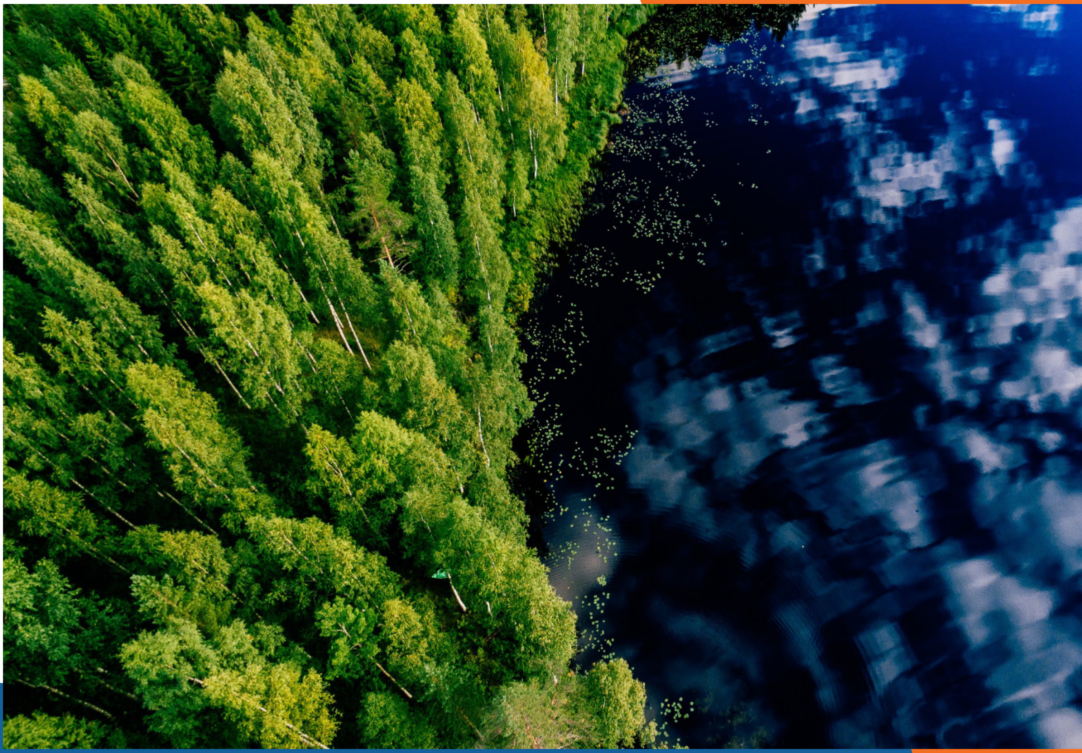

NWBC 2022

The 10th Nordic Wood Biorefinery Conference

25-27 October 2022, Helsinki, Finland

VTT TECHNOLOGY 409

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NWBC 2022

The 10th Nordic Wood Biorefinery Conference

Atte Virtanen (Ed.)

VTT Technical Research Centre of Finland Ltd.

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Nordic Wood Biorefinery Conference 2022 - NWBC2022

The focus of Nordic Wood Biorefinery Conference 2022 conference is on latest discoveries and innovations in bio-based materials, chemicals, and products from wood biorefineries.

25-27 October 2022

Helsinki, Finland

Conference organizers

Preface

The 10th edition of the Conference, and this book of proceedings, continue the tradition of NWBC on building the foundation of a sustainable bio-economy. This requires that the many aspects of the foundation are systematically considered, including for example societal issues, design and consumer needs, technological performance and economics of production. Furthermore, findings both from industrial experiences from all linked sectors in implementation and R&D projects and academic research needs to be communicated to close the loop. The organizers hope that the selected scientific contributions, industrial viewpoints and the conference format are able to contribute to building yet another layer on this foundation.

It is our great pleasure to welcome you to the 10th Nordic Wood Biorefinery Conference. The Conference takes place in Helsinki, in Scandic Park Hotel from the 25nd to the 27th of October. A magnificently renovated hotel is located right next to Helsinki city centre and close to excellent transport connections.

The organisers of the NWBC 2022 wish to thank all people involved in the process of making the conference; Programme Scientific Committee, Award Jury, all speakers, poster presenters and their co-authors, student pitchers for their valuable contributions to the contents of the conference. Special thanks to Merja Laamanen and Jessica Vepsäläinen for their contribution in planning and executing the conference agenda and to Päivi Vahala-Partanen for graphical design and technical editing.

Enjoy the conference!

With best wishes,

On behalf of the whole Organizing Committee

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Biomaterial
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and products, VTT
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and products, VTT
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Table of contents

Nordic Wood Biorefinery Conference 2022 - NWBC2022 1

Preface 2

Table of contents 3

Keynote Speakers 9

Scientific Committee 14

Site Visit and Social Events 15

Side Event: Nordic Research and Technology Infrastructure Workshop 16

10th Nordic Wood Biorefinery Conference – Scientific Programme 17

ORAL PRESENTATIONS

Tuesday 25 October

Nordic RTOs Collaboration on Testbeds and Technology Infrastructures Strengthens the Impact on European Green Transition 24
Mika Härkönen, Karin Johnson, Pauliina Tukiainen, and William Mackintosh

FinnCERES Flagship – A Competence Centre for the Materials Bioeconomy 25
Tekla Tammelin, Stina Grönqvist, Jukka Hassinen, Monika Österberg, and Orlando Rojas

Engineered Lignin Products

Learnings and Aspects on Kraft Lignin Separation and Valorisation 29
Per Tomani, Anders Arkell, Ewellyn Capanema, and Omid Hosseinaei

LignoForce™ Lignin as a Biopolyol in Rigid Polyurethane Foams 30
Adil Mazar, and Michael Paleologou

A New Biorefinery Approach for Production of Lignin-Carbohydrate Functional Hybrids 36
Mikhail Balakshin, and Ewellyn Capanema

LigniOx Lignins as Sustainable Bio-Based Dispersants 43
Jouko Vyörykkä, Marc Schmitz, Neethi Rajagopalan, Minna Vikman, Olesya Fearon, Tiina Liitiä, and Anna Kalliola

Fibenol’s Biorefinery – from Secondary Woody Biomass to Chemical Building Blocks 48
Gert Preegel, Karl Peebo, and Uku Erik Tropp

Low emission biorefineries and side-stream valorization

New Methods to Control the Sodium and Sulphur Balance of Kraft Pulp Mills 53
Rickard Wadsborn, and Erik van Zessen

Valorization of Industrial Spruce Bark by Alkaline Extraction 60
Marc Borrega, Anna Kalliola, Marjo Määttänen, Anna S. Borisova, Atte Mikkelson, Panu Lahtinen, and Elisa Spönla

Preparation, Characterization, and Application Evaluation of Different Sawdust-Based Green and Versatile Chemicals and Materials for Sawdust Valorization 62
Jiebing Li

Demonstration and Assessment of a Novel Biorefinery Concept for the Integration of Beechwood-Based Products as Platform and Fine Chemicals 68
Roy Nitzsche, Jakob Köchermann, Kathleen Meisel, Hendrik Etzold, and Arne Gröngröft

Wednesday 26 October
Circularity of Wood Sourced Carbon and Emerging policies

Current and Emerging Solutions for Carbon Neutrality in Wood Based Biorefinery 77
Marko Hakovirta, Janne Keränen, Jaakko Asikainen, and Ali Harlin

Novel Cellulose Modifications

Preparation of Dialdehyde Cellulose (DAC) from Cellulose Pulp and its Applications as Reversible Wet Strength Additive 88
Gerrit Schaper, Julian Häntzschel, Bana Alomari, and Martin Zahel

Nanocellulose-Based Antimicrobial Microparticles as an Alternative to Toxic Nano-Biocides 93
Vanja Kokol, Monika Kos, Vera Vivod, Sara Novak, Veno Kononenko, Nina Gunde-Cimerman, and Damjana Drobne

Efficient New Extraction Method for Highly Charged Phosphorylated CNC 98
Marcel Kröger, Olamide Badara, Timo Pääkkönen, Sami Hietala, and Eero Kontturi

Progress on Cellulose Esterification – Control Over Surface to Bulk Modification 104
Tetyana Koso, Marco Beaumont, and Alistair King

Structure – Function – Performance Interrelations in Materials Engineering

Multifunctional and Biobased Coating Aided by Digital Material Design 105
Monika Österberg

Simulating the Impact of Nozzle Hole Locations and Diameters on Film Thickness in Spinning Process 107
Kaarlo Nieminen, Eva Gonzáles, and Michael Hummel

Capturing Colloidal Nano- and Microplastics with Plant-Based Nanocellulose Networks 111
Ilona Leppänen, Timo Lappalainen, Tia Lohtander-Piispa, Christopher Jonkergouw, Suvi Arola, and Tekla Tammelin

High Performance Cellulose-Based Substrates for Flexible Printed Electronics 112
Tia Lohtander-Piispa, Akio Yamamoto, Vinay Kumar, Petri Widsten, Ilona Leppänen, Alexey Khakalo, Mohammad Behfar, Katariina Torvinen, and Tekla Tammelin

Low Emission Biorefineries and Side-Stream Valorization

When Historical Partners, METSA and FIRMENICH, Combine Technical Expertise to Improve both Recovery Yields and Quality of Crude Sulfate Turpentine 117
Emmanuel Cazeils, and Thomas Fant

Size Based Monitoring of Cellulose Hydrolysis Reaction for the Cellulose Nanocrystal (CNC) Production 118
Shubhankar Bhattacharyya, Öjvind Sundvall, Liselotte Uhlir, Björn Källman, and Tommy Nordin

LigniOx Process Concept to Produce Lignin Dispersants at a Kraft Pulp Mill and an Organosolv Biorefinery 124
Anna Kalliola, Tiina Liitiä, Iris Winberg, Katariina Kemppainen, Outi Poukka, Julien Davin, Hanne Wikberg, Pieter Vandezande, Pauliina Sjögård,and Lauri Pehu-Lehtonen

High performing wood-based products for industrial scale

Scalable Industrial Process for the Production of Nanofibrillated Cellulose Oxalate 130
Jonatan Henschen, Jonas Engstrand[1], and Monica Ek

Low emission biorefineries and side-stream valorization

Delignification of Kraft Pulp with Oxygen, Air and Nitrogen - Effect on Selectivity and Pulp Brightness 134
Jenny Sjöström, Raghu Deshpande, Gunnar Henriksson, Mikael E. Lindström, Tomas Vikström, Hans Theliander, and Olena Sevastyanova

Techno-Economic Analysis for Novel Biorefinery Concept Producing Biobased Acetic Anhydride 139
Kristian Melin, Daniel Klüh, Harri Nieminen, Arto Laari, and Tuomas Koiranen

Catalysis solvolysis of Novel Organosolv Lignin into Phenolic Monomers 144
Saravanan Kasipandi, Sari Rautiainen, Silja Känsäkoski, Taina Ohra-aho, and Juha Lehtonen

Thursday 27 October
Wood Based Textile Solutions

Spinning of Regenerated Fibres from Paper Grade Pulp 147
Taina Kamppuri, Jenni Rahikainen, Simo Hannula, Elisa Spönla, Antje Potthast, Irina Sulaeva, Stina Grönqvist, and Ali Harlin

Spinning and Additive Manufacture for Multiscale Cellulose Structures on Textiles and 3D Printed Materials 152
Guillermo Reyes, Alistair W. King, Harri Kosonen, and Orlando J. Rojas

Sustainable Chemistries for Cellulosic Textiles 158
Anna-Stiina Jääskeläinen, Mari Myöhänen, Saara Hanhikoski, Jörg Schöner, Mats Berg, and Kaisa Karisalmi

Engineered Lignin Products

Unlocking the Potential of Lignin in Material Applications via its Simultaneous Isolation and Multi-Functionalization ... 162
Stefania Bertella, Vijay Kumar Rana, Peyman Karami, Łukasz Richter, Francesco Stellacci, Dominique Pioletti, and Jeremy S. Luterbacher

Lignin Based Polyacids to Substitute Fossil-Based Materials in Coatings Formulations ... 166
Olesya Fearon, Viviana Polizzi, Pieter Vandezande, and Anna Kalliola

Sustainable Lignin Polymer in Thermoformed Fiber Products ... 171
Mihaela Tanase-Opedal, and Jost Ruwoldt

Product Development and Scale-Up of The Lignin Platform in an Aldehyde-Assisted Fractionation (AAF) Biorefinery ... 176
Monique Bernardes Figueiredo, Ydna Questell-Santiago, Chloé Wegmann, Antoine Bourgeois, Justine Charmillot, Etienne Gatt, Philip Scholten, Florent Héroguel, and Remy Buser

LignoCity – Flexible Production of Tailor-Made Lignin ... 177
Maria Ölmhult, and Anders Arkell

Lignin Nanoparticles-Based Antibacterial Coatings for Development of Antimicrobial Surfaces ... 182
Maria Morits, Roberta Teixeira Polez, Satu Salo, Petri Widsten, Kristoffer Meinander, Donika Morina, Stina Grönqvist, and Monika Österberg

Upgrading Biorefinery Lignins Through Green and Cost-Efficient Reactive Extraction ... 187
Davide Rigo, and Mikhail Balakshin

POSTER PRESENTATIONS

Assessing Environmental Aspects

Oxygen Delignification – its Strong Oxidative Power to Increase Mechanical Pulp Properties and Reduce Energy Requirements ... 193
Cláudia Esteves, Olena Sevastyanova, Sören Östlund, and Elisabet Brännvall

Engineered Lignin Products

LigniOx Lignins - Sustainable Depressants for Froth Flotation in Mineral Processing ... 195
John Bachér, Olesya Fearon, Tuomo Mäkelä, and Anna Kalliola

Lignin-Based Carbon Materials for Energy Storage Applications ... 197
Chamseddine Guizani, Virpi Siipola, Olli Sorsa, Marja Vilkman, Antti Pasanen, Petri Widsten, Olesya Fearon, Taina Ohra-aho, Tommi Virtanen, Anna Kalliola, Mikko Mäkelä, and Katariina Torvinen

Potential of a Bio-Based Additive in the Prevention of Lignin-Induced Recalcitrance under Severe Pretreatment Conditions ... 199
Miriam Kellock, Anna S. Borisova, Hannu Maaheimo, Jenni Rahikainen, Ulla Holopainen-Mantila, Marc Borrega, Kaisa Marjamaa, John Ralph, Claus Felby, Kristiina Kruus, and Tarja Tamminen

Enzymatic Upgrading of AqSO Biorefinery Cellolignins for High Value Applications ... 201
Madina Muratova, Dmitry Tarasov, Davide Rigo, Popova Yuliya, Daryna Diment, MiJung Cho, and Mikhail Balakshin

UV Spectrophotometry of Lignin Revisited - Exploring Solvents with Low Toxicity ... 207
Jost Ruwoldt, and Mihaela Tanase-Opedal

Customized Catalytic Hydropyrolysis of Biomass to High-Quality Bio-Oil Suitable for Co-Processing in FCC Refining Unit 209
Hoda Shafaghat, Ann-Christine Johansson, Olov G.W. Öhrman, and Prakhar Arora

High Performing Wood Based Products for Industrial Scale

Reconstructing Lignocellulose Biomass Wastes into Construction Materials 211
Svitlana Filonenko, and Markus Antonietti

High-Performing Functionalized Cellulose Materials via High Consistency Processing 213
Ali Harlin, Marianne Vehviläinen, Marjo Määttänen, and Stina Grönqvist

Low Emission Biorefineries and Side-Stream Valorization

Purification of Organic Solvents Contaminated with Wood Extractives: a Liquid-Liquid Extraction Process Using Fully Recyclable Biomimetic Solvents 215
Lukas Almhofer, Daniela Bammer, Klaus Schlackl, Christian Paulik, and Robert Bischof....215

Recovery and Characterization of Low-Molecular-Weight Lignin from Ultrafiltered Kraft Black Liquor.... 217
Mariona Battestini Vives, Omar Abdelaziz, Johan Thuvander, Anders Arkell, Christian Hulteberg, and Frank Lipnizki

Microbial Expansin Related Proteins for Improved Enzymatic Action for Conversion of Lignocellulose to Platform Sugars 219
Deepika Dahiya

Adaptive Bayesian Optimization for Alkaline Oxidation of Birch Wood 221
Hanna Hörhammer, Hannu Rummukainen, Jorma Kilpi, Jari Sirviö, Pirkko Kuusela, and Mikko Mäkelä

Production of Water-Soluble Carbohydrates from Aspen Wood Flour with Hydrogen Chloride Gas .223
Antti Topias Kilpinen, and Eero Kontturi

Hydrodeoxygenation of Black Liquor HTL-Oil Model Compounds in Supercritical Water....229
Sari Rautiainen, Felix Hyppönen, Tyko Viertiö, Juha Lehtonen, Luděk Meca, and Pavel Kukula

Electrochemical Reduction of Aldonic Acids into the Corresponding Aldoses in the Presence of Electrolytes Reflecting SSL Composition.... 231
Maria Wolfsgruber, Robert Bischof, Christian Paulik, and Adam Slabon

Thermochemical Process Wastes as Carbon Material Sources 233
Aivars Zhurinsh, Galina Dobele, Aleksandrs Volperts, Ance Plavniece, and Vilhelmine Jurkjane

Novel Cellulose Modification

Wood Derived Natural Microcrystalline Cellulose with the Functionality of Nanocellulose - New Perspective for Industry....235
Gert Preegel

Structure – function – performance interrelations in materials engineering

Mapping The Properties and Performance of Nanocellulose- and Alginate-Based Cell Factory Matrices for Sustainable Photosynthetic Chemicals Production 237
Ville Rissanen, Vilja Siitonen, Tuukka Levä, Lauri Nikkanen, Sergey Kosourov, Maria Heilala, Josphat Phiri, Thaddeus Maloney, Mikko Mäkelä, Yagut Allahverdiyeva, and Tekla Tammelin

Solid-State Photosynthetic Cell Factories for Sustainable Chemicals Production Using Nanocellulose-Based Cross-Linked Functional Structures 239
Tuuli Virkkala, Ville Rissanen, Tuukka Levä, Sergey Kosourov, Suvi Arola, Eero Kontturi, Yagut Allahverdiyeva, and Tekla Tammelin

Nanocellulose as Bio-Template for Synthesis of Photo-catalytically Active Porous Silica 241
Maryam El Hajam, Noureddine Idrissi Kandri, Abdelaziz Zerouale, Xiaoju Wang, Jan Gustafsson, Luyao Wang, Ermei Mäkilä, Leena Hupa, and Chunlin Xu

Wood based textile solutions

Organosolv Catalytic Fractionation of Nordic Forestry Wood Residues to Textile Fibers 243
Kiran Reddy Baddigam, Kuntawit Witthayolankowit, Anuja Kane, Birgitta Gustafsson, Manzoorahmed Shaikh, Björn Sjöstrand, Deepika Gupta, Helena Håkansson, Joseph S. M. Samec, and Aji Mathew

From Industry 4.0 to Research 4.0. a Modular Approach for the Development of Cellulosic Fibres ... 245
Steffen Müller-Probandt, and José Canga Rodríguez

Spindyeing Man-Made Cellulose Fibres with Vat Dyes 259
Nicole Nygren, Marike Langhans, Marja Rissanen, and Michael Hummel

Functionalized Biocelsol - Regenerated Cellulosic Fibres with Improved Dyeability with Anionic Reactive Dyes.. 261
Marianna Vehviläinen, Marjo Määttänen, Harri Setälä, and Marja Rissanen

Enzymatic High-Consistency Processing of Softwood and Eucalyptus Kraft Pulps for Textile Fibres ...263
Elisa Spönla, Jenni Rahikainen, and Stina Grönqvist

Author Index 266

List of Tables 269

Table of Figures..270

Keynote Speakers

Marcus Wallenberg Prize 2022 winner
Organic superbase salts (ILs) for cellulose dissolution and biomass processing

Professor Ilkka Kilpeläinen
University of Helsinki

Marcus Wallenberg Prize 2022 winner
Novel cellulose fibers from steam-exploded birch wood as the main product in a new biorefinery concept

Professor Herbert Sixta
Aalto University

Please see following links:
Sustainable concept for wood-based textile fibres: The Marcus Wallenberg Prize (mwp.org)

CONFEDERATION OF EUROPEAN PAPER INDUSTRIES biomass into high-performance textile fibres (cepi.org)

The Green Deal with Wood Biorefineries

Jori Ringman, Director General
Cepi

Circularity of wood sourced carbon and emerging policies Current and Emerging Solution for Carbon Neutrality in Wood based Biorefinery

Research Professor Ali Harlin
VTT

Nordic RTOs collaboration on testbeds and technology infrastructures strengthens the impact on European green transition

Karin Johnson, CEO
RISE Processum AB

Professor of Practice Mika Härkönen
VTT

FinnCERES Flagship - A Competence Centre for the Materials Bioeconomy

Research Professor Tekla Tammelin
VTT

Multifunctional and biobased coating aided by digital material design

Professor Monika Österberg
Aalto University

PANEL DISCUSSION I:
The challenges and opportunities of Lignin

Ms. Ananda Dias, New Business Manager
Suzano

Mr. Mikael Hannus, SVP of Group R&D, Stora Enso

Assistant Professor Mika Sipponen
Stockholm University & Co-Founder at Lignoflow Technologies

Mr. Per Tomani, Director Research & Business Development, RISE

PANEL DISCUSSION II:
Turning research success to commercial success

Mr. Johannes Bogren, Vice President
Södra

Ms. Åsa Ek, Acting SVP Head of Innovation
Division Biomaterials, Stora Enso

Professor Kristiina Kruus,
Dean in the School of Chemical Engineering
Aalto University

Pia Nilsson, Director
Global Platform Development R&D, UPM

Niklas von Weymarn, CEO
Metsä Spring Oy

Scientific Committee

- Per Tomani, RISE
- Florian Graichen, SCION
- Mikael Hannus, Stora Enso
- Gustav Nyström, EMPA
- Lauri Sikanen, LUKE
- Kristiina Kruus, Aalto
- Emily Cranston, UBC
- Orlando Rojas, Aalto / UBC
- Hanna Hörhammer, VTT
- Peter Axegård, C-Green Technologies
- Paul Stuart, Polytechnique Montrèal & EnVertis Inc.
- Marcelo C.S. Muguet, Klabin

Site Visit and Social Events

Site Visit to Bioruukki


Photo: VTT

Visit VTT Bioruukki Pilot Centre on Monday 24.10.2022 afternoon at 15.00-17.00. The site visit fee per person is 50,00 € (incl. VAT) and you can save your seat when registering to the conference.

We will organise transportation from hotel Scandic Park to Bioruukki and back to the hotel after the visit. Travel time is about 30 min one way.

NOTE: Limited amount of 60 seats available!


Photo: Flickr – Olli Ronimus

Helsinki City Reception

The City of Helsinki will host a reception to NWBC attendees in Helsinki City Hall (Pohjoisesplanadi 11-13) on 25.10 at 19.00 – 20.30.


Photo: Restaurant Pörssi

Conference Dinner

The dinner will take place at Restaurant Pörssi. Pörssi, the Gray Granite House, was built between 1911 and 1912. The building is commonly kept as one of the 20th century's most impressive works of Finnish jugend-architecture. Designed by architect Lars Sonck. Brokers left the house in the early 1990s when the stock exchange moved to electronic securities trading.

Location: Pörssi Restaurant (Fabianinkatu 14) is 2 km from Scandic Park Helsinki, 30 min walk or 15 min by tram (No 4).

Side Event: Nordic Research and Technology Infrastructure Workshop

Welcome to the Nordic Research and Technology Infrastructure Workshop to identify Nordic collaboration opportunities, strengths and industry needs for Nordic bioeconomy testbeds on 24.10.2022 at 11.30-14.30.

We invite all stakeholders (Research Infrastructure owners, companies, public authorities, funding authorities, innovation organizations…) with an interest in bioeconomy Research and Technology Infrastructures (RI/TI) to participate in the Nordic Research and Technology Infrastructure Workshop.

The purpose of this workshop is to discuss about Nordic Research Infrastructure collaboration and funding opportunities, strengths and industry needs from Nordic perspectives.


Photo: VTT Bioeconomy infrastructure

10th Nordic Wood Biorefinery Conference

Monday 24 October 2022

11.30 - 14.30	Side Event: Nordic Research and Technology Infrastructure Workshop
15.00 - 17.00	Visit to Bioruukki Bus Transportation from Scandic Park Hotel and back, bus leaves from the hotel at 14.30
16.00 - 18.00	Pitching Training Session Students Wonder, Future Hub VTT Technical Research Centre of Finland, Tekniikantie 21, Espoo

Tuesday 25 October 2022

8:30 - 17:30	Registration
8:55 - 9:00	Guidance and Practicalities
9:00 - 9:15	Opening of the Conference Dr. Antti Vasara, President & CEO, VTT
9:15 - 9:50	Keynote: The Green Deal with Wood Biorefineries Jori Ringman, Director General, Cepi Cepi is the European association representing the paper industry
9:50 - 10:50	Keynote: Nordic RTOs Collaboration on Testbeds and Technology Infrastructures Strengthens the Impact on European Green Transition Dr. Karin Johnson, CEO at RISE Processum AB Professor of Practice Mika Härkönen VTT Keynote: FinnCERES Flagship – A Competence Centre for the Materials Bioeconomy Research Professor Tekla Tammelin, VTT
10:50 - 11:20	Coffee & poster viewing

11:20 - 12:40	Engineered lignin products Learnings and Aspects on Kraft Lignin Separation and Valorisation Mr. Per Tomani, RISE LignoForce^{TM} Lignin as a Biopolyol in Rigid Polyurethane Foams Dr. Michael Paleologou, FPInnovations LigniOx Lignins as Sustainable Bio-Based Dispersants Dr. Jouko Vyörykkä, DOW Fibenol's Biorefinery – from Secondary Woody Biomass to Chemical Building Blocks Mr. Uku Erik Tropp, Fibenol
12:40 - 13:40	Lunch
13:35 - 15:00	Low emission biorefineries and side-stream valorization New Methods to Cntrol the Sodium and Sulphur Balance of Kraft Pulp Mills Dr. Rickard Wadsborn, Stora Enso Mr. Erik van Zessen, Paques Valorization of Industrial Spruce Bark by Alkaline Extraction Dr. Marc Borrega, VTT Preparation, Characterization, and Application Evaluation of Different Sawdust-Based Green and Versatile Chemicals and Materials for Sawdust Valorization Dr. Jiebing Li, RISE Demonstration and Assessment of a Novel Biorefinery Concept for the Integration of Beechwood-Based Products as Platform and Fine Chemicals Mr. Roy Nitzsche, DBFZ
15:00 - 16:30	Coffee & Poster Session
16:30 - 17:30	Student´s Pitching Program
19:00 - 20:30	Helsinki City Reception Helsinki City Hall, Pohjoisesplanadi 11-13

Wednesday 26 October 2022

8.00 - 9.00	Student Breakfast, Only for Invitees
8:30 - 17:00	Registration
9:00 - 9:30	Marcus Wallenberg Prize 2022 winner keynote Organic Superbase Salts (ILs) for Cellulose Dissolution and Biomass Processing Professor Ilkka Kilpeläinen, University of Helsinki
9:30 - 11:10	Circularity of wood sourced carbon and emerging policies Current and Emerging Solutions for Carbon Neutrality in Wood Based Biorefinery Research Professor Ali Harlin, VTT Novel Cellulose Modifications Preparation of Dialdehyde Cellulose (DAC) from Cellulose Pulp and its Applications as Reversible Wet Strength Agent Mr. Gerrit Schaper, Papiertechnische Stiftung (PTS) Nanocellulose-Based Antimicrobial Microparticles as an Alternative to Toxic Nano-Biocides Professor, Dr. Vanja Kokol, University of Maribor Efficient New Extraction Method for Highly Charged Phosphorylated CNC Mr. Marcel Kröger, Aalto University Progress on Cellulose Esterification – Control Over Surface to Bulk Modification Dr. Alistair King, VTT
11:10 - 11:40	Coffee & poster viewing
11:40 - 13:00	Structure – function – performance interrelations in materials engineering Multifunctional and Biobased Coating Aided by Digital Material Design Invited speaker Professor Monika Österberg, Aalto University Simulating the Impact of Nozzle Hole Locations and Diameters on Film Thickness in Spinning Process Dr. Kaarlo Nieminen, Aalto University Capturing Colloidal Nano- and Microplastics with Plant-Based Nanocellulose Networks Ms. Ilona Leppänen, VTT High Performance Cellulose-Based Substrates for Flexible Printed Electronics Dr. Vinay Kumar, VTT
13:00 - 14:00	Lunch

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Ms. Ananda Dias, New Business Manager, Suzano
Mr. Mikael Hannus, SVP of Group R&D, Stora Enso
Assistant Professor Mika Sipponen, Stockholm University &
Co-Founder at Lignoflow Technologies
Mr. Per Tomani, Director Research & Business Development, RISE

14:30 - 15:50 Low emission biorefineries and side-stream valorization

When Historical Partners, METSA and FIRMENICH, Combine Technical Expertise to Improve Both Recovery Yields and Quality of Crude Sulfate Turpentine
Dr. Emmanuel Cazeils, Firmenich
Mr. Thomas Fant, Metsä Fibre

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Scalable Industrial Process for the Production of Nanofibrillated Cellulose Oxalate
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15:50 - 16:30 Coffee & poster viewing

16:30 - 17:30 Delignification of Kraft Pulp with Oxygen, Air and Nitrogen - Effect on Selectivity and Pulp Brightness
Ms. Jenny Sjöström, KTH

Techno-Economic Analysis for Novel Biorefinery Concept Producing Biobased Acetic Anhydride
Dr. Kristian Melin, Lappeenranta University of Technology (LUT)

Catalytic Solvolysis of Novel Organosolv Lignin into Phenolic Monomers
Dr. Sari Rautiainen, VTT

19:00 - 23:00 Conference Dinner, The Gullichsen Award & The Boreal Alliance Award
Restaurant Pörssi, Fabianinkatu 14

Thursday 27 October 2022

8:00 - 16:00	Registration
9:00 - 9:30	Marcus Wallenberg Prize 2022 winner keynote Novel Cellulose Fibers from Steam-exploded Birch Wood as the Main Product in a New Biorefinery Concept Professor Herbert Sixta, Aalto University
9:30 - 10:30	PANEL DISCUSSION: Turning Research Success to Commercial Success Johannes Bogren, Vice President, Södra Åsa Ek, Acting SVP Head of Innovation Division Biomaterials, Stora Enso Dean Kristiina Kruus, School of Chemical Engineering, Aalto University Pia Nilsson, Director, Global Platform Development R&D, UPM Niklas von Weymarn, CEO, Metsä Spring Oy
10:30 - 11:00	Coffee & poster viewing
11:00 - 11:20	Lignin-Based Functional Fillers - a Disruptive Innovation Invited speaker, Dr.-Ing. Tobias Wittmann, SunCoal Industries GmbH
11:20 – 12:20	Wood based textile solutions Spinning of Regenerated Fibres from Paper Grade Pulp Dr. Taina Kamppuri, VTT Spinning and Additive Manufacture for Multiscale Cellulose Structures on Textiles and 3D Printed Materials Dr. Guillermo Reyes, Aalto University Sustainable Chemistries for Cellulosic Textiles Dr. Anna-Stiina Jääskeläinen, Kemira
12:20 - 13:20	Lunch
13:20 - 14:40	Engineered lignin products Unlocking the Potential of Lignin in Material Applications via its Simultaneous Isolation and Multi-Functionalization Ms. Stefania Bertella, Aalto Lignin Based Polyacids to Substitute Fossil-Based Materials in Coatings Formulations Dr. Olesya Fearon, VTT Sustainable Lignin Polymer in Thermoformed Fiber Products Dr. Mihaela Tanase-Opedal, RISE PFI

Product Development and Scale-Up of the Lignin Platform in an Aldehyde-Assisted Fractionation (AAF) Biorefinery
Dr. Monique Bernardes Figueiredo, Bloom Biorenewables

14:40 - 15:10 Coffee

15:10 - 16:10 LignoCity – Flexible Production of Tailor-Made Lignin
Ms. Maria Ölmhult, RISE
Mr. Anders Arkell, RISE

Lignin Nanoparticles-Based Antibacterial Coatings for Development of Antimicrobial Surfaces
Dr. Maria Morits, Aalto University

Upgrading Biorefinery Lignins Through Green and Cost-Efficient Reactive Extraction
Dr. Davide Rigo, Aalto University

16:10 - 16:20 Closing the Conference and Announcing the next NWBC

ORAL
Presentations

Tuesday
25.10.2022

Keynote

Nordic RTOs Collaboration on Testbeds and Technology Infrastructures Strengthens the Impact on European Green Transition

Mika Härkönen[1] Karin Johnson[2], Pauliina Tukiainen[1], and William Mackintosh[2]

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Abstract

In 2019 the Nordic Research and Technology Organisations (RTOs) signed a MoU on collaboration around testbeds and technology infrastructures. In the same year a mutual research infrastructure cooperation agreement on bio- and circular economy technologies was signed between VTT and RISE. Impacting applied research and scale-up requires not only top level competence but also state-of-the-art experimental testbeds including well equipped laboratories and pilot plants. The primary reasons for the collaborative initiatives were to learn from each other by sharing knowledge and experience and working together through testbeds.

Now after three years it is time to discuss what has been achieved and what are the key actions in the coming years. The analysis of the technology infrastructures of VTT and RISE revealed surprisingly low amount of directly overlapping facilities, and several research fields had clearly complementary testbeds. This forms a solid basis for collaboration in further development of the testbed offering, for example in the form of INN-PRESSME project and other networks. The knowledge of each other's facilities has helped in planning the major research infrastructure investment projects such as RISE Bioeconomy Arena and VTT Bioruukki Pilot Centre.

SINTEF joined as partner for the assessment of Nordic research landscape, available research infrastructures, funding schemes and development actions. The Nordic governments are equally committed to United Nation's sustainability goals and EU green transition targets, and the national research priorities are relatively similar. The complementary and specialized test beds give opportunities for Nordic collaboration in terms of use, development and impact.

Infrastructure collaboration have the potential to enhance the impact on research, commercialization and society. Information exchange through collaboration agreements and personal contacts illuminate synergies and lead to smarter solutions.

Keynote

FinnCERES Flagship – A Competence Centre for the Materials Bioeconomy

Tekla Tammelin[1], Stina Grönqvist[1], Jukka Hassinen[2], Monika Österberg[2],
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Abstract

FinnCERES is a Competence Centre formed between Aalto University and VTT Technical Research Centre of Finland (www.finnceres.fi). This combination yields a unique combo of highly ranked fundamental and applied research in the area of forest-sourced materials. In addition, the strength of the alliance derives from its state-of-the-art research infrastructure including pilot capabilities, and global research and industrial networks. We aim at holistic material sustainability considering today's demands on the smart use of biomass. In the current materials design, the specific inherent properties and added value of lignocellulosics are emphasised even more than merely their renewable origin or biodegradability.

We consider plants as our future material bank since cell wall components, structure and functions are an endless source for inspiration for the materials science and engineering. The aim of the research programme is to bridge the gap between fundamental and applied research as well as to provide a fast track for scientific findings towards real innovations and industrial implementation.

This presentation highlights the latest scientific advances from the research programme which is divided into five major research themes: 1) Fundamentals: Interactions and advanced characterisation, 2) Future biorefineries, 3) Clean air and water, 4) Lignocellulosics beyond plastics, and 5) Electronics, optics, and energy applications. In addition, the recent progress and actions within the FinnCERES Ecosystem including the Boreal Alliance will be communicated.

Highlights of the FinnCERES research programme

FinnCERES investigates and develops bio-based material solutions, and its efforts are well aligned with the national and global bioeconomy targets on transitioning from fossil-based resources to renewables. We strive for scientifical and technological breakthroughs by bridging fundamental and applied research in order to realize sustainable growth. The principal goal of the FinnCERES research is to harness the natural properties of lignocellulose to create new sustainable materials. FinnCERES

Competence Centre is a multidisciplinary community bringing together experts from various fields such as bio-based materials science, inorganic, organic and materials chemistry, enzymology, condensed matter physics, and computational modelling to name few. Our aim is to reveal what wood and plants can provide.

Our outputs are crystallized in three scenarios: 1) lignocellulose is a viable value-added raw material which is complementing and partly replacing fossil-based counterparts in high-volume applications, 2) wood-derived building blocks and their water-responsive character provide pathways to construct bioinspired air and water purification materials 3) inherent features of lignocellulose-based materials provide performance and functionality for textiles, packaging, diagnostics, electronics, optics, and energy harvesting. We envision that our sustainable outcomes will bring us closer to *the new era of bio-based materials*.

The FinnCERES research programme is divided into five major research themes, and recent advances include:

"Fundamentals: Interactions and Advanced Characterization" aims to address fundamental questions on the structure of the lignocellulosic building blocks and their assemblies. In cellulosic products, the hygroscopicity is often seen as a detriment because water uptake can greatly impair the strength of paper or reduce the gas barrier performance of cellulose films, for instance. Our core approach is not only to accept the presence of water but to thoroughly understand its role as a structural element. The approach will introduce new solutions to tackle the effect of water in lignocellulosic products. More importantly, one of our strategic aims is to exploit water as a functional asset and we utilize the presence of water in newly built lignocellulose architectures in contemporary materials such as sensors with electrochemical (Durairaj et al., 2021) or optical response (Orelma et al., 2020) nano- and ultrafiltration membranes Pöhler et al., 2022), and encapsulating scaffolds of living cells (Rissanen et al., 2021). This approach is novel and can yield radically new materials that do not exist yet.

"Clean Air and Water," endows lignocellulosic building blocks with selective and efficient capturing ability, for purification and detection of valuables, rare elements and pollutants. The highlight of the theme demonstrates how FinnCERES deals with the microplastics challenge. We have addressed the primary need on how to collect and bind the most challenging nanosized plastic fraction and how to quantitatively analyse the fraction (Leppänen et al., 2022). Today, we are able to bridge the significant methodological gap related to efficient entrapment and filtration of the most harmful fraction of nanosized plastic particles. We have introduced a versatile solution, whose efficiency to collect microplastics is not dependent on any specific chemical interaction. Instead, the entrapment of particles is a result of a synergistic feature provided by the nanocellulose network: high hygroscopicity coupled with high active surface area - features which are naturally granted by nanocellulose.

"Future Biorefineries" theme involves the preparation of lignocellulosic building blocks to meet the demands of future advanced materials. Future biorefineries and side-stream valorisation with novel modification routes are integral parts of the programme when considering smart utilization of all available biomass fractions for value-added materials. Lignin valorisation for materials applications is in a central role when considering the reduction CO_2 emissions of the pulp industry. In this realm (Henn et al., 2022) showcased the potential of lignin nanoparticles as sustainable and formaldehyde-free high-strength adhesives for wood panels (Henn et al., 2022). Nuutinen et al., combined keratin proteins (a side stream from poultry industry) with lignin nanoparticles and cellulose using nanoscale design approach which enables good affinity between components - a highly important feature not only in composites but also in many other applications such as hydrogels for biomedicine and cosmetics (Nuutinen et al., 2022). This work is part of the fresh doctoral thesis of Dr. Nuutinen (2022).

Following the same lines on valorisation of valuable side streams, FinnCERES teams have successfully demonstrated post-functionalisation strategies enabling resource efficient textile dyeing of manmade cellulose fibres (Rissanen et al., 2022). Furthermore, many biocolorants show bioactivity enabling simultaneous functionalisations like antioxidant activity, UV protection and antimicrobial properties. For example, cellulose films treated with willow bark extract effectively block UVA and UVB radiation (Lohtander et al., 2020; 2021) as recently highlighted in the doctoral thesis of Dr Lohtander-Piispa (2022). These recent advances are part of the FinnCERES theme “Lignocellulosics Beyond Plastics” where the target is to further develop high-volume materials for packaging, biocomposites and textiles.

“Electronics, Optics, and Energy Applications” theme includes the development of lignocellulose-based ion conductors, photonic and optoelectronic devices, and applications for energy storage and harvesting, including batteries and solar cells. The theme goes beyond the conventional paper-based substrates for optoelectronics showcasing the cellulose-based optical fibers (Orelma et al., 2020; Jaiswal et al., 2022), nanocellulose-based thermoresponsive optical modulation devices Jaiswal et al., 2021 and optically tunable nanocellulose films where excellent light transmittance is couple with the possibility to tune optical haze by surface patterning (Khakalo et al., 2020).

To achieve the desired societal and economic impact of the research findings, industrial collaboration is crucial. FinnCERES is well aligned with the excellent development of industrial investments in bio-based materials in Finland. Currently, in September 2022, FinnCERES has 15 co-creation members to which we provide a front-row access to world-class bio-based materials research. We facilitate fruitful discussion ensuring that the FinnCERES research lines meet the future needs of the industry, and work as a catalyst for sustainable solutions. The close collaboration between the Flagship and Finnish industry ensures quick exploitation of the novel material solutions created in the Flagship, which can be transformed into successful business and new jobs.

As we are facing global climate and resource challenges, collaboration across borders is needed more than ever. To tackle these grand challenges, FinnCERES Flagship and Bioproduct Institute at the University of British Columbia launched Boreal Alliance, a research collaboration network for bio-based materials innovations (www.borreal-alliance.org). Boreal Alliance, established in 2021, joins forces within academia and research institutes around the globe, aiming to identify opportunities that translate bio-based materials science to sustainable innovations. So far, five prestigious Affiliate Members have joined the Boreal Alliance network: Swiss Federal Laboratories for Materials Science and Technology (Empa), Natural Resources Institute Finland (Luke), Treesearch, University of Oulu, and UNITE Flagship. The Alliance fosters international research exchanges, supports science-based policy making, and encourages cross-disciplinary collaboration to advance circular and renewable bioeconomy.

Conclusions

FinnCERES investigates and develops bio-based material solutions, and its efforts are well aligned with the national and global bioeconomy targets on transitioning from fossil-based resources to renewables.

- Ambitious scientific agenda
- Supporting industrial renewal
- Internationally recognized competence centre in materials bioeconomy

Acknowledgements

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Engineered Lignin Products

Learnings and Aspects on Kraft Lignin Separation and Valorisation

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Abstract

Process-integrated, continuous, separation of lignin from kraft pulp mills which results in a lignin with low ash content (0.05-1 %) is relatively new technology compared to traditional kraft pulping sub-processes, like recovery boilers, lime kilns, white liquor preparation etc. The LignoBoost technology was demonstrated in 2007 and the first commercial full-scale process started in 2013, delivered to Domtar by Valmet. This means that this concept now has been in commercial scale operation for almost 10 years. There is also an alternative commercialized concept available today from another supplier, NORAM International. The idea to integrate lignin separation into a kraft pulp mill is today quite proven commercial technology.

This paper will discuss different learnings, experiences, from the early development of the LignoBoost process, which includes handling of the separated lignin followed by drying. The dust explosion risk is relatively high for dry kraft lignin due to a high kst value – so the paper will also discuss if there are opportunities to reduce this risk. The paper will also briefly discuss promising product segments for kraft lignin.

LignoForce^{TM} Lignin as a Biopolyol in Rigid Polyurethane Foams

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Abstract

This study focussed on evaluating the use of unmodified LignoForce^{TM} kraft lignin as a partial petroleum-based polyol replacement in rigid polyurethane foams (PU). Three different approaches were selected for evaluation:

- LignoForce^{TM} lignin was mixed with the commercial polyol before making the PU foam by adding p-MDI and catalyst (conventional approach)
- LignoForce^{TM} lignin was mixed with p-MDI, before making PU foam by adding the commercial polyol and catalyst
- LignoForce^{TM} lignin was mixed with p-MDI and catalyst to make a p-MDI lignin pre- polymer, before adding the commercial polyol

In this study, the effect of incorporating lignin at several levels of polyol replacement on the thermal, mechanical and physical properties and structure of the PU foams was investigated. GPC (Gel Permeation Chromatography) and ^{31}P NMR (Phosphorus 31 Nuclear Magnetic Resonance spectroscopy were used to evaluate the molecular weight distribution and hydroxyl group content, respectively of the lignins used.

The results showed that the lignin extracted from a black liquor of a Western Canadian kraft mill had an Mw of 4836 Da and a polydispersity index (PDI) of 3.98. The total hydroxyl group content was 6.6 g/mol comprised of 0.58, 2.31, 1.63, and 2.05 g/mol of carboxylic, non- condensed phenolic, condensed phenolic and aliphatic hydroxyl groups, respectively – this made this lignin a good candidate polyol for rigid PU foam production. The results also showed that the second and third approaches were the most advantageous ones for making PU foams since their use led to the production of lignin-based PU foams with up to 45 % polyol replacement by lignin with mechanical and physical properties comparable to those of the control.

Introduction

During the kraft pulping process lignin is removed by cooking wood chips with white liquor (a mixture of sodium hydroxide and sodium hydrosulphide) at high temperatures and pressures. The lignin ends up in the residual weak black liquor which is concentrated by evaporation to about 70 % solids before being fired into the recovery boiler where it is combusted in order to generate steam, electricity and cooking chemicals for internal mill use (Kouisni et al., 2016). In addition to its use as a biofuel, lignin has the potential to be used in several high value applications such as adhesives (Ang et al., 2019), coatings (Carlos de Haro et al., 2019), insulation foams (Hayati et al., 2018) and thermoplastics (Ortiz-Serna et al., 2020). The extraction and use of kraft lignin in high-value applications can bring additional benefits to kraft pulp mills while concurrently meeting customer demand for low-carbon footprint materials. However, it is well known that the use of lignin in most applications is limited to low substitution levels. This is mainly due to the heterogeneity of lignin as evidenced by its high

polydispersity and the reduced accessibility of its functional groups to various common chemical reagents – these lead to variable physical and chemical properties which make the use of lignin in several industrial applications rather difficult (Sun and Tomkinson, 2001).

Polyurethanes are one of the most used synthetic polymers in the world. They are produced by reacting a diisocyanate or polyisocyanate such as toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI)) with a diol or polyol (such as polyethylene adipate and poly(tetramethylene ether)glycol). This reaction leads to the formation of urethane linkages. The presence of two or more hydroxyl and isocyanate groups on the polyol and polyisocyanate molecules, respectively, leads to the production of polyurethane polymers. Polyols and isocyanates are commonly synthetized from petroleum sources. Due to the increasing demand for polyurethane materials and their high cost, it is essential to come up with new approaches for replacing petroleum based polyols and/or isocyanates with renewable, less expensive alternatives.

In this study, lignin was first produced from the black liquor of a Western Canadian mill using the LignoForceTM process and characterized. This lignin was then used, as is, as a substitute for petroleum-based polyols in rigid polyurethane foams using three different approaches. Finally, the PU foams made were tested for several physical and mechanical properties of interest and compared with a reference foam (no lignin used).

Lignin extraction and characterization

The LignoForceTM process was used for the extraction of lignin from 38 wt.-% solids black liquor from a Western Canadian mill. As done in this process, 100 L of black liquor was first oxidized at 85-100 °C using oxygen (O_2). The oxidation was carried out in a 200-L reactor equipped with a sparger and stopped when the sulfide (S2-) concentration in black liquor reached the 0-1 g/l range. Carbon dioxide was then used to acidify the oxidized black liquor. The pH and temperature of acidification were adjusted at 9.8 and 74-80 °C, respectively. 13.5 kg of lignin slurry was fed to a LAROX filter press during the first filtration step. The temperature of filtration was adjusted at 25-35 °C. Subsequently, the lignin cake was washed to remove impurities. Three washing steps were applied for each run: a first acid wash using sulfuric acid at 2 %, a second acid wash using sulfuric acid at 0.2 % and, a water wash. The obtained lignin was characterized, and its main features are summarized in *Table 1* shows that the solids content of the obtained lignin is high while the levels of ash, sodium, sulfur, soap and carbohydrate are relatively low. This indicates that this lignin was washed well.

Table 1. Characteristics of the obtained LignoForceTM lignin.

Analysis	LignoForce^{TM} lignin
Total solids, %	56.4
Ash content, % (OD)	0.75
Na, % (OD)	0.21
S, % (OD)	1.34
Carbohydrates, % (OD)	2.48
Mw, g/mol	4836
Mn, g/mol	1214
Mw/Mn	3.98
Soap, % (OD)	1.92
Calorific value, BTU/lb	11856
First decomposition temperature, °C	241.26

Table 2. Lignin hydroxyl functional groups

Hydroxyl functional groups, mmol/g	Lignin-Domtar April
COOH - Terminal	0.25
COOH - Benzene ring	0.33
Total -COOH	0.58
Phenolic –OH (guaiacyl)	2.15
Phenolic –OH (syringyl)	0.00
Free Phenolic –OH	0.16
Total non-condensed phenolic-OH	2.31
Total aliphatic-OH	2.08
Condensed phenolic units – DPM	0.56
Condensed phenolic units - 4-O-5′	0.53
Condensed phenolic units - 5-5′	0.54
Total condensed phenolic units	1.63
Total hydroxyl units:	6.6

The main hydroxyl functional groups of the lignin produced were determined using ^{31}P NMR analysis. As seen in Table 2, the obtained LignoForceTM kraft lignin produced contained relatively high levels of carboxylic acid, aliphatic, non-condensed phenolic and condensed phenolic hydroxyl groups. Based on its main structural features as presented above, it was determined that this lignin could be used in several high-value applications including phenol formaldehyde resins and polyurethane foams.

Lignin-based rigid polyurethane (PU) foams

The dried lignin was used to prepare PU foams using three different approaches:

- LignoForceTM lignin was mixed with the commercial polyol before making the PU foam by adding p-MDI and catalyst (conventional approach)
- LignoForceTM lignin was mixed with p-MDI, before making PU foam by adding the commercial polyol and catalyst (Method 1)
- LignoForceTM lignin was mixed with p-MDI and catalyst to make a p-MDI-lignin prepolymer, before adding the commercial polyol (Method 2)

The lignin was mixed with isocyanate (or commercial polyol) in a 500-mL cup for 5 min using a high-speed mixer to get a homogenous mixture. The desired amounts of isocyanate (or commercial polyol), surfactant, catalyst and blowing agent were mixed in a separate cup. The mixture obtained was then mixed with lignin and isocyanate (or commercial polyol) at 2000 rpm for 4-6 s. Subsequently, the mixer was immediately removed, and the foam was left to rise in free expansion. The obtained foam was kept at room temperature for 24h to ensure complete curing before characterization.

Figure 1 shows the effect of incorporating kraft lignin using the methods cited above on PU foam physical and mechanical properties. The lignin-based PU foams produced had a slightly higher density compared to the reference. When the conventional method was used, up to 30 wt.-% polyol replacement by lignin, the lignin-based PU foams showed comparable physical and mechanical properties to those of the reference foam, except for the modulus which was lower (32 vs 64 kPa). When Method 1 or 2 was used, up to 45 wt.-% polyol replacement by lignin, the lignin-based PU foams obtained had comparable or better physical and mechanical properties than those of the reference foam. In fact, the lignin-based PU foams obtained using Method 1 or 2 displayed a thermal conductivity of 0.0286 and 0.0275 W/m.K, respectively, compared to 0.0303 W/m.K for the reference foam. The same trend was observed when it comes to water absorption - the lignin-based PU foams obtained using Methods 1 and 2 showed a significantly higher resistance to water absorption since the water gain was only about 50 and 26 %, respectively, of the original dry foam mass compared to about 121 % for the reference foam. The Max stress and Modulus obtained, however, are similar for the lignin-based PU foams and the reference. These results clearly demonstrate the effectiveness of Methods 1 and 2 when it comes to the preparation of high-quality lignin-based PU foams at high petroleum- based polyol replacement levels by lignin as compared to the conventional method.

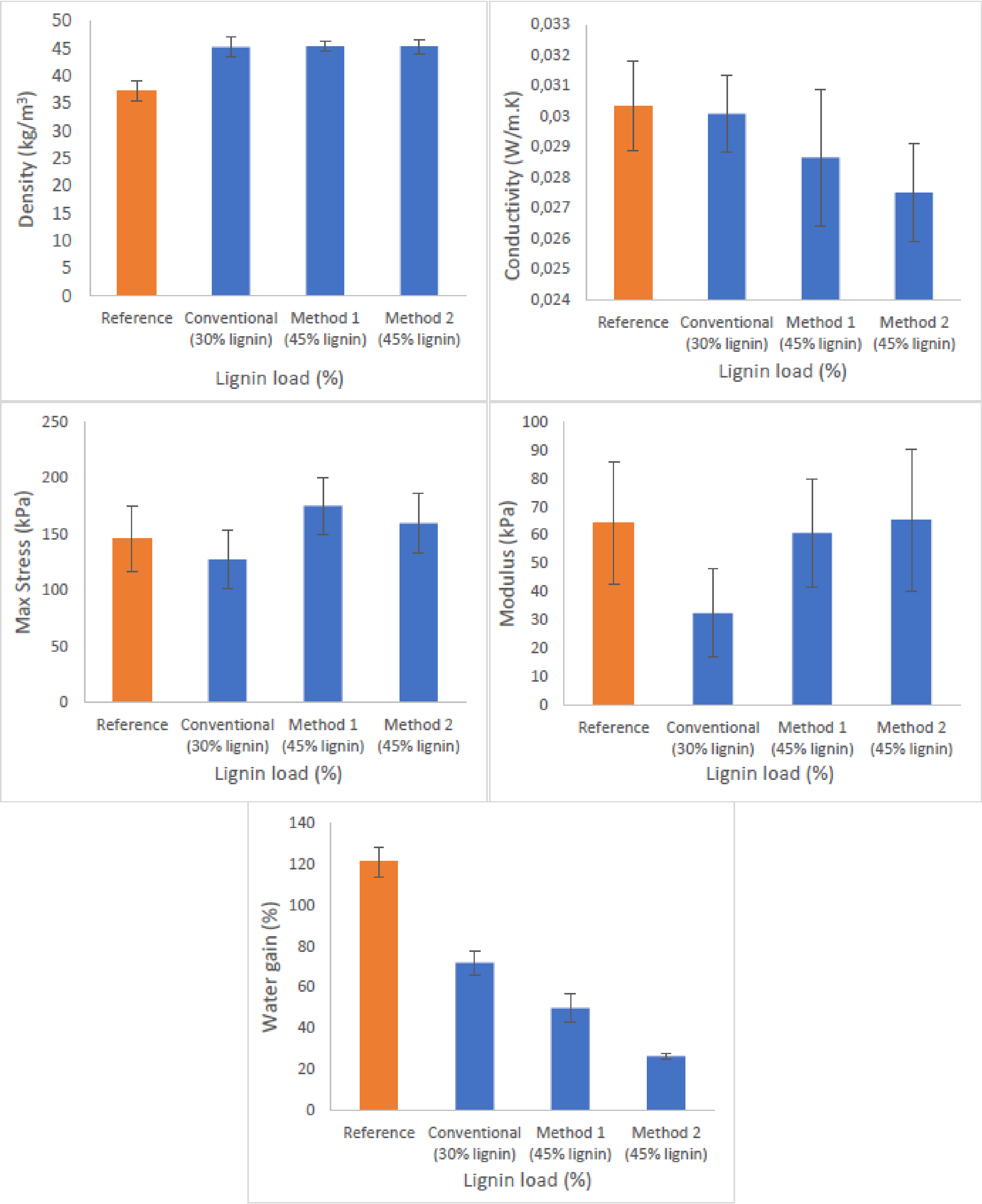

Figure 1. Mechanical and physical properties of the PU foams produced in this study.

Conclusions

Based on the results obtained in this work, incorporating kraft lignin in PU foams by solubilizing/dispersing the lignin in the polyol (conventional method) is technically possible up to the 30 wt.-% petroleum-based polyol replacement level without any major negative impact on foam properties. However, incorporating kraft lignin in PU foams by solubilizing/dispersing the lignin in the isocyanate (Methods 1 and 2) appears to enable the use of lignin in PU foams up to the 45 wt.-% petroleum-based polyol replacement level. In fact, in the latter case, the thermal conductivity and water absorption properties are better than the control while the strength properties are comparable to the control. It also appears from the data that Method 2 is somewhat better than Method 1 in terms of the thermal conductivity and water resistance of the foams made.

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Engineered Lignin Products

A New Biorefinery Approach for Production of Lignin-Carbohydrate Functional Hybrids

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Abstract

Traditional biorefineries focus on maximal separation of the main biomass components to produce the highest purity of biorefinery products assuming their best application performance. However, recent studies demonstrated advanced performance of lignin-carbohydrate mixtures in specific applications implying lignin-carbohydrate synergism. Examples of lignin-carbohydrate hybrids (LCHs) include various lignin-carbohydrate complexes (LCCs), where lignin and carbohydrate are chemically linked, physical mixtures of lignin and crystalline cellulose (CelloLignins and LignoCelluloses) as well as their combinations. Therefore, it makes sense optimizing different biorefinery processes for the best performance of these LCHs thus avoiding severe, expensive and often environmentally damaging purification of the biorefinery streams. Herein, we present a green, simple, and flexible biorefinery concept for integrated utilization of all major biomass components for high-value applications with the focus on lignin-carbohydrate functional hybrids (LCHs). The suggested biorefinery concept allows much greater flexibility in optimizing LCH characteristics desirable for specific applications than traditional pulping processes. Such LCH engineering, at the same time, requires an efficient strategy capable of handling large datasets to find correlations between process variables, LCH composition, structures and properties and finally their performance in different applications.

Introduction

Plant biomass is a potential source of renewable energy, but by far not the only one: other alternatives might be more successful. However, plant biomass is the main source of renewable chemicals. The valorization of polymeric and oligomeric lignin, hemicelluloses and cellulose for high-value products is desirable for best benefits from integrated biorefineries as a sound alternative to the current bioethanol or monomeric sugars production (Balakshin et al., 2021; Ragauskas et al., 2014; Mikkonen, 2020)

Importantly, the traditional biorefinery approaches, both industrial and emerging, imply maximal separation of the biomass components targeting high-purity products (Sixta, 2006); there is also an assumption on direct correlation between the purity of a product and its value. Biorefinery lignins – lignins from sugar-based, biofuel-targeting biorefineries – are usually considered as low value products of approximately fuel value, which is primarily due to their low lignin purities (Balakshin et al., 2021; Ragauskas et al., 2014; Balakshin & Capanema, 2016). However, harnessing lignin-carbohydrate synergism of biorefinery streams, demonstrated recently (Balakshin et al., 2021; Mikkonen, 2020) is a very promising direction for advanced biorefineries showing better performance (at lower costs) of lignocellulosic hybrids (LCH). A few examples are so-called Cellolignins (lignins with minor amounts of cellulose) and Lignocelluloses (celluloses with minor amounts of lignin) in specific applications than that of pure lignin or cellulose. This approach may be considered as novel because it shows a conceptional difference compared to the exhaustive biomass fractionation.

Lignin-Carbohydrate Complexes (LCCs) represent another good example for the synergism between lignin and carbohydrates and therefore can be very valuable biorefinery products. LCCs combine chemically linked aromatic and carbohydrate moieties exhibiting amphiphilic properties that create unique possibilities for their compatibility with different bioproducts (Balakshin et al., 2014). The main limitation in the LCC valorization is the lack of industrially relevant methods for LCC isolation and low yields 0.4-0.8% of the original biomass (Tarasov et al., 2022).

Thus, biorefinery approaches providing different high-value streams from all biomass components is of top importance. In particular, engineering of LCH in the new biorefinery concept and their further exploitation is of high interest. To develop an advanced integrated and industrially feasible biorefinery approach, a Hydrothermal Treatment (HTT) and Supercritical Water Hydrolysis (SWH) were used.

Results and discussion

Cellulose-containing biorefinery crude lignins as high-value products

The first part of the work has been mainly conducted with a specific type of biorefinery lignins, so called Omno PolymersTM, products of the Plantrose technology, which consists of a 2-stage process involving subsequent subcritical and supercritical water hydrolysis (SSWH) of plant biomass (Balakshin & Capanema, 2016). SSWH lignins were tested in direct replacement of PF adhesives using the Automatic Bond Evaluation System (ABES) test. Surprisingly, the crude lignins containing 20-45 % residual cellulose exhibited superior performance in lignin – plywood PF blends (30 % substitution), superior to the corresponding high-purity lignins without cellulose accompaniment (Figure 2). A sample with about equal amounts of lignin and cellulose performing best. Similar results were obtained with lignin-PF resin blends for oriented strand boards (OSB). The ratio of lignin to cellulose is not the only influencing factor; cellulose characteristics have also a strong effect on the bond performance (Balakshin & Capanema, 2016). Pilot trials on plywood and OSB panel production showed that about 35 % of resin could be replaced with SSWH lignin without any increase in the hot press time, which is the usual bottleneck in production.

Selected SSWH lignins showed significantly higher bond performance than other technical lignins that originated from various pulping processes (Kraft, soda, organosolv) and different biomass (SW, HW, non-wood) (Figure 2). The performance of cellulose-free lignin (SHL-50), extracted out of SSWH, was similar to that of the reference lignins. These data underline the key role of the cellulose part in the SSWH lignins.

To explain the superior performance of crude biorefinery lignins, it was suggested5 that the crystalline cellulose in crude biorefinery lignins might have a similarly positive influence on lignin performance as CNC reviewed recently (Balakshin et al., 2021). Although the effect of the residual crystalline cellulose in crude biorefinery lignins on lignin performance is not as pronounced than that of pure CNC, the production costs of crude biorefinery lignins are dramatically lower than those of pure CNC ($5-7/kg). The Plantrose^{TM} process also produces highly crystalline cellulose streams containing minor amounts of lignin for which the above-discussed lignin-CNC/CNF synergism could also be valid (Balakshin et al., 2021) The understanding of the mechanism of this lignin-cellulose synergism and the optimum cellulose characteristics (MW, degree of crystallinity, crystal dimension, cellulose I/II ratio) are of primary importance for a purposeful engineering of optimal biorefinery lignins for specific applications (Balakshin & Capanema, 2016).

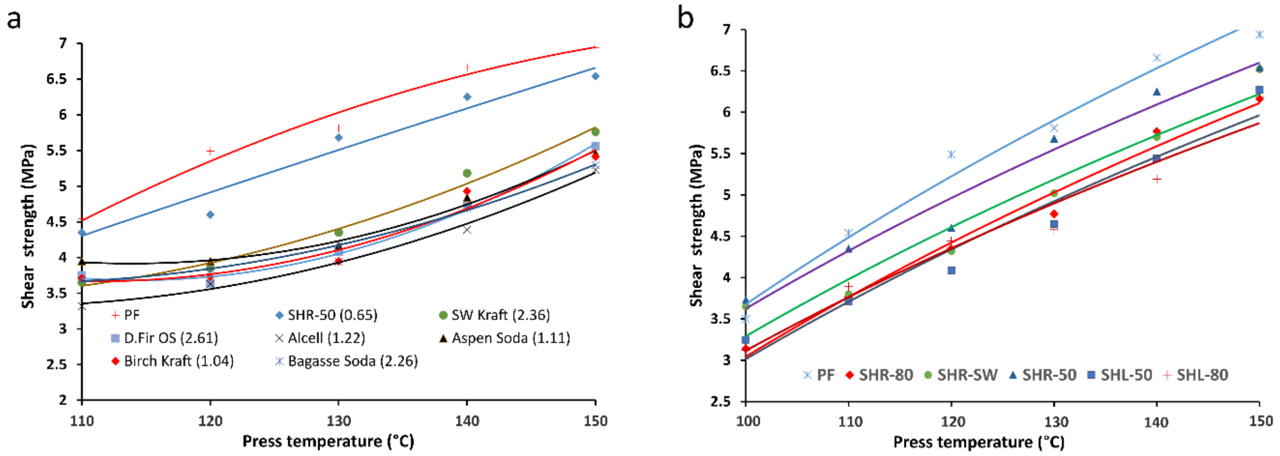

*Figure 2. ABES bonding strength (at 90 s press time) of plywood PF blended with lignins (70:30 w/w); Left: SSWH lignin (SHR-50) versus different technical lignins; right: different SSWH lignins. * SHR: supercritical hydrolysis residue (hardwood), the number corresponds to the lignin content; SHR-SW: supercritical hydrolysis residue produced from softwood (pine); SHL: supercritical hydrolysis lignin extracted from the corresponding SHR.*

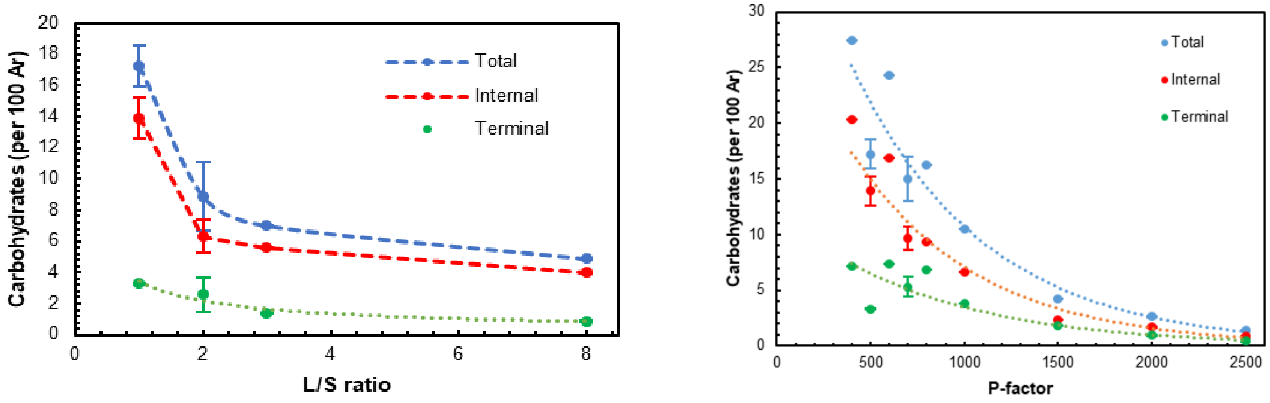

Figure 3. The effect of the L/S ratio (P-factor = 500) and P-factor (L/S=1) on the carbohydrate contents in acetone-extracted LCCs (AELs).

LCH from AqSO process

The positive lignin-cellulosic synergism discovered with SSWH LCH was one of the main points in the development of a new biorefinery process in our very recent studies Tarasov et al., 2022. The established process consisted of a modified hydrothermal treatment (HTT) of birch wood followed by solvent extraction of the resulting solids and is therefore named as AquaSolv Omni (AqSO) biorefinery. AqSO biorefinery produces three major streams: hydrolysate (hemicelluloses-derived products), solvent-extracted lignin-carbohydrate complexes (LCCs) and cellulose-rich fibers. Specific process conditions were found to facilitate production of LCCs of different types in high yields as a new valuable and industrially realistic process stream.

Surprisingly, acetone-extracted LCC (AEL) with significant carbohydrate content was produced at the Liquid-Solid (L/S) ratio of 1 (Figure 3a). LCC linkages were confirmed by 2D NMR. A low HTT severity (P factor~400-600) resulted in AELs with the highest carbohydrate content, which was significantly reduced as the severity increased (Figure 3b). A part of the extractable LCC apparently originated from partially cleaved native LCC that enables its extraction with the solvent. Another part of LCC was hypothesized to be formed during HTT. This was in agreement with the highest LCC content at the lowest L/S ratio (AEL-1); the low L/S ratio increased the concentrations of lignin and carbohydrates in the reaction mixture and thus facilitated the formation of new LCC linkages. An increase in the L/S ratio resulted in degradation of LCC linkages (Figure 3a), likely due to higher amount of water in the reaction system shifting the competition between the hydrolysis and formation of LCC to the former. Eventually, the amount of carbohydrates in AELs decreased with increasing severity (Figure 3b) due to degradation of LCC linkages as well as carbohydrate (mainly Xyl) moieties in LCCs themselves.

Lignin nanoparticles (LNPs) have emerged as a rapidly growing field in lignin research and have found to be relevant building blocks in many applications ranging from biomedicine to composites (Moreno & Sipponen, 2020). We reported the first successful LCC nanoparticle (LCCNP) production, from the produced AELs (in the whole range of AqSO conditions) and elucidate their basic properties and potential applications. Among different potential applications of LNPs, their use as stabilizers for oil-water Pickering emulsions is very attractive. In this context, the behavior of LCCNPs for the stabilization and radical polymerization of tetrahydrofurfuryl methacrylate (THFMA)-based Pickering emulsions was investigated (Figure 4a) (Tarasov et al., 2022). Eventually, LCCNPs from AEL-500 and PLCC (a pine native LCC preparation) were selected as model particles due to their different tendency to interfacial agglomeration (Figure 4, compare a and c).

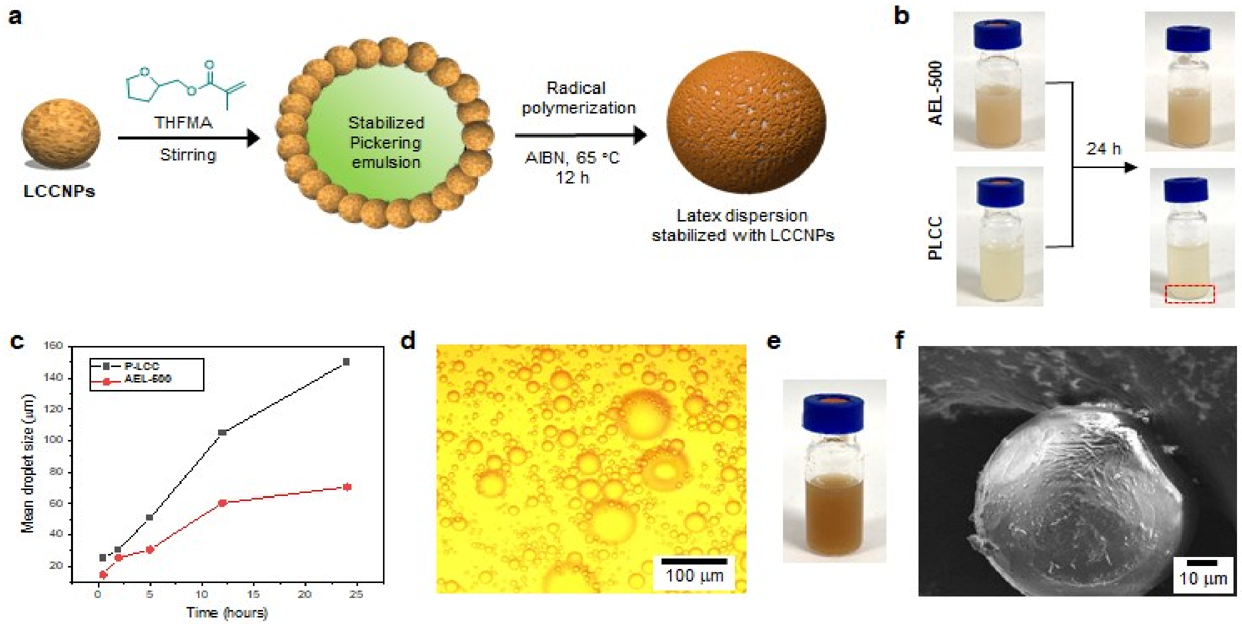

Figure 4. (a) Schematic diagram of the use of LCCNPs as surfactants in Pickering emulsion polymerization process. (b) Digital images of THFMA-Pickering emulsions stabilized with LCCNPs from AEL-500 and PLCC at different time. (c) Time evolution of mean droplet size of THFMA-Pickering emulsions stabilized with PLCC NPs and AEL-500 NPs. (d) Optical microscopic and (e) Digital images of latex dispersion after polymerization process. (f) A SEM image of the P-LCC NPs-coated poly(THFMA) microbeads after free radical polymerization at 65 °C.

Here, it is important to note that THFMA-Pickering emulsions stabilized with LCCNPs from AEL-500 were found significantly more stable in contrast to those obtained from a native PLCC (smaller droplet size and no visual phase separation, compare Figure 4b and c). Therefore, free radical polymerization (FRP) of THFMA-based Pickering emulsions using LCCNPs from AEL-500 and AIBN as a thermal initiator at 65 °C was studied (Figure 4a). Stable latex dispersions were obtained from the polymerization (Figure 4e). SEM and optical light microscopy methods revealed uniform spherical polymeric microbeads with a similar size to that of the initial monomer droplets (Figure 4d and f). The microscopic images clearly showed that the THFMA microspheres contained a thin amorphous layer of LCCNPs (Figure 4f), which indicate that LCCNPs can enable the polymerization process in aqueous media, Thus, AqSO LCCNPs have the potential to be used as building blocks to produce bio-based composites. Importantly, the best AEL preparation was found, and its properties were more suitable than those of reference native LCCs.

Integrated biorefinery approaches

The new integrated biorefinery approach summarized in Figure 5 suggests application of all process streams for quite high-value products in contrast to the traditional current biorefinery focused largely on the biofuel or monomeric sugar part. The AqSO biorefinery provides three major streams, namely hydrolysate (mainly hemicelluloses-derived products), solvent-extracted lignin/LCC (AEL) and cellulose-rich fiber (Lignocellulose). Additional streams are possible under more advanced scenarios, e.g., adding enzymatic hydrolysis/modification to the overall process. Although the process can provide rather efficient fractionation of wood components producing high purity products, it is of higher interest to explore the use of ligno-carbohydrates hybrids (LCH), such as Cellolignins and Lignocelluloses (Figure 5) in high-value applications where they have better performance than pure lignin and carbohydrates (Balakshin et al., 2021, Balakshin & Capanema, 2016). The unnecessity of deep fractionation of the wood components would also simplify the process and reduce its production costs. Furthermore, this option gives us more degree of freedom in products engineering.

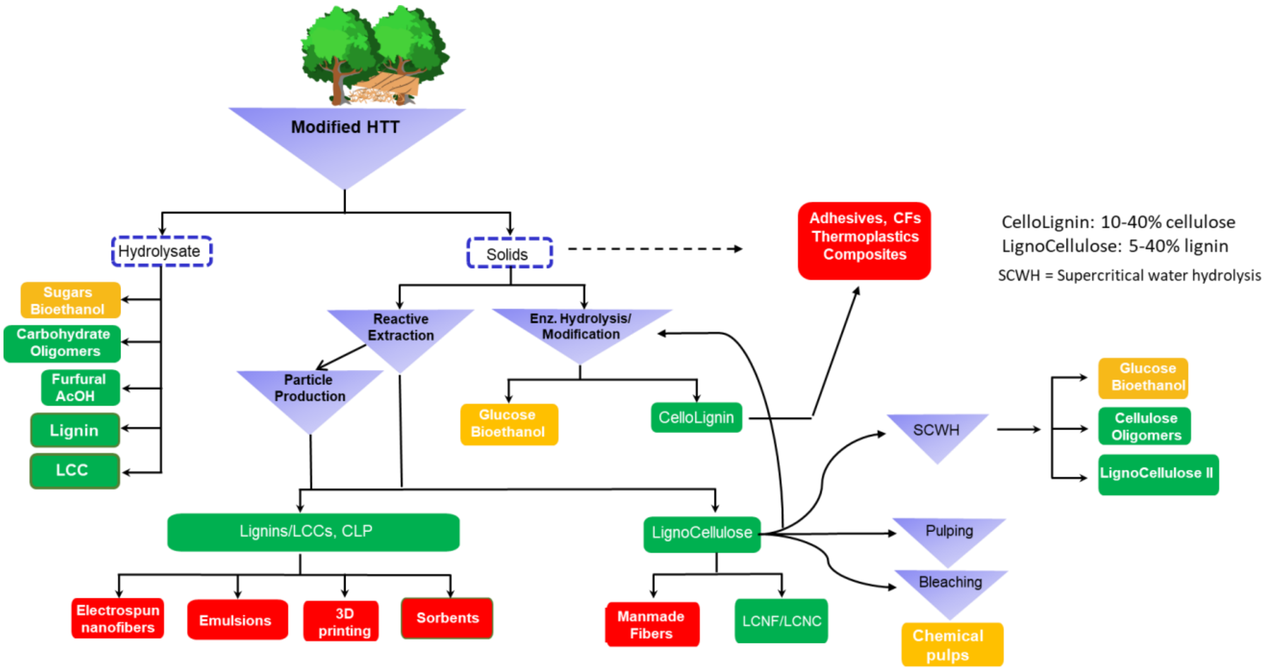

Figure 5. Examples of different scenarios for AqSO process as an advanced integrated biorefinery. Orange boxes show the traditional biorefinery products while green ones indicate additional valuable AqSO biorefinery streams and their potential applications (red)

In addition to Cellolignins and Lignocelluloses, our studies showed the possibility to produce LCC-type precursors as a new valuable process stream (Tarasov et al., 2022). This finding is of great importance as, despite of large interest in potential LCC applications, there is almost no process to manufacture industrially relevant LCC products at high yields yet; our discovery creates this opportunity. The produced LCCs possess special characteristics (e.g., higher share of lignin content, short carbohydrate chains) that should allow this LCC type to find an optimal niche in the application roadmap. One of them is LCCNPs production, for the first time, directly from the process stream and their application in specialty products, such as THFMA-Pickering emulsions stabilizer that enable the polymerization (Tarasov et al., 2022).

The hydrolysate can be traditionally used for sugars/bioethanol or/and preferably further fractionated to isolate specific useful products, such as oligosaccharides, lignin and LCC or used as is for high-value applications, e.g. surfactants (Mikkonen, 2020).

The Lignocellulose have the potential to be suitable precursors for Ioncell textile fiber production based on earlier studies with unbleached Kraft pulps (Ma et al., 2018). Further optimization of the properties of the solids to the application requirements is likely possible manipulating the process variables. On the other hand, solids with higher lignin content should be suitable for Ioncell CFs production (Trogen et al., 2021). High concentration of LCC linkages expected in the substrate should be important i). to avoid phase separation between cellulose and lignin and ii). to prevent lignin leaching in the coagulation bath and thus facilitate the recovery of ionic liquid used in the Ioncell process (Tarasov et al., 2022). In addition, Lignocelluloses can be used for production of lignin containing LCNF/LCNC (Balakshin et al., 2021) or/and processed through supercritical water hydrolysis biorefinery, pulping and/or bleaching.

Enzymatic hydrolysis or/and different types of enzymatic modifications of the solids can also be used to optimize the produced LCHs (e.g., their lignin:cellulose ratio, lignin and cellulose characteristics optimal for CFs, PF resins etc.) and to produce glucose as a co-product. It is important to highlight that, in contrast to the traditional biorefinery, the application of enzymes will be focused on the LCHs engineering rather than on the glucose yield.

The AqSO biorefinery allows for a wide range of structure and properties characteristics giving a large room for products engineering per required characteristics. Therefore, it can provide with LCH precursors to a wide variety of applications: from lignin-based carbons or carbon fibers to lignin containing thermoplastic blends, colloids and surfactants by simply tuning the process conditions without any additional input of chemicals or additives.

AqSO biorefinery should have a rather different niche vs various OS and new advanced “lignin-first” biorefineries processes (Abu-Omar et al., 2021). The latter is designed to provide lignins suitable for aromatic monomers production via lignin decomposition and has clear advantage in this area. However, the AqSO biorefinery is much simpler than the OS and “lignin-first” processes. Therefore, the application of its products in replacement of commodity petrochemicals of high market sizes would be more economically feasible, while OS and “lignin-first” biorefinery products should be used in specialty applications. Thus, these biorefinery approaches complement each other in expanding the area of sustainable biomass-derived products rather than compete for the same market. The decision on optimum integrated biorefinery approaches and specific conditions must be made based on sound process-structure-performance correlations for all involved biorefinery streams and considerations of economic aspects.

Closing remarks

Current biorefinery concepts should be elaborated and optimized for integrated utilization of all products in high-value applications rather than focusing on bioethanol, biofuels or sugars only, as is still common at present. Engineering of lignin and LCH for high-value applications will be a game changer within these efforts. Biorefinery lignins and LCH will become the main target in such optimized biorefineries, while sugars/bioethanol are still utilized and valued, although now actually being by-products.

From this angle, recently developed AqSO biorefinery looks very promising as a green, simple and flexible process for advanced integrated biorifenery allowing valorizarion of all biomass components for high-value products. First examples for high potential of AqSO products were reported. LCC nanoparticles were produced for the first time directly from the solvent extract. The LCCNPs had unique properties and showed good application potential, e.g., in stabilization of THFMA-Pickering emulsions for the corresponding polymer production. In addition, AqSO LCHs showed promising results in direct replacement of PF resins used in wood adhesives. The cellulose-rich solids with low lignin content (<7 %) can be a good precursor for Ioncell textile fiber production. High amounts of chemical linkages between lignin and polysaccharides is expected to give additional benefit for the application performance of AqSO products. The high flexibility of the process enables engineering of the resulted products in a wide range of chemical composition, structure and properties and therefore allows a large space to optimize the products for specific high-value applications. Thus, AqSO Biorefinery should be a new and valuable contribution to the existing biorefinery scenarios expanding biorefinery portfolio.

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Engineered Lignin Products

LigniOx Lignins as Sustainable Bio-Based Dispersants

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Abstract

Recently, a concept of an alkali-O_2 oxidation (LigniOx) process for producing lignin dispersants at a kraft pulp mill has been introduced. The LigniOx process uses O_2 gas to increase the anionic charge of lignin and the final oxidised lignin product can serve as a concrete plasticiser or versatile dispersant. Besides kraft lignin, the oxidation has been applied to other lignin by-streams, such as organosolv and hydrolysis lignin, to provide water-soluble anionic lignin dispersants.

Anionic dispersants cover most of the dispersant market. Concrete plasticisers are anionic dispersants that disperse cement particles to allow good workability of fresh concrete and ensure good strength properties of the matured concrete. Similarly, anionic dispersants are used in preparing paints and coatings containing a high portion of different inorganic pigments. LigniOx dispersants have been demonstrated to work in these applications. Their performance has been measured to be superior to the commercial lignosulphonate products and even to compete with some of the synthetic superplasticizers.

Lately, several novel application areas for LigniOx lignins have been explored. These evaluations include testing of LigniOx lignins as gypsum plasticizer, anti-scaling agent, flotation aid (depressant) and as a component in agricultural products. In addition to the results of concrete studies, results of selected examples of the new end uses of LigniOx lignins will be presented. Furthermore, the biodegradability of LigniOx lignins in soil and aquatic environment was followed by measuring CO_2 evolution. Kraft lignin and a lignosulfonate product were tested for comparison. The study indicated that oxidation of lignin increases their biodegradation. Based on an environmental life cycle assessment, the LigniOx product outperformed the fossil-based superplasticiser and polyacrylic acid in several impact categories, including reduced effect on climate change.

Introduction

LigniOx (alkali-O_2 oxidation) process was developed to provide new and higher value end- uses for lignin from various biorefinery processes. Today only small fraction of lignin at kraft pulp mills are separated and used in other applications than for energy production. There is also growing interest to consider new biorefinery processes that also result to lignin by-streams, which could be valorized. Recently, a concept of LigniOx process for feasible production of lignin dispersants at a kraft pulp mill has been introduced (Kalliola et al., 2022). The focus of the application studies has been in concrete and gypsum applications where LigniOx can reduce the needed water amount and therefore resulting to higher strength concrete and lower energy use in gypsum board production.

Experimental

Oxidized lignin samples

Molar mass (Mw) of oxidized lignins (originating from kraft, organosolv, and hydrolysis lignin) varied from 3750 to 25890 Da and the anionic charge at pH 6 from 2.1 to 3.5 (Vilkman et al., 2022). The anionic charge can be attributed to carboxylic acids and hydroxyl-p-quinones introduced in lignin during oxidation and more overturning lignin into a biobased dispersant. While the oxidized lignins are soluble under the conditions of pH 6, the charge could be determined unlike for kraft lignin, which is only soluble under highly alkaline conditions (Kalliola, 2015).

Results and discussion

Mortar and Gypsum results

In mortar and gypsum test LigniOx samples were compared to standard plasticizers used in these applications (*Table 3*).

Table 3. Plasticizer materials used in the mortar and gypsum experiments.

Material abbreviation	Material description
LS	Lignosulfonate
SNF	Sodium naphthalene sulfonate
PCE	Polycarboxylate ether
LigniOx A	Oxidized kraft lignin A
LigniOx K1	Oxidized kraft lignin 1
LigniOx K2	Oxidized kraft lignin 2

Mortar tests were performed by slump test according to EN 1015-3. Comparison of different plasticizer chemistries were performed in mortar by analyzing initial slump. Higher slump

indicates better dispersion and results to lower viscosity, which allows to reduce water amount and achieve higher strength in cured concrete. Figure 6 display comparison of the different typical chemistries against LigniOx A. It is evident in this comparison that LigniOx A is clearly better than Lignosulfonate and had currently performance between naphthalenesulfonate and polycarboxylate ether.

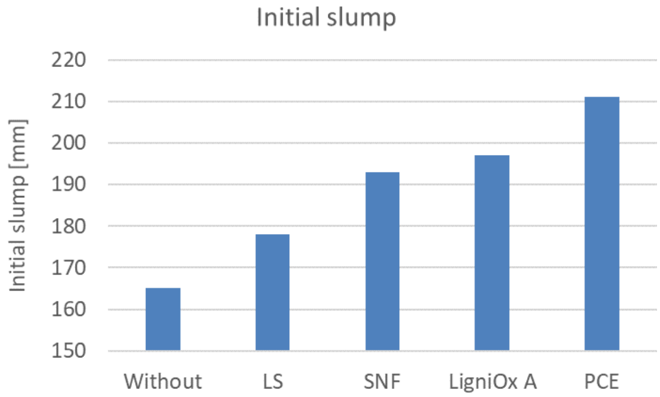

Figure 6. Initial slump values for different plasticizer chemistries commonly used in concrete production

The gypsum slump tests were performed by lifting a ring (Ø 5cm and height 10 cm) filled with gypsum slurry and measuring the slump. LigniOx K1 and K2 were compared in gypsum formulation against reference material SNF (Figure 7). With addition level of 0.20 % the slump results with both LigniOx samples were close to the reference. The post treatment of the LigniOx materials were different indicating that K2 has slightly better slump performance.

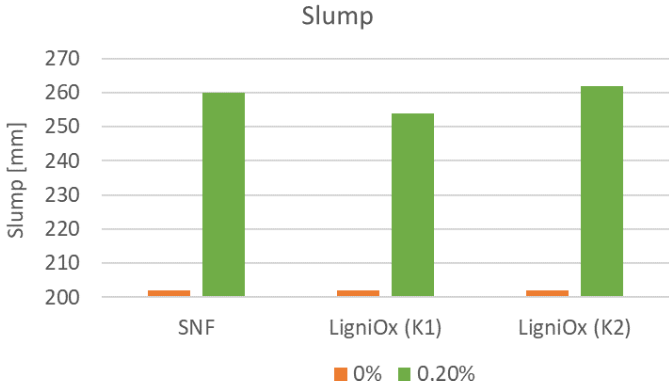

Figure 7. Slump values for polynaphthalenesulfonate and LigniOx K1 and LigniOx K2 in gypsum.

Biodegradability of LigniOx lignin

Any dispersants used in an agricultural product or in water treatment can end-up in the soil, fresh water, or the marine environment. Therefore, to ensure environmental safety, biodegradability is an important property. Biodegradability is not dependent on the origin of material (biobased or synthetic); rather, it is a function of the physicochemical properties (Sapea 2021). The biodegradability of alkali-O_2 oxidized lignins (kraft, organosolv, and hydrolysis lignin) was evaluated in a recent study by Vikman et al., (2022). The oxidized lignins exhibited higher biodegradation in soil and in aquatic environments in comparison to a commercial kraft lignin and a commercial lignosulfonate. In soil, the biodegradabililties of oxidized lignins were 19 to 44 %, whereas the reference lignins exhibited only 5 to 12 % conversion to CO_2 (*Table 4*). Biodegradation.of the oxidized lignins and references in the aquatic environment increased in a similar order as in the soil environment, although the degradation in each sample was slightly smaller, than in the soil. The improved biodegradability of the oxidized lignins was due to the altered chemical structure of lignin. Compared to the untreated lignin, the oxidized lignin contained structures formed in aromatic ring opening reactions, making the lignin more accessible to microbial degradation. In addition, the oxidized lignin contained carbon originating from small organic compounds, which are easily biodegradable.

Improved biodegradability of the lignin products will support the approach towards more sustainable processes and consumables. However, the biodegradability study could be complemented by a more detailed investigation on environmental safety of the novel dispersants produced from the oxidized lignins.

Table 4. Biodegradation and relative biodegradation of oxidized Lignins in soil and aquatic environments

Sample	Lignin (% of dm)	Biodegradation (%)		Biodegradation in relation to MC (%)	
		Soil 6 months	Aquatic 5 months	Soil	Aquatic
Microcrystalline cellulose, MC	-	66	81		
LigniOx-KL	70.8	19	11	28	14
LigniOx-OSL	77.1	28	21	42	26
LigniOx-HL	62.6	39	29	59	36
Crude LigniOx-OSL	59.2	45	30	68	38
KL-Ref	94.6	5	7	7	9
LS-Ref	82.0	12	14	18	13

Life cycle assessment of LigniOx lignin

Recently, Neethi et al., (2022) completed a life cycle assessment (LCA) of LigniOx kraft lignin in comparison with a concrete superplasticizer product and PAA (polyacrylic acid, a dispersant product) (Figure 8). In this study, the production of LigniOx lignin was integrated into an existing kraft pulp mill. The results demonstrated that oxidized lignin performs clearly better than the commercially available oil-based products in most of the impact categories of the LCA assessment. The majority of environmental impacts of LigniOx lignin were from the main kraft pulping process, e.g., eutrophication that originates from the fly ash purging as well as chlorine dioxide and acidification that originate from chlorine dioxide bleaching of kraft pulp fibers. The study indicated that the production of LigniOx lignin is more attractive than the production of conventionally recovered kraft lignin. In addition, the results of LigniOx lignin were better when compared with other bio-based products, such as polyacrylic acids and carboxymethylated cellulose.

Conclusions

LigniOx products show comparable or better performance to existing market references in cement and gypsum applications. It clearly outperforms biobased Lignosulfonate in mortar application and show promising comparison against fossil-based naphthalene sulfonate.

LigniOx process has been found to enhance the biodegradation of lignin in soil and aquatic environments. In addition to the adequate biodegradability of the oxidized lignins, the better performance in environmental factors in the LCA demonstrates the high potential of oxidized lignins as an environmentally friendly alternative for oil-based products.

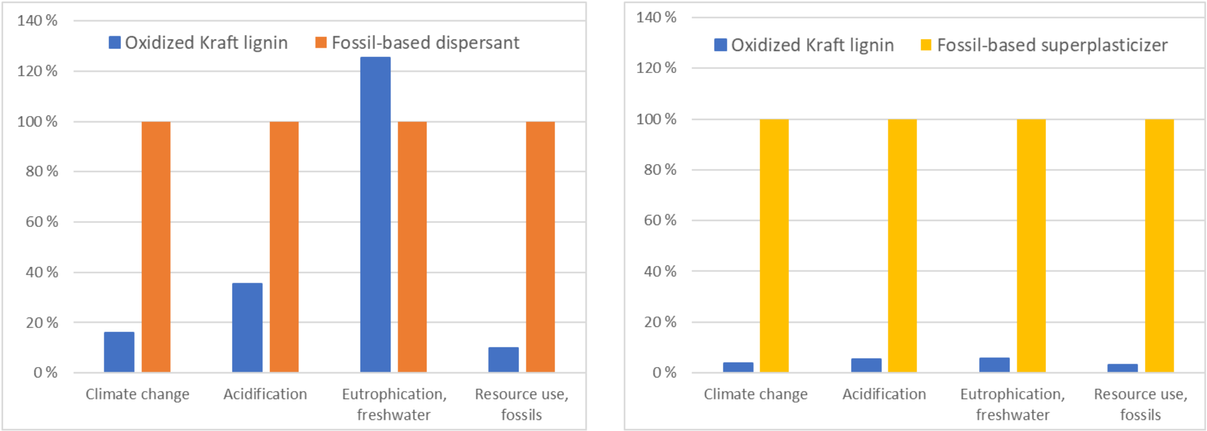

Figure 8. Comparison of oxidized kraft lignin (LigniOx lignin) with fossil-based dispersant (left) and fossil- based superplasticizer admixture (right).

Acknowledgements

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Fibenol's Biorefinery – from Secondary Woody Biomass to Chemical Building Blocks

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Abstract

Fibenol is constructing a unique biorefinery (operational in 2023) to valorise 30 000 t/a of residual hardwood into chemical building blocks, namely lignin, cellulosic sugars, and microcrystalline cellulose. These products help to make the chemical industry more sustainable by replacing fossil chemicals with bio-based chemicals.

The biorefinery uses Sunburst™ pre-treatment technology, which combines mechanical grinding, dilute acid catalysis and steam explosion in under 30 seconds. Compared to commercially available Kraft lignin, the resulting extrusion-based lignin (LIGNOVA™) is near-native in structure and contains almost no sulphur, thus making it odour-free. The cellulosic sugars are comparable with food-based sugars in quality, but have a significantly lower water and land use. Fibenol's microcrystalline cellulose is a versatile raw material for many industries, acting as a rheology modifier, barrier material or a strength additive.

In this work, Fibenol's technology, materials and end-use applications are explored in detail.

Introduction

Fibenol is an Estonian company, aiming to make the chemical industry more sustainable by replacing fossil chemicals with bio-based chemicals. To achieve that, a unique biorefinery is currently under construction (expected to be commercially operational in 2023) to valorise 30 000 t/a of residual hardwood into chemical building blocks, namely lignin, cellulosic sugars, and microcrystalline cellulose. Currently birch is used as the main raw material, although other hardwood species (such as alder) are also promising.

Fibenol's biorefinery, constructed in Imavere, Estonia, is based on Sunburst™ pre-treatment technology. By using a specialized extruder, mechanical grinding, dilute acid catalysis and steam explosion are combined to convert solid hardwood chips into slurry in under 30 seconds. The hemicellulose component of wood is already depolymerized into water-soluble sugar monomers, whereas lignin and cellulose remain in the solid phase. The resulting wood-based suspension is then subjected to a series of downstream processing steps, resulting in cellulosic sugars, lignin and/or microcrystalline cellulose, depending on the process route.

Fractionation – from slurry to materials

Figure 9 displays Fibenol's main fractionation process, which yields C5 sugars (rich in xylose, derived from hemicellulose), C6 sugars (rich in glucose, derived from cellulose) and lignin (LIGNOVA Crude). First, water-soluble C5 sugars are separated and concentrated to roughly 60 % solid content. Remaining solid lignin-cellulose cake is enzymatically treated to hydrolyse cellulose to glucose monomers. After separation, LIGNOVA Crude and C6 sugars (rich in glucose, later concentrated to 60 % solid content) are obtained.

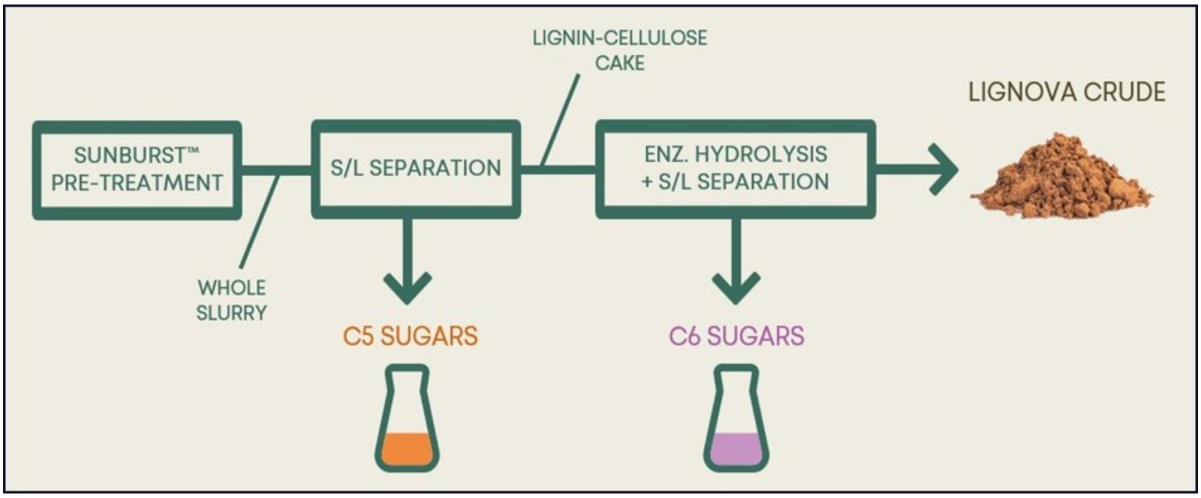

Figure 9. Fibenol's main process route: pre-treated biomass separation to cellulosic sugars and LIGNOVA Crude.

Alternatively, a more advanced process route (Figure 10) may be taken to obtain microcrystalline cellulose and LIGNOVA Pure instead of C6 sugars and LIGNOVA Crude, respectively. The key difference between the standard process route is the lignin-cellulose cake handling stage: instead of hydrolysing cellulose to glucose, lignin is dissolved in alkali and separated. This yields microcrystalline cellulose (subjected to further refining), whereas alkaline lignin is precipitated and separated to produce higher-purity lignin (LIGNOVA Pure).

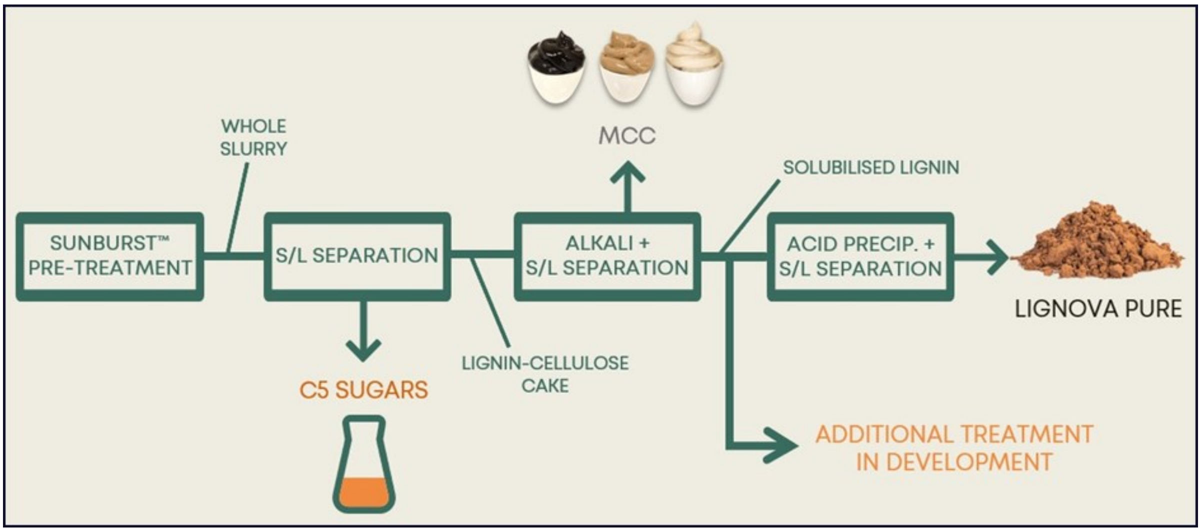

Figure 10. Fibenol's advanced process route: pre-treated biomass separation to C5 sugars, microcrystalline cellulose and LIGNOVA Pure.

Cellulosic sugars – replacing food with wood for sugar production

Two different streams of cellulosic sugars may be produced – either rich in xylose (C5 sugars) or rich in glucose (C6 sugars), detailed comparison shown in *Table 5*. Compared to conventional food-sourced sugars, cellulosic sugars have a lower water and land use and do not compete with farmland.

Table 5. Comparison of C5 and C6 sugars.

	C5 sugars	C6 sugars
Composition (% of dry matter)		
Pentose	50-55	8-13
Hexose	20-25	80-85
Oligomers	4-6	1-3
Organic acids	2-4	1-2
Ash	8-13	1-3
Lignin	3-5	1-3
Properties		
Overall solid content (%)	50-65	50-65
pH	4.0-4.5	5.5-6.0

End-use applications for Fibenol's cellulosic sugars include fermentation to single cell protein, ethanol or other chemical building blocks such as 1,4-butanediol.

LIGNOVA – extrusion-based lignin for replacing fossil-based aromatics

As seen in Figure 9 and Figure 10, the production methods for LIGNOVA Crude and Pure are different. Although both grades are near-native in structure, there are notable differences in composition and properties, outlined in *Table 6*.

Table 6. Comparison of LIGNOVA Crude and Pure.

	LIGNOVA Crude	LIGNOVA Pure
Composition		
Lignin (%)	88-90	93-95
Cellulose (%)	4-6	0
Ash (%)	1-2	1-2
Sulphur (%)	<0.2	<0.2
Properties		
Molecular weight, Mw (kDa)	16	10
Aliphatic OH-content (mmol/g)	2.5	2.2
Phenolic OH-content (mmol/g)	2.2	3.0
Melt behaviour onset temperature (°C)	N/A	180

Both LIGNOVA grades have end-use applications in various industries. Depending on the exact application, the cellulose content and higher molecular weight of LIGNOVA Crude may be beneficial or detrimental compared to LIGNOVA Pure. In addition to being a sustainable bio- based raw material and reducing the carbon footprint if replacing fossil-based materials, LIGNOVA may bring various other benefits in as described in *Table 7*.

Table 7. LIGNOVA in the composite and PF resin industries

Application	Examples	Adding LIGNOVA…
Composite materials	Injection moulded engineering details, plastic bags and films, extrusion moulded profiles	• Reduces the melt viscosity of bio-based composites • Increases rigidity of the composite • Increases antioxidant capacity
Phenol formaldehyde resins	Plywood resins, phenolic foams, impregnation resins	• Reduces hazards from handling phenol and formaldehyde • May increase adhesive strength

Furthermore, promising developments have been made by using LIGNOVA for developing asphalt roads (bitumen replacement), polyurethane materials (polyol replacement), personal care products (UV-blocking active ingredient), carbon materials and other areas.

Compared to common fossil-based chemicals, there are significantly less greenhouse gas emissions related to LIGNOVA. For example, the emissions related to phenol production, a common fossil building block, are roughly 3.0 kg CO_2 eq/kg product[1], whereas the emissions related to the production of LIGNOVA Crude are approximately 0.3 kg CO_2 eq/kg product.

Microcrystalline cellulose – micro-scale material with nano-scale properties

Table 8. Crude, blonde and white microcrystalline cellulose.

	Crude MCC	Blonde MCC	White MCC
Composition (% of dry matter)			
Glucose monomers	65-75	85-95	90-100
Hemicellulose	1-2	1-2	1-2
Lignin	25-30	5-10	2-5
Inorganic material	5-10	3-6	2-5
Sulphur	<0.05	<0.05	<0.05
Properties			
Total solid content (%)	15-20		
Crystal structure	Native cellulose Iβ		
Degree of polymerisation	<100		

The structure of Fibenol's microcrystalline cellulose (MCC) is defined by the pre-treatment technology: the amorphous bonds in the cellulose structure are broken and mainly crystalline cellulose material is obtained. This leads to significantly smaller cellulose molecules compared to the cellulose fibres seen in the pulping industry, which in turn presents unique properties. There are similarities with cellulose nanomaterials, although Fibenol's specialty cellulose is aggregated to microscale particles, thus easing handling.

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[1] Ecoinvent v3.8 database

Microcrystalline cellulose (MCC) is produced along with LIGNOVA Pure. After separating solubilised alkaline lignin, the remaining MCC is subjected to bleaching to reduce the lignin content. Overall, three MCC grades are available: crude, blonde and white, differences outlined in *Table 8*.

Given the unique properties of Fibenol's specialty cellulose, there are a myriad of applications where this material could be used as shown in Table 9. Given the crystalline structure, MCC performs as a shear-thinning rheology modifier: the viscosity of a system increases, but applying shear reduces the viscosity exponentially. This property finds uses in paints and adhesives as well as concrete mixtures. Furthermore, MCC can be used as a strength additive in the paper industry.

Table 9. Microcrystalline cellulose applications.

MCC function	Industry
Rheology modification	Paints, adhesives, concrete mixtures
Strength improvement	Pulp and paper
Grease and oxygen barrier improvement	Coatings, films, packaging

Conclusions

Fibenol is building a biorefinery in Imavere Estonia to fractionate residual birch into lignin, cellulosic sugars and microcrystalline cellulose. The fractionation is based on Sunburst™ pre- treatment technology, which combines mechanical grinding, dilute acid catalysis and steam explosion in under 30 seconds. The mild technology yields sulphur-free products with small environmental footprint.

Each biorefinery product has numerous application areas: cellulosic sugars find applications in biofuels as well as fermentation processes to produce other chemical building blocks. Lignin can be used as a bio-based aromatic polymer in the plastic industry, adhesives, foams, etc. The rheology modification properties combined with barrier and strength additive properties make microcrystalline cellulose an attractive material for paints, coatings, adhesives, construction as well as pulp and paper.

Acknowledgements

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New Methods to Control the Sodium and Sulphur Balance of Kraft Pulp Mills

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Abstract

This paper discusses and introduces a new, more selective removal method for sulfur, applicable for the kraft pulping process. The process is based on a technique previously utilized in other industries, but not previously utilized within the kraft pulping process: bacterial treatment of a part of the green liquor flow, which produces elemental sulfur as the main product.

Background information of the technique combined with piloting experiences performed on- site at a softwood kraft pulp mill in the Nordics during a period of two years is discussed. The aim is that by introducing this technique, a more selective purge of sulfur from the kraft process is obtained, thus paving the way for the introduction of additional biorefinery concepts into the kraft pulp mill system with smaller impact upon the process economy.

Introduction

The sodium and sulfur balance of a kraft pulp mills is essential to maintain production at the mill, both from a cost and environmental perspective but also from a processing perspective.

Main input of sulfur in the regular softwood kraft pulp mill is related to production of crude tall oil, as well as the use of chemicals such as magnesium sulfate and others in fiber lines. Implementation of biorefinery techniques into the softwood mill, such as lignin production, often involves the use of sulfuric acid, leading to a change in the sodium/sulfur balance of the mill.

This balance is normally maintained by the removal of so-called recovery boiler dust, or ESP -dust which composition varies from mill to mill. Normally, the dust is composed of a large fraction of sodium sulfate and minor fractions of sodium carbonate and alkali chlorides. This means that the loss of sodium is considerable when removing the ESP-dust for sulfur reasons, and the need for replacing the lost sodium with fresh chemicals arises. Fresh, or make-up, NaOH is normally used, which is adding to the production costs of the mill.

In the light of the above, more selective methods to remove sulfur is needed. Options involving electrochemical methods have been proposed (Cloutier et al, 2014), and so also methods based on removing sulfur containing gases to produce either sodium bisulfite or sulfuric acid. In this work we are proposing a new method to remove sulfur from the kraft pulp mill based on bacterial technology previously used for treatment of sulfur containing gases in various industries.

The method is based on the utilization of the Thiopaq-technique (Janssen et al, 2009), utilizing green liquor as feed while producing elemental sulfur, see Figure 11.

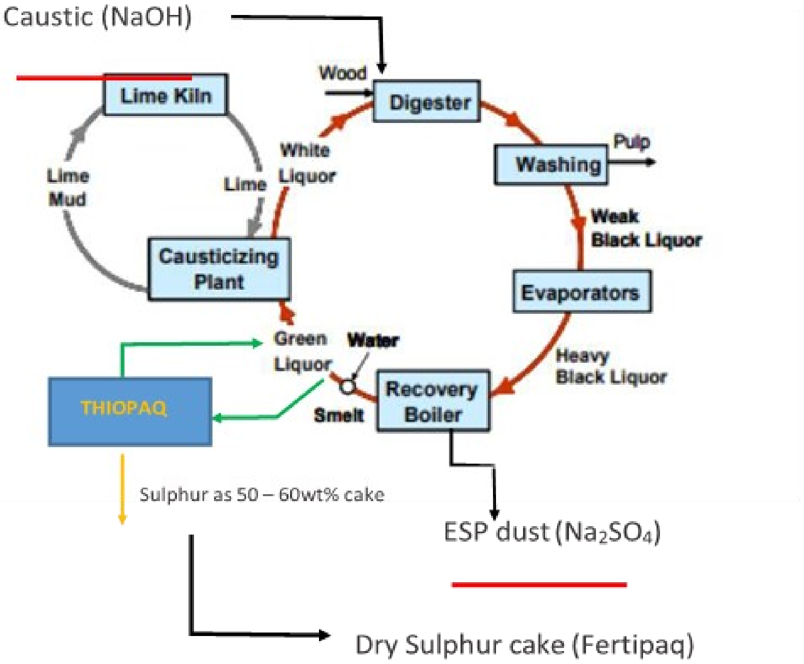

Figure 11. Ultilization of the Thiopaq techniqe to produce elemental sulfur from the green liquor.

The work presented here is based on the filing of two patent applications (van Zessen et al, 2019a, b) where further details are found.

Biological processes for sulfur removal

Basically, in the newly developed technology the sulfide is converted to elemental sulfur and caustic. This conversion can be carried out by aerobic autotrophic sulfide oxidizing bacteria. The produced caustic will result in an increase in pH to such an extent that without any precautions the pH would be over 12. Therefor the presence of carbonates, and the addition of CO_2 is applied to keep the pH around 10. The general reaction for this is showed below, equation 1.

$$2\ NaHS + O_2 + CO_2 \rightarrow Na_2CO_3 + 2\ S + H_2O \qquad (1)$$

It should be realized that green liquor is an alkaline solution high in salt, in which bacterial activity is normally not encountered. However, there are the so-called salt lakes that have bacterial sulfide oxidizing activity. These lakes can be found throughout the world. Examples are the lakes in Altai Mountains, salts lakes in Mongolia, China and Egypt, but also the salt planes in South America. A typical example of a salt lake is Mono Lake in the USA. Bacteria found in these lakes can convert sulfide to elemental sulfur solemnly relying on CO_2 as carbon source (Sorokin et al., 2005).

The activity of two different wildtype sulfide oxidizing strains as a function of salt concentration and pH is shown in Figure 12. Obviously, there are bacteria that can tolerate the harsh environment of the green liquor with respect to pH and salt concentration. The temperature though needs to be controlled to between 25 °C and 30 °C.

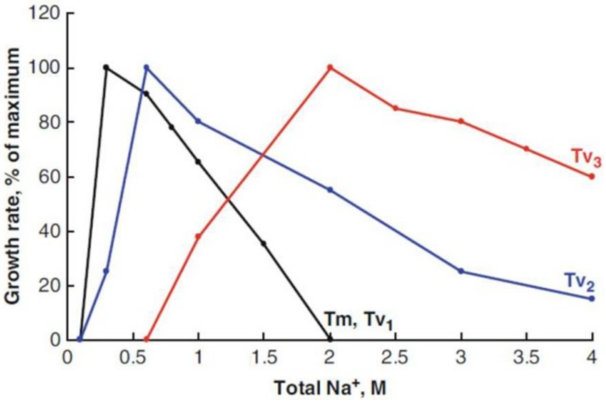

Figure 12. Activity of bacteria as a function of the salt concentration and pH is 10. Data adapted from (Sorokin et al 2005). Tm and Tv1 are low salt tolerant; Tv2 extremely natronotolerant;Tv3 extremely natronophilic.

Experimental

Laboratory trials

In a first explorative research project the possibility of treating the green liquor with bacteria in a small 2L bioreactor was tested. This bioreactor was continuous fed with green liquor supplied from a Stora Enso mill. The bioreactor was inoculated with biomass from a full-scale operating plant treating sulfide rich process water. The main conclusion was that the bacteria were able to survive and multiply and the major challenge observed in the laboratory trial was to prevent the scaling of sodium bicarbonate ($NaHCO_3$), Figure 13. This was accomplished by operating the bioreactor at pH ~ 10.

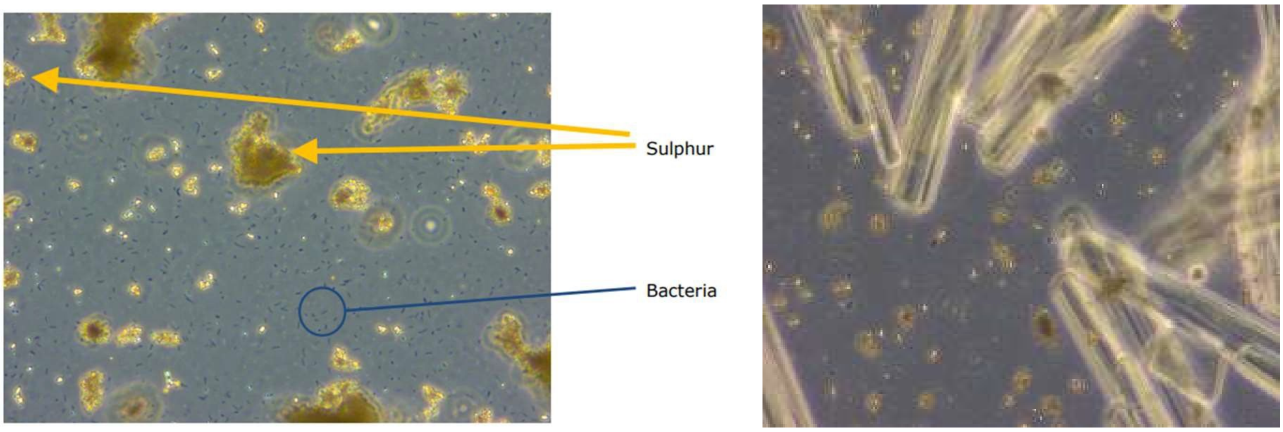

Figure 13. Sulfur produced and the bacteria in the laboratory trials (left) and crystals of sodium bicarbonate formed during the initial trials (right).

Demonstration Plant

In the next phase of the project, a larger demonstration plant was designed, built, and operated at one of the production sites of Stora Enso. A bioreactor of 5 m^3 operating volume was used, and the pilot plant was placed in the vicinity of the recausticizing plant, see Figure 14. Filtered green liquor directly from the production was used as main raw material for the process. Additional utilities to the pilot plant such as carbon dioxide, water, compressed air were supplied by the mill. After cooling down the green liquor it was mixed outside the bioreactor with the bioreactor liquid, and the bioreactor temperature was controlled with additional cooling. Air was added with a blower, nutrients to support the growth of the bacteria were added, and the pH was controlled by dosing CO_2. Produced sulfur was separated through gravity settling. The feed flow of the green liquor was controlled with a flow meter. In case dilution water was needed it was dosed based on fixed ratio with the green liquor.

The demonstration plant was operated by the mill itself, and the operation lasted from 2019 till 2021.

Figure 14. Picture of the demonstration/pilot plant used in the mill environment.

Results and discussion

In the first year of operation the green liquor was only cooled and any dilution with additional water was not applied. Temperature of the process was maintained well around 35 °C, and the pH, through the addition of CO_2, was kept above 9.5. Any scaling of $NaHCO_3$ was not observed, and stable performance was reported, Figure 15.

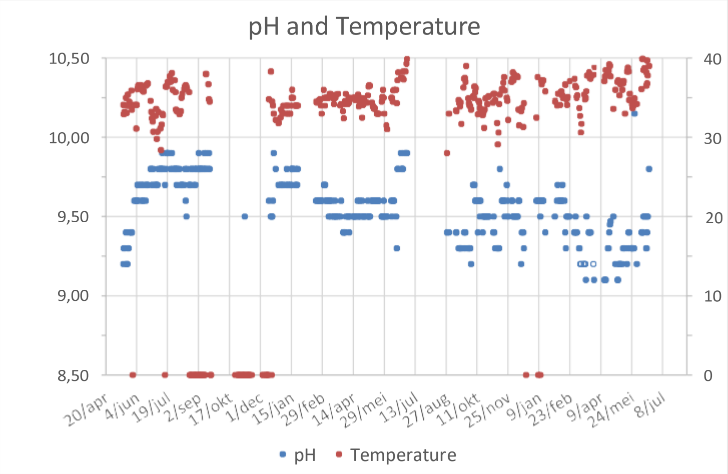

Figure 15. Temperature and pH profile of the reactor liquor in the demonstration plant over two years of operation.

In the first year it was noted that the throughput of green liquor was limited due to the amount of air available in the reactor. It also became clear that the control of the oxygen supply with air was limited through the low solubility of oxygen in the sodium rich process liquor. Based on the overall water balance, it was deemed possible to dilute the green liquor. Consequently, the green liquor throughput could be increased (almost 5 times), Figure 16. In the second year and the final months of the demonstration work, the throughput could easily be increased, without experiencing any operational issues. The dilution was limited to maximum 1:1 dilution of the green liquor.

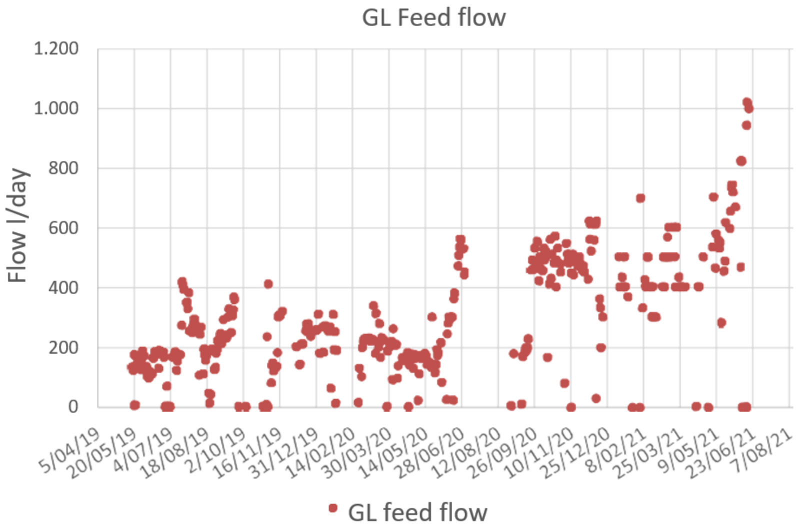

Figure 16. Flow of green liquor to the reactor over two years of operation.

During the demonstration period of almost two years the pulp mill experienced scheduled and unscheduled maintenance outages. The duration of the outages lasted from several days to several weeks. During these maintenance periods, the pilot plant was put on standstill and the bacteria were kept in the bioreactor without any additional measures. Directly after the maintenance of the mill was completed, the demonstration plant was started. Within two days the demonstration plant could recover the load again. During the complete demonstration period, the bioreactor was not reseeded with fresh bacteria at all. Any upset condition, either in the causticizing plant or demonstration plant itself, could be dealt with by the bacteria which recovered to full activity without reseeding.

The green liquor is a highly concentrated sulfide solution. However, during the complete two- year demonstration period, sulfide smell in the off gas of the bioreactor, sulfide smell when taking bioreactor samples or sulfide smell of effluent flow of the gravity settler was not noted.

Sulfur produced

The bacterial conversion of sulfide with air will yield elemental sulfur (eq 2). In case of over- aeration also sulfate can be produced according to equation 3 below.

$$NaHS + ½\ O_2 + 0.66\ CO_2 \rightarrow 0.33\ NaHCO_3 + 0.33\ Na_2CO_3 + S(s) + 0.33\ H_2O \qquad (2)$$

and

$$NaHS + NaHCO_3 + 2\ O_2 \rightarrow Na_2SO_4 + H_2O + CO_2{}' \qquad (3)$$

The typical sulfur percentage, or yield, produced was 70 % on average, but up to 80% sulfur yield was measured, meaning that up to 80 % of the ingoing hydrogen sulfide was turned into elemental sulfur. The produced sulfur is hydrophilic and can be easily dispersed in water. The particles are of sufficient size that they can be easily separated with gravity settling,

Table 10 shows the sulfur and sodium contents of the unwashed and washed solid sulfur cake, compared to sodium sulfate. Unwashed cake contained a relatively high level of sodium, as green liquor is forming the basis of the surrounding liquor. Simple washing trials in the laboratory revealed that the sodium contamination may easily be decreased to below 1 %, thus enabling a high recovery rate of the sodium back to the pulp mill. As comparison, sodium sul fate has a lower fraction of sulfur compared even to the unwashed sampled, meaning that purging even a poorly washed sulfur cake could be viable compared to purging ESP-dust.

Table 10. Sodium and sulfur content in recovered pilot sulfur cake, washed and unwashed compared to sodium sulfate.

Sample	Sodium content (mass-%)	Sulfur content (mass-%)
Unwashed sulfur	36 %	62 %
Washed sulfur	0.1 %	99.4 %
Na_2SO_4 (as comparison)	33.4 %	22.5 %

Scaling experiences

Green liquor is produced at the mill at highest possible salt concentration to decrease the evaporation need of the resulting black liquor. If salt concentrations in green liquor are too high, scaling of sodium salts, predominantly pirssonite, may appear that hamper the production in the recausticizing area (Frederick et al, 1990). This is known within the industry, and production measures to avoid scaling exist.

In the present work it was expected that the scaling risk within the reactor was severe, and that one obvious problem would be to prepare and arrange cleaning and reseeding of the 6 m^3- reactor during the project. However, no scaling was observed in the reactor, apart from the green liquor feeding line entering the reactor. This is explained by the lower pH in the reactor compared to green liquor, as well as partial dilution of the green liquor during the later phase of the project.

Conclusions from the piloting study

In this work, a bacterial process to remove sulfur selectively was piloted in the kraft pulp mill environment, and the following conclusions may be drawn from the study:

- The bacterial process is stable over time and recovers well after mill shutdowns and outages.
- Bacteria used in the process survives green liquor conditions, reseeding was never performed.
- Scaling of sodium salts such as pirssonite was not experienced in the pilot plant, neither in the reactor itself of surrounding piping, due to pH adjustment and dilution of the green liquor.
- Sulfur yield in the conversion was >70 % without optimization, measured as conversion of sulfide in treated green liquor to elemental sulfur
- Elemental sulfur produced showed a high purity after laboratory washing
- Compared to removal of ESP-dust, this method could decrease the need for NaOH-make- up at the mill scale.
- Mill implications and impacts are mill specific and needs to be treated separately. Acknowledgements

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Low Emission Biorefineries and Side-Stream Valorization

Valorization of Industrial Spruce Bark by Alkaline Extraction

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Abstract

Industrial bark is an abundant side-stream from the debarking of wood logs by the forest industries. Nowadays the bark is mainly treated as energy source in the mills but other applications of bark are also being sought. Softwood bark is composed of cellulose, non-cellulosic polysaccharides, lignin, high amounts of tannins and other extractives, and inorganic compounds. Alkaline extractions of spruce bark conducted under a wide range of process conditions showed that between 20-27 % of the bark could be extracted as polyphenols, mainly tannins and some lignin, with a molar mass of about 2-3 KDa (Borrega et al., 2022). For comparison, the polyphenol yield from water extractions conducted under similar temperature and time was only about 4 % on bark.

The polyphenols in the black liquor from two selected extractions, conducted at 100 ˚C with 15 % NaOH and at 160 ˚C with 24 % NaOH, were recovered by acidic precipitation and tested as surfactants. The composition of the polyphenol-rich precipitates was dependent on the extraction conditions; lower extraction temperature increased the share of carbohydrates while higher temperature increased the share of lignin. Nonetheless, despite the different composition, the polyphenol-rich precipitates were able to decrease the surface tension in aqueous solutions and showed surface activity similar to that of a commercial biosurfactant (Borrega et al., 2022). The polyphenol-rich materials could also be used to partly replace phenol in resins for wood adhesives. Moreover, the utilization of alkali extracted polyphenols as preservative component in construction wood is currently being investigated.

In addition to extraction of polyphenols in high yield, alkaline extractions of bark leave a cellulose-rich bark residue that may be exploited in various applications. For instance, the utilization of residual spruce bark (after alkaline extraction) in saccharification trials demonstrated that up to 94% of the polysaccharide fraction could be hydrolyzed into monosugars (Borrega et al., 2022). The bark residues may also be used in pulping or to prepare nanofibrillated cellulose films with barrier properties. These results, coupled with preliminary techno-economic analyses, demonstrate that alkaline extraction is a promising and scalable technology for valorization of industrial bark side-streams.

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Low Emission Biorefineries and Side-Stream Valorization

Preparation, Characterization, and Application Evaluation of Different Sawdust-Based Green and Versatile Chemicals and Materials for Sawdust Valorization

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Abstract

Two biorefinery processes have been established, beyond the present-state-of-the-arts with sound technical and economic feasibilities, to convert softwood sawdust to green and versatile products for value added applications. There are five biorefinery products, namely glucomannan (GM), ammoxidated lignin, hydrophilic micro- & nano- fibre (MNF) (i.e., carboxymethylated MNF, CM-MNF), hydrophobic MNF (i.e., alkylated CM-MNF), and neat CM-MNF or GM--CM-MNF film. They have been examined as films for water vapor & oxygen barriers and for water or oil absorptions, as dispersed powder in PLA polymer, or as fire retardant agent for spruce wood.

Introduction

Sawmill production is one key business in forest industry worldwide. It is especially important for Södra whose overall industry includes 51,000 forest owners to retailers/consumers. There is today an annual 15.9 million m^3 of sawnwood production in Södra's sawmills, which is one of the largest sawmill operations in Europe. However, sawmills experience a low profit margin; only ca. 50 % of sawlogs ends up as sawnwoods. It should be vital to improve the sawmill side streams' value. In fact, there is a large quantity of sawdust (SD), annually ca. 4 million m^3, that is co- produced in Södra (by a rule of thumb of 1/4 of the sawnwood production). Today, SD is used mainly as biofuel in thermal power stations and for particleboard production with limited values. SD should be further valorised by exploration of its better and new applications. Generally, biorefinery processing of SD could disintegrate it into its building chemical components, namely cellulose, hemicelluloses and lignin, and convert them further to value-added products in an integrated way to maximize the economic value of SD while reducing waste production. So far, however, no biorefinery process of SD, neither for component isolation, nor for component processing, is yet commercially running in Sweden. In this "ProfSaw" project funded by Södra, we have worked on a new concept of SD biorefinery that most uniquely not only all SD's chemical components will be extracted, processed, and utilized, but also the minuscule sizes will be taken as an advantage to produce micro- & nano- fibre (MNF) as nanocellulose or carboxymethylated cellulose

(CMC)-like material and its derived hydrophobic alkylated MNF as well as nitrogen containing lignin etc. for different novel or higher value (more profitable sawmill) applications.

Experimental

Dried softwood SD from Södra was size fractionated using a vibrating screen equipment. For the small size SD fractions (0.5-2 mm), microwave-assisted extraction (MAE) was conducted by two steps, first by 0.05 % NaOH at 200 °C for 8 min to prepare glucomannan (GM) by post- extraction ethanol precipitation of the solution and then by 1 % NaOH at 150 °C for 20 min for the residue to open SD fibre structure further. For the big size SD fraction (> 2 mm), extended impregnation (EI) was conducted at 110°C for 40 min using the white liquor for Kraft cooking. Ammoxidation (Ammo) was then conducted on the MAE- or EI treated SD using 40 % ammonia and 30% hydrogen peroxide in an autoclave by heating at 120 °C for 1 h to obtain MNF from MAE treated SD or delignified SD from EI treated SD as residues together with ammoxidated lignin (N-lignin) from the solution after freeze-drying. The MNF was then reacted with monochloroacetic acid in NaOH solution to obtain carboxymethylated MNF (CM-MNF) from which CM-MNF gel was prepared after homogenization using a fluidizer. The gel was finally dried and alkylated using diethyl carbonate to obtain alkylated CM-MNF (Alk-CM-MNF).

Different circular films were prepared in a membrane filtering system from ~0.1 % CM-MNF gel with or without pre-blending with GM. Alk-CM-MNF film was prepared after similar diethyl carbonate alkylation of dried CM-MNF film. CM-MNF and Alk-CM-MNF film strips were submerged into water or oil for 24 hours, the oil and water absorbed were measured as indicated by the changes of their weights. Alk-CM-MNF-PLA composites were prepared by blending PLA chloroform solution with Alk-CM-MNF particles followed by casting and then slow evaporation. For fire retardant property of N-lignin, a cone calorimeter was used at an irradiance of 50 kW/m2, using the spruce wood in 10 cm×10 cm×1.3 cm size impregnated with N-lignin solution first under vacuum and then under pressurised N2. Sample and property characterizations include also chemical composition, Maldi-TOF-MS, N-content, surface charge, contact angle, mechanical strength and water vapor and oxygen permeability.

Results and discussion

SD consists of different size fractions as revealed by vibration screening. 41.9 % is larger than 2 mm and termed “Big size fraction”. More SD, 51 %, is between 0.5 and 2 mm and termed “Small size fractions”. The rest, 6.3 %, has sizes <0.5 mm; this fraction is found difficult to be processed e.g., by filtration so it is excluded from our investigation.

There are two size dependent processes established (Figure 17). The primary, unique and new concept process is based on the small size fractions to use not only the chemical components but also the minuscule size advantage. It starts from MAE that is more heating-efficient than conventional heating and one of the advantageous green extraction methods. A two-step MAE has been conducted, to extract GM and then to further open SD fibre structure. The former has been optimized in terms of so-called unavoidable GM yield-molecular size compromise (Gulbrandsen et al., 2015) for the best GP yield but keeping GP’s high DP. The latter has been optimized for the best fibre opening indicated by the highest residue yield loss. The MAE treated SD is then reacted with ammonia and an oxidative agent (here hydrogen peroxide), commonly termed “Ammoxidation” (Ammo) by which lignin’s aromatic ring structure is attacked, forming different nitrogen containing structures jointly termed as nitrogenated lignin or N-lignin (Tyhoda, 2008). The N-lignin is mostly dissolved in the solution leading to SD delignification. The setup has been optimized as repetitive Ammo treatments for reaching such a total delignification extent that the treated SD could be homogenized by a fluidizer but keep some amounts of residual lignin. This residual lignin will innovatively contribute to MNF's extra barrier, hydrophobicity, and UV-screening properties. Two such samples with 4.7 and 3.0 % KL contents, termed high lignin-MNF (HL-MNF) and low lignin-MNF (LL-MNF), are prepared after two and three repetitive Ammo steps, respectively. Commonly, nanocellulose or CMC is produced by fluidization or homogenization from bleached chemical pulp with almost no residual lignin. Prior to the fluidization the pulp also needs to be defibrated by milling with a high energy consumption. As one major targeted product, our hydrophilic nanocellulose or CMC-like MNF is prepared after carboxymethylation of MNF, instead of using TEMPO oxidation (Vallejos et al., 2016), to introduce charges onto the fibres which facilitates fibrils' disintegration. This allows us starting from residual lignin containing MNF, skipping the pre-defibration before the fluidization and reducing the energy consumption in the fluidization itself. As a result, very hydrophilic nanocellulose-like CM- MNF gels are easily produced. Finally, all the hydrophilic OH groups including the methylcarboxyl groups in CM-MNF are ethylated using a green chemical, diethyl carbonate, to prepare a hydrophobic Alk-CM-MNF.

The secondary process is based on the big size fraction to fully use all SD. It starts from a so-called extended impregnation (EI) that was reported being effective for selective removal of hemicellulose from spruce without altering too much the other components (Wang et al., 2011). The second treatment is Ammo by adapting the optimized conditions mentioned above for the primary process to produce N-lignin and the residue termed "Delignified SD". No further treatment in this process has yet been investigated (Figure 17).

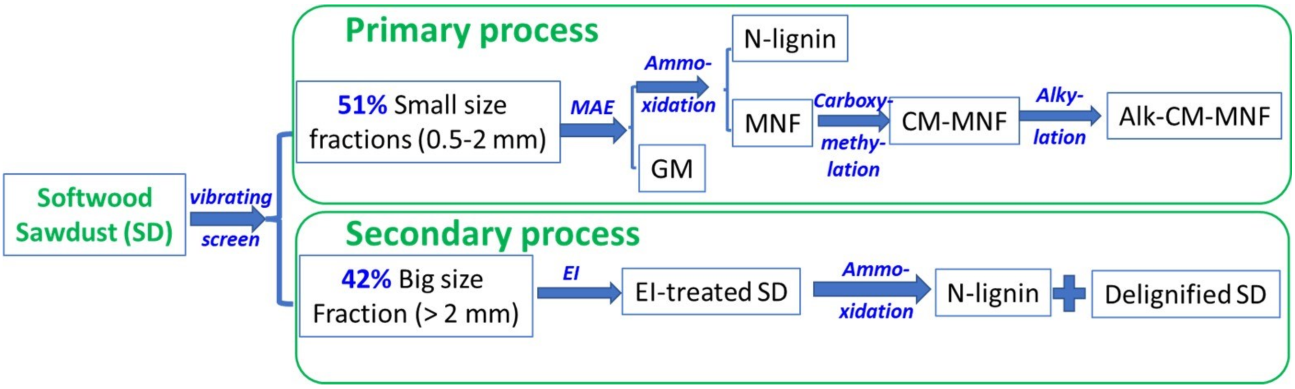

Figure 17. Size-dependent sawdust biorefinery processes

There are five biorefinery products prepared:

1. GM is obtained in a yield of 3.3 %, slightly higher than the highest yield of 2.7 % by (Chadni et al., 2019). It has a Mp (molecular weight at the peak) of 2000 Da corresponding to DP 12, as revealed by Maldi-TOF-MS analysis that also shows a clear pattern of 162 Da MS difference between all neighbouring peaks, indicating good GM purity.
2. N-lignin is obtained from e.g., the primary process in yields of 16.9 and 14.8 % from the first and second Ammo, respectively. They contain 17.7 and 13.8% nitrogen, 15.0 and 32.5 % KL and 0.9 and 1.1 % carbohydrates, respectively.
3. CM-MNF are prepared as CM-LL-MNF and CM-HL-MNF with surface charges of 469 and 610 µekv/g respectively. Their 0.5% gels have a viscosity of 676 and 689 Pa•s respectively. The viscosity difference reflects perhaps the cellulose degradation extent difference as the former has been prepared after one more time of Ammo than the latter (three vs. two times). The cellulose DP of LL-

MNF is 300-350 as revealed by a viscosity determination. Due to the presence of residual lignin, CM-MNF gels have yellow colors, absorbing UV-lights with maximums at e.g., 205 and 280 nm.

4. Alk-CM-HL-MNF is obtained after a total product recovery from the reaction mixture. It shows apparent electrostatic phenomenon when placed in a glass beaker, the powders attaching to the wall. This is due to their very high hydrophobicity that results in a reduction of water content making the fibers more easily to be charged after their frictions against the glass.
5. Neat CM-MNF films and GM—CM-MNF composite films are also novel products from this project. All films have contact angles lower than 90 degree (*Table 11*), implying all being hydrophilic as expected from the compositions' structures since both CM-MNF and GM are hydrophilic. Comparatively, the contact angles from neat and composite CM-HL-MNF films are larger than their CM-LL-MNF counterparts, owing to the residual lignin's hydrophobicity. Addition of hydrophilic GM into the GM-CM-MNF composite films slightly reduces the contact angles compared to the neat film counterparts (Table 1).

Table 11. Comparisons of different films prepared

Film	Contact angles (at 0.5s)	Tensile Strength Index kNm/kg	Water Vapor permeance (g/m^2/d)	Oxygen permeance (cc/m^2/day)	absorption (g/g)	
					water	oil
CM-LL-MNF	58.1	97,08	167,2	-	32,55	0,849
GM (50 %) - CM-LL-MNF	56,4	95,01	164,2	-	-	-
CM-HL-MNF	70,1	106,40	208,7	2807	73,71	0,566
GM (18 %) - CM-HL-MNF	68,5	93,55	226,9	2616	-	-
Reference CMC film	-	152,48	-	-	-	-

Several application potentials have been evaluated:

All hydrophilic CM-MNF and GM—CM-MNF films demonstrate good mechanical properties. Although their tensile strengths are lower than the chemical pulp-based CMC reference, all values are close to 100 kNm/kg that is considered strong enough for packaging and coating applications (*Table 11*). The film with a higher lignin content is stronger. This does not necessarily imply a positive effect from the residual lignin, but from the less degraded cellulose as discussed above. We believe that due to the presence of residual lignin all these films would have the UV-screening properties from their gels (see above) which is unique compared to the market CMC-based films.

In addition, the films have water vapor permeances between 160 to 230 g/m^2/day (*Table 11*). This barrier capability is appreciable since the rate in normal fabrics can measure up to several thousand g/m^2/day. The permeance is higher for the films with the higher lignin content. In addition, certain oxygen barrier capabilities could be observed for two CM-HL-MNF films (*Table 11*). Comparatively, the addition of GM improved the barrier property to oxygen. This might be due to the film's reinforcement by the GM addition and the hydrophilicity from the GM.

Furthermore, very effective water absorption is observed, up to 33 and 74 times of water compared to the original film weights could be absorbed by the CM-MNF films with low and high residual lignin contents respectively (*Table 11*).

Hydrophobic CM-MNF, i.e., Alk-CM-MNF, has been evaluated for dispersion in non-polar polylactic acid (PLA) polymer and it has shown an excellent compatibility with PLA which implies the application potential for its PLA composite production with e.g., improved mechanical strength and barrier properties. In addition, Alk-CM-MNF films have substantially improved oil absorption capacities, boosted from the original 0.8 (CM-LL-MNF film) and 0.6 g/g (CM-HL-MNF film) (*Table 11*) to 5.0 (Alk-CM-LL-MNF film) and 2.9 g/g (Alk-CM-HL-MNF film), respectively.

N-lignin has been evaluated as fire-retardant for its impregnated spruce wood and it shows slightly but certainly positive effect in reducing the maximum heat release rate from both the 5 % and 2.5 % N-lignin impregnated samples against the blank wood sample (Figure 18). This reveals the possibility for further development of the N-lignin in this novel water-borne fire-retardant area.

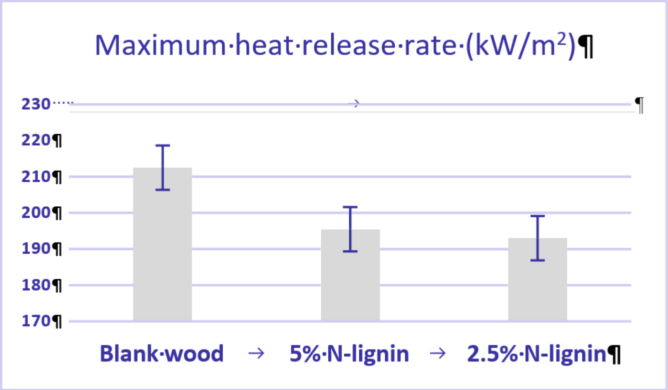

Figure 18. Maximum heat release rate comparison

Conclusions

Two SD size dependent processes have been developed in this project. The primary process is greener and more energy-saving than the conventional pulping-bleaching-energy intensive defibration sequence for the nanocellulose or CMC production from wood chips. As one of the most unique products, hydrophilic CM-MNF is indeed an excellent, better, and more cost-effective nanocellulose- or CMC like material. Their films with or without pre-blending with GM have comparable strengths to the market CMC film. They have not only vapor and oxygen barrier properties but also a unique UV-light screening property due to the extra presence of residual lignin. The films can further work as good water absorbent. Apart from their packing and coating application potentials, there are also other expected CM-MNF application potentials such as production of hydrogel and for paper and bag production and so on. As a derived product, the very hydrophobic Alk-CM-MNF has excellent compatibility with PLA which implies the application potential for its PLA composite production with e.g., improved mechanical strength and barrier properties. It has also application potentials for better particle board or novel thermoplastics or thermoplastic composite productions. Moreover, the Alk-CM-MNF films have substantial oil absorption capacities to be used as oil absorbent. The third unique product, N-lignin, has a good potential as novel fire-retardant for its impregnated spruce wood application. There are other expected application potentials reported in the literature for the N-lignin, such as slow/control release fertilizer and soil modifier (Tyhoda, 2008). All these results would recommend stopping the present low value applications but starting these better and innovative high value processing and applications for SD. This could eventually boost up the profits of the sawmills e.g., in Södra.

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Demonstration and Assessment of a Novel Biorefinery Concept for the Integration of Beechwood-Based Products as Platform and Fine Chemicals

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Abstract

A novel lignocellulose biorefinery (LCB) for the integration of beechwood-based products as platform and fine chemicals was experimentally demonstrated and assessed. The process sequence included organosolv pulping followed by pulp bleaching, hydrothermal conversion of hemicellulose to xylose and its purification, fermentation of xylose to malic acid, and base-catalyzed depolymerization (BCD) of lignin. The resulting products were dissolving pulp, phenolic BCD-oligomers, and malic acid. Based on the findings of the experimental work, a LCB converting 50,000 dry metric tonnes of beechwood annually was simulated. Mass and energy balances showed that 14,616 dry metric tonnes of dissolving pulp, 5,174 dry metric tonnes of BCD-oligomers, and 4,077 dry metric tonnes of malic acid annually could be produced. The overall energy efficiency was 40.3 %. The calculation of specific production costs demonstrated the marketability of dissolving pulp (1,350 €/t) and BCD-oligomers (2,180 €/t), while malic acid (4,750 €/t) is not yet competitive. Environmental assessment showed reduced greenhouse gas (GHG) emissions from the production of BCD-oligomers and malic acid, and higher GHG emissions from the production of dissolving pulp compared to the reference product.

Introduction

One of the urgent measures to stop global warming is the replacement of fossil resources as a feedstock of the global economy. An important part of this challenge is to develop technologies for the efficient conversion of biomass to fuels and chemicals. Due to its ubiquitous availability, wood has the potential to become a valuable resource. In Germany, beechwood was identified as a promising feedstock for prospective LCB (Michels 2009). While traditional pulping processes focus mainly on the valorization of cellulose, it is important for the overall efficiency of LCB that hemicellulose and lignin are also recovered. New pulp mills already show a strong tendency to include the production of specialty products from these unused wood components. Thus, they not only produce pulp for the paper and board industry but also products for the chemical industry. Novel biorefinery concepts for the processing of all of the major wood components into value-added products should therefore be developed.

The aim of this study was the practical demonstration and assessment of such a novel LCB producing dissolving pulp from cellulose, malic acid from hemicellulose, and BCD-oligomers from lignin. To do so, the whole process chain starting from organosolv pulping and followed by pulp bleaching, xylose valorization from hemicellulose hydrolysate (HH), fermentation of xylose to malic acid, and BCD of lignin (Figure 19) was realized. State of the art for these technologies was considered to be the experimental proof of concept and their validation at laboratory- to pilot- scale, corresponding to a Technology Readiness Level (TRL) of 3–4. However, the individual processes had not yet been carried out with real feedstocks and their integration and optimization into one LCB could increase the TRL to 5. The results of the experimental studies were transferred to commercial scale by process simulation and based on the mass and energy balances of the LCB specific production costs and the attributable greenhouse gas emissions were calculated. More detailed information of this study can be found in literature (Nitzsche et al., 2020).

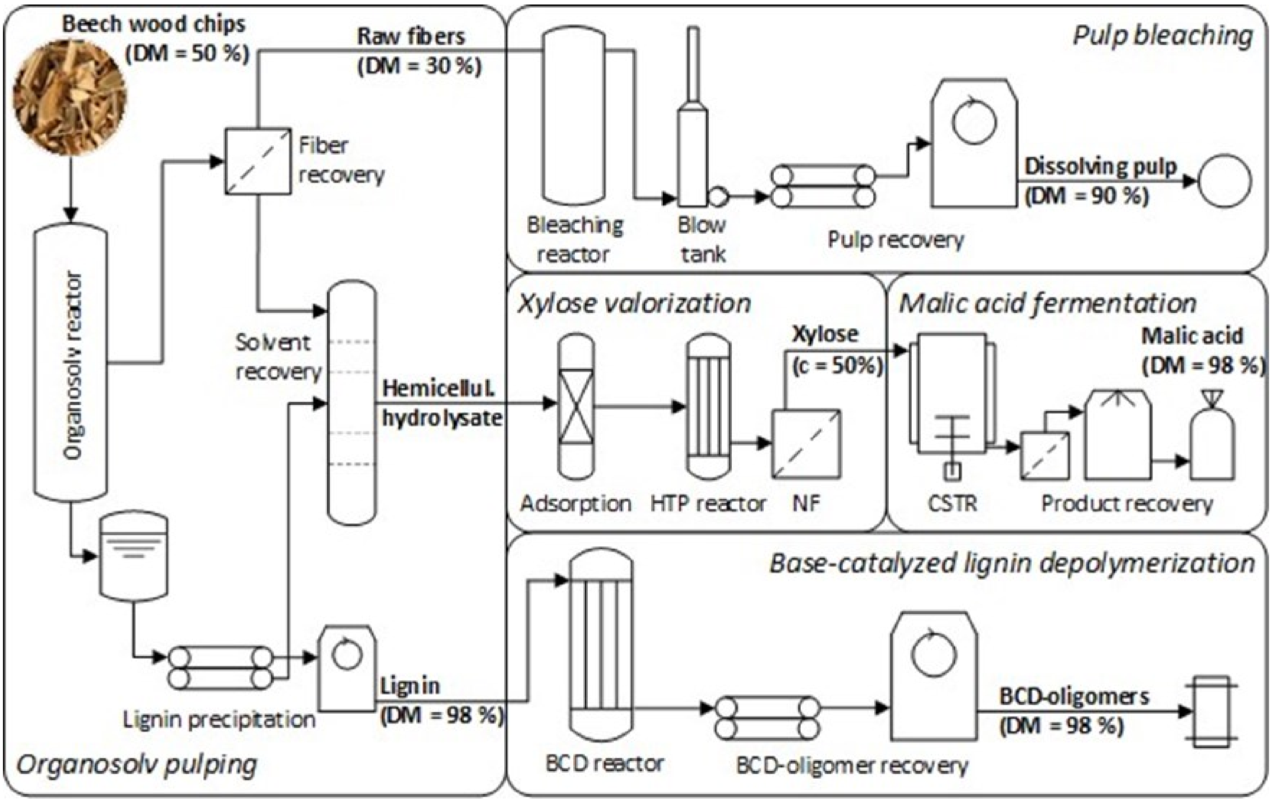

Figure 19. Simplified scheme of the lignocellulose biorefinery for the production of dissolving pulp, malic acid and BCD-oligomers from beechwood (DM: dry matter, c: concentration)

Materials and Methods

Process Demonstration

Organosolv pulping was conducted in the LCB pilot plant of the Fraunhofer CBP in a 400 L batch reactor. Screened beechwood chips were used as feedstock. Pulping conditions were a pressure of 2.0 MPa, a temperature of 170 °C, and a residence time of 130 min. A 1:1 ethanol-water mixture was used as solvent at a liquor-to-wood ratio of 3.2:1. In addition, H_2SO_4 was added as a catalyst. The resulting fiber suspension was dewatered in a screw press and from the liquid extract lignin was precipitated by a distillation process (Leschinsky et al., 2014). From the remaining supernatant ethanol was recovered by rectification, leaving the HH as residual liquid product. It contains oligomeric sugars, monomeric sugars, furans, and carboxylic acids hydrolyzed from the hemicellulose during pulping as well as residual lignin.

In pulp bleaching experiments, executed at the University of Hamburg, cellulose fibers from the organosolv pulping were treated to produce dissolving pulp for use in the viscose process.

For this purpose a bleaching sequence was developed consisting of

1. pulp screening and washing,
2. cold caustic extraction with NaOH (T = 35 °C, t = 30 min, pH = 13),
3. oxygen delignification (p = 0.8 MPa, T = 80 °C, t = 90 min, pH = 12.7),
4. chlorine dioxide bleaching (T = 60 °C, t = 180 min, pH = 6.7), and
5. hydrogen peroxide bleaching (T = 60 °C, t = 120 min, pH = 11.4).

To obtain fermentable xylose from HH, a purification sequence consisting of removal of lignin by adsorption, conversion of oligomeric hemicellulose to xylose, and purification of xylose by nanofiltration (NF) was applied. Adsorption was performed in batch experiments using the resin SP700 at a 1:5 adsorbent-to-solution ratio (T = 25 °C, t = 90 min). The oligomeric hemicellulose in the HH was hydrolyzed to xylose by hydrothermal treatment in a continuous tube reactor (d = 7 mm, L = 6.8 m) at a pressure of 5.0 MPa, a temperature of 180 °C, and a residence time of 2.8 min. NF to remove fermentation inhibitors and concentrate xylose was carried out at a transmembrane pressure of 3.0 MPa, a temperature of 35 °C, and a cross-flow velocity of 1.1 m/s.

Malic acid was fermented from purified xylose using the microorganism Aspergillus oryzae ATCC 56747. The process was conducted in a 1000 L bioreactor at the Fraunhofer CBP. It was operated at a pressure of 0.15 MPa, a temperature of 35 °C, an aeration rate of 0.25 vvm, and an initial stirrer speed of 239 rpm. Downstream processing was performed by

1. acidification with H_3PO_4,
2. inactivation of microorganisms,
3. removal of residual biomass and other solids by filtration,
4. cooling crystallization,
5. filtration of crystals, followed by vi) drying of crystals by freeze-drying.

BCD was carried out continuously in a plug flow reactor (Rößiger et al., 2017). The lignin was fed at 5 % in a 2.5 % NaOH solution with a flow rate of 20 kg/h. The reaction was carried out at 25.0 MPa and 300 °C. The reaction product was continuously collected and acidified with H_2SO_4 to a pH of 1.0 to precipitate the oligomeric fraction, which was subsequently removed by filtration. The filter cake was washed with deionized water until almost all salts were removed. Finally, the resulting BCD-oligomers were dried at 50 °C until a constant mass was reached.

It was assumed that the LCB would be located in Germany at an existing chemical site where all required utilities and waste water treatment can be provided. A plant capacity to process 50,000 dry metric tonnes of beechwood annually and 8,000 operating hours per year were assumed to be reasonable for a demonstration plant (Takkellapati et al., 2018). Conceptual designs of process flowsheets were developed for each process step of the novel biorefinery concept (Figure 20). Process simulation using Aspen Plus® was chosen as the appropriate method for calculating mass and energy balances, energy efficiency, as well as sizing of the plant equipment. The input data for the process simulation came from the experimental results.

To estimate the economic competitiveness, the specific production costs were calculated in line with VDI 6025. All relevant costs were allocated to the cost groups capital-linked costs, consumption-linked costs, operation-linked costs, and other costs. Capital-linked costs were determined based on equipment costs estimated according to Peters et al., (et al., 2004) and Chauvel et al., (2003). Plant-specific surcharge factors were used to account for direct costs and indirect costs leading to fixed-capital investments (FCI). Consumption-linked costs were based on usage and prices of raw materials, auxiliaries, process energy, and disposal costs. Operation-linked costs include estimations for labor. Other costs include administration, insurance, and uncertainties. General assumptions for the costing are summarized in *Table 12*. Specific production costs were determined by dividing total annual production costs by annual product volume.

Table 12. Main assumptions for costing

Parameter	Value	Unit
Average cost of capital	5.3	% p.a.
Assessment period	20	Years
Maintenance, repairs	2	% of FCI p.a.
Administration	20	% of operating costs p.a.
Insurance, uncertainties	1.5	% of FCI p.a.
Annual labor costs	80,000	EUR/person

Life cycle assessment (LCA) was conducted in accordance with ISO 14040 and 14044 standards to calculate and compare the GHG emissions of each LCB product. CO_2 equivalents (CO_2-eq) were calculated as an indicator of the global warming potential. The calculated mass and energy balances were transferred to a life-cycle model using Umberto LCA+ software. To estimate potential GHG savings, each LCB product was compared to a conventional reference product that would likely be substituted (*Table 13*). The emission data for these reference products were obtained from the ecoinvent database v2.2 and v3.4 (Frischknecht et al., 2005, Wernet et al., 2016).

Table 13. LCB products, reference products with emission factor and substitution ratio

LCB products	Reference products	Emission factor [kgCO_2-eq/kg]	Substitution ratio
Dissolving pulp	Pulp (sulfite process)	1.21	1:1
BCD-oligomers (in polyurethane)	Polyol (in polyurethane)	4.32	1:1
Malic acid	Citric acid	3.09	1:1.21

Results and Discussion

Mass and Energy Balances

The biomass and energy flow through the LCB processing 50,000 dry metric tonnes of beechwood annually are presented in Figure 20. The conversion rates of the starting material to products, which are described in the individual process steps and in the Sankey diagram below, refer to the dry matter of the respective components, meaning water content (w) is 0 %.

During organosolv pulping, 46.4 % of the beechwood is converted to cellulose fibers, 15.2 % to lignin and 15.7 % to hemicellulose sugars in the HH. This process stage is characterized by a high water demand, as water is used in large quantities as a solvent and as wash water for cellulose and lignin. This high water consumption results in a high waste water load of 13.4 m^3 per metric tonne of cellulose fibers (w = 0 %). Due to an efficient ethanol recovery the need for fresh ethanol could be reduced by 99.4 %. During pulp bleaching, 63.0 % of the raw cellulose fibers are converted to dissolving pulp. In this process stage, water is by far the largest mass flow, where it is used for the dilution of pulp during pulp screening and cold caustic extraction as well as for pulp washing in the oxygen delignification, chlorine dioxide bleaching, and hydrogen peroxide bleaching. Due to the high water demand, recirculation is essential. In this study, it was assumed that 11 m^3 of waste water per metric tonne of dissolving pulp (w = 0 %) arise. The consumption of chemicals, especially of NaOH (1.34 t/h in the cold caustic extraction) and ClO_2 is also very high. During xylose valorization and purification from hemicellulose, at first 95 % of the lignin is removed from the HH by adsorption, then 90 % of the oligomeric hemicellulose in the HH is converted to xylose, which is finally concentrated to 126 g/l by NF. The advantage of this process stage is the low requirement of further input streams, such as water and other chemicals. For the desorption of lignin from the adsorbent SP700, 2.36 t/h ethanol is needed. Efficient recovery reduces the need for fresh ethanol by 99.5 %. For each metric tonne of xylose (w = 0 %), 39.5 m^3 of waste water is produced. This is mainly due to the large water input within organosolv pulping. During the malic acid fermentation, 58.0 % of the xylose is processed to malic acid. This comparatively low yield is attributed to the formation of by-products (e.g., succinic acid, fumaric acid) and high losses during the purification processes. Process water is used for the dilution of the xylose solution during the cultivation of the microorganisms and the preparation of a 70 % H_3PO_4 solution for the acidification of the fermentation broth. The waste water load is 11.2 m^3 per metric tonne of malic acid (w = 0 %). During lignin depolymerization, 67.5 % of lignin is converted to BCD-oligomers. Large amounts of water, H_2SO_4, and NaOH are consumed in this process stage. The demand for water is mainly due to the washing of the BCD-oligomers (53.9 %) as well as for the preparation of the 2.5 % NaOH solution (33.4 %) and the 30 % H_2SO_4 solution (4.7 %). A highly contaminated waste water with a volume of 86.2 m^3 per metric tonne of BCD-oligomers (w = 0 %) results from the process.

The energy efficiency for the primary products dissolving pulp and BCD-oligomers is 21.0 % and 15.6 %, respectively, and for the secondary product malic acid 3.7 %. Hence, the overall energy efficiency of the LCB is 40.3 %. An increase in energy efficiency could be achieved by optimizing the recovery of malic acid or by the conversion of xylose to other or higher caloric products. It must be considered, however, that most of the processes studied were tested here for the first time at a pilot-scale and that a comprehensive optimization has not yet taken place.

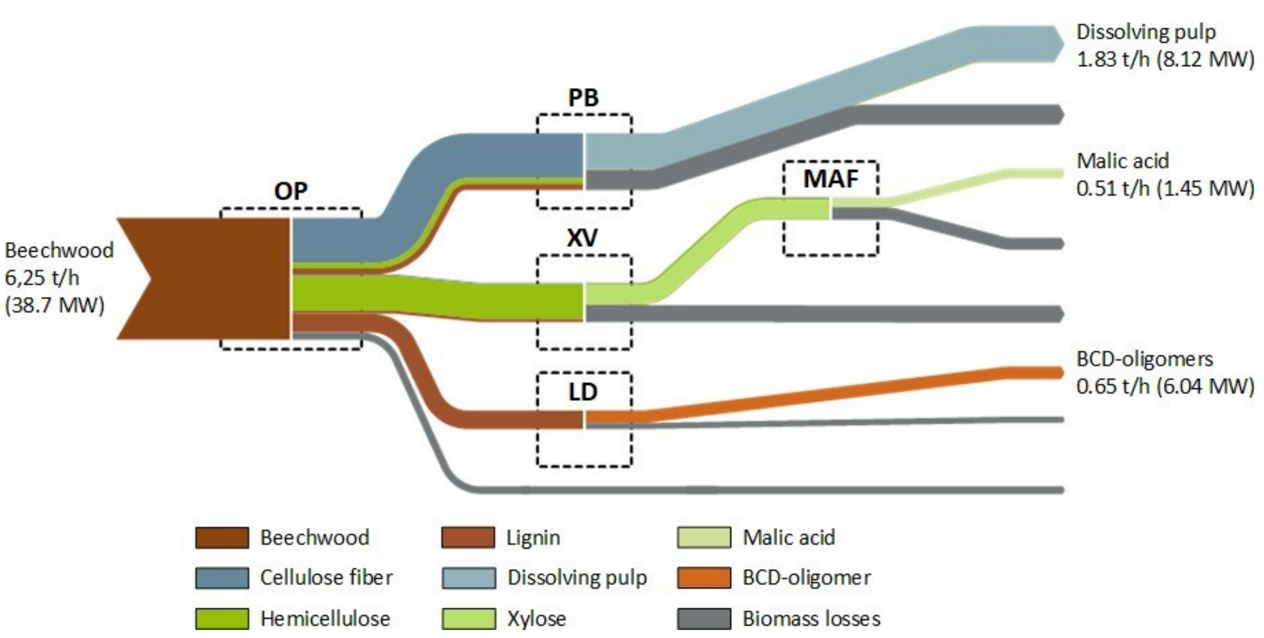

Figure 20. Sankey diagram of the biomass and energy flow through the studied lignocellulose biorefinery (OP: organosolv pulping, PB: pulp bleaching, XV: xylose valorization, MAF: malic acid fermentation

Costing

Investment and annual costs for the individual process steps in the LCB are summarized in *Table 14*. Organosolv pulping has the largest share (28 %) of the total investment, before malic acid fermentation (22 %), BCD (20 %), pulp bleaching (16 %) and xylose valorization from hemicellulose (14 %). The main drivers for the annual costs are consumption-linked costs, in particular for beechwood during pulping and auxiliaries and operating materials for the other processes.

Table 14. Investment and annual costs of the lignocellulose biorefinery concept (OP: organosolv pulping, PB: pulp bleaching, XV: xylose valorization, MAF: malic acid fermentation, LD: lignin depolymerization)

		OP	PB	XV	MAF	LD
Investment sum	[kEUR]	30,830	18,150	15,390	24,710	22,500
Capital-linked costs	[kEUR/a]	3,140	1,870	1,580	2,530	2,320
Depreciation	[kEUR/a]	1,540	910	770	1,240	1,130
Interest	[kEUR/a]	1,000	600	500	800	740
Maintenance	[kEUR/a]	600	360	310	490	450
Consumption-linked costs	[kEUR/a]	9,380	9,790	2,710	3,880	5,050
Raw Material	[kEUR/a]	5,000	-	-	-	-
Auxiliary and operating material	[kEUR/a]	1,140	7,800	1,090	3,320	3,000
Energy Supply	[kEUR/a]	2,490	1,540	970	450	940
Disposal costs	[kEUR/a]	750	450	650	110	1,110
Operation-linked costs	[kEUR/a]	2,300	1,660	1,290	1,100	1,000
Labor Costs	[kEUR/a]	2,300	1,660	1,290	1,100	1,000
Other costs	[kEUR/a]	1,090	600	550	690	540
Administration	[kEUR/a]	640	330	320	320	200
Insurance	[kEUR/a]	300	180	150	250	230
Uncertainties	[kEUR/a]	150	90	80	120	110

Specific production costs for dissolving pulp (1,350 EUR/t) and BCD-oligomers (2,180 EUR/t) are close to market prices. The costs for malic acid production (4,750 EUR/t) are significantly higher than the market price and are currently not competitive. The specific production costs of the three products have a similar cost distribution: Consumption-linked costs account for the largest share (49 %–66 %), followed by capital-linked costs (16 %–26 %), operation-linked costs (12 %–16 %), and other costs (5 %–8 %).

Environmental Performance

Implementing the LCB in the market and substituting the conventional reference products would contribute to a mitigation of global warming. The production of BCD-oligomers and malic acid would each cause lower GHG emissions compared to their reference products as can be seen in Figure 21 However, the GHG emissions of pulp production are higher than those of the reference pulp production. The main reasons for that are a high consumption of NaOH and a relatively high emission factor of ClO_2 used for pulp bleaching. Within the biorefinery concept, the highest GHG saving is reached by the substitution of polyol with BCD-oligomers in polyurethane.

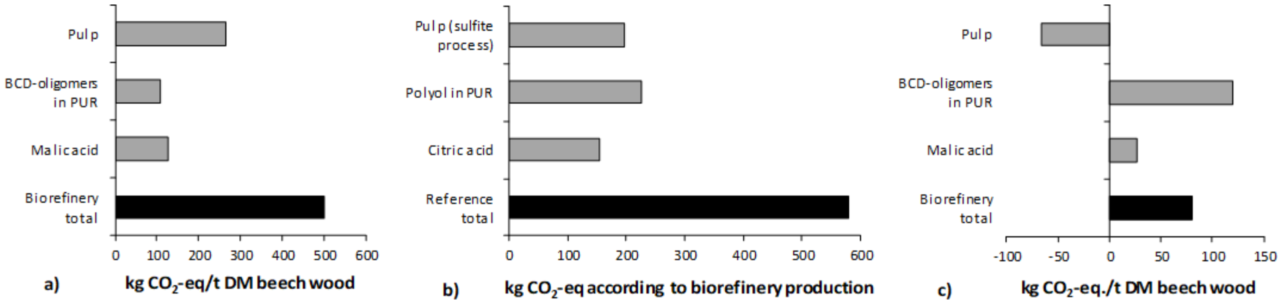

Figure 21. Greenhouse gas (GHG) emissions of a) the lignocellulose biorefinery products, b) of the reference products, and c) savings (PUR: polyurethane, CO_2-eq: CO_2 equivalent).

Conclusions

Within this study a novel LCB including the process steps of organosolv pulping, pulp bleaching, hydrothermal conversion of oligomeric hemicellulose to xylose and its purification, malic acid fermentation, and BCD of lignin was demonstrated and assessed. It was shown that beechwood can be converted into the three products dissolving pulp, phenolic BCD-oligomers, and malic acid. The production of dissolving pulp and BCD-oligomers is already marketable, while malic acid is currently not competitive. Environmental assessment showed that the examined LCB would in total contribute to the mitigation of global warming. By integrating and optimizing the single process steps into one LCB, the TRL could be increased from 3-4 to 5.

Acknowledgement

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Biography

Roy Nitzsche completed his master's degree in environmental engineering in 2012. Right after he joined the German Biomass Research Center (DBFZ) as a research associate in the working group Separation Technologies and Process Design in the department Biorefineries. Research focuses are on the recovery of valuable substances from lignocellulosic hydrolysates and fermentation broths as well as the conceptual design and simulation of individual separation cascades and entire biorefinery concepts. In cooperation with the Technical University of Berlin, he is doing his doctorate on the subject "Demonstration and Assessment of Adsorption and Membrane Filtration for the Separation and Valorization of Hemicellulose from Organosolv Beechwood Hydrolysates".

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Current and Emerging Solutions for Carbon Neutrality in Wood Based Biorefinery

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Abstract

Industry transformation process toward sustainable bioeconomy is on-going in pulp and paper industry. Focus is on energy and material efficiency of own operations, sustainability of the supply chain, and new innovation towards more sustainable products and services with replacement or reduction of use of less sustainable materials. This chosen industrial strategic agenda demands continuous investments in innovation and R&D and higher speed to market, and development of partnerships across various industries. Reaching the goal of low-carbon or carbon zero bioeconomy by 2050 remains challenging. Most companies in pulp and paper industry have already defined and committed to strict goals in reducing their greenhouse gas (GHG) emissions. New breakthroughs and radical innovation are needed targeting at major achievements in climate change mitigation. In this article we assess the potential for improving energy efficiency and reducing GHG emissions in the pulp and paper sector of the bioeconomy. Bottom-up and top-down approaches are used to discuss the existing and future options and necessary technology developments and investments. Analysis remains on a conceptual level as each mill is different. We conclude that a combination of investments in both short- and long-term technologies that are necessary.

Introduction

Industrial transformation of pulp and paper industry (PPI) towards bioeconomy is still ongoing (D'Amato et. al., 2017). This review of PPI decarbonization reveals the potential for change for further reduction in CO_2 emissions in pulp and paper industry, yet still fulfilling the market needs with the traditional pulp and paper and more advanced sustainable products it manufactures. PPI is natural base for new business models in circular economy and the full scope use of wood and wood fiber in various new products. The opportunities for new value add and positive contributions to low carbon society are vast and include biofuels and chemicals, traditional wood products, packaging and tissue and novel product substitutes for the traditionally fossil based economy products in textiles, pharmaceuticals, and cosmetics. This direction has created major opportunities for growth, innovation and partnerships. PPI is also involving many new industries and brand owners that are committed to driving global sustainability agendas (Liao et al., 2021). The latest somewhat complementing challenge in the PPI comes from widely accepted goals for low-carbon society and company specific commitments to carbon neutrality. A good example of this is the commitment of the Confederation of the European Paper Industry (CEPI) to decarbonize by 80% and to reach climate-neutrality by 2050 (Cepi, 2021a). It is also an industry associated with very high capital investments and low margins (Eib.org. 1997; Csimarket.com, 2022). With the advancement of manufacturing technologies and processes in its own operations it has arguably evolved to be highly efficient in materials, energy, and water utilization with manufacturing capacity utilization rates above 85 % (Statista, 2022; www150.statcan.gc.ca, 2022). The PPI is highly energy intensive and considered to be the third or fourth most energy-intensive worldwide, contributing to about 6% of industrial energy use globally. It also has third highest Gross Value Added (GVA) emissions intensity (tCO_2e/£1000 GVA) after cement and aluminum production (Ecofys, 2013; Rogers et al., 2013). The cost of energy related to the produced product (scope 1) is ranging from 7-13 % (Stora-Enso, 2022; Metsä Board, 2022). However, it has been considered as one of the least CO_2 emitting industrial sectors worldwide. This is due to the exceptionally large utilization of biomass as its primary energy source and has been considered as carbon-neutral by e.g. EU and UK. (Ter-Mikaelian et al., 2015). However, this consideration is being debated and is about to change (Nrdc.org, 2021; Energymonitor, 2021; Mather-Gratton et al., 2021). How will this emerging change in frame of reference influence PPI and how long does it take to make an impactful response to the needed change? Especially if the necessary technologies are not mature enough for implementation. Both the development and investment to new manufacturing processes and technologies takes time to respond and when investments are implemented, the technological manufacturing platforms are fixed for long time; investment cycles are 30-60 years (Pita, 2015).

Many of the technical solutions for carbon neutrality in PPI are being perceived as part of modernization and operational efficiency and cost reduction goals (Mäki et al., 2021). Some of the technologies that enable the changes needed are illustrated. In this article we review these more operational and tactical approaches as well. There is also a relatively long list of Emerging Technologies (ET) that include topics such as Carbon Capture and Storage (CCS) (Onarheim et al., 2018), Black Liquor Gasification (BLG) (Naqvi, et al., 2010), Biorefineries (Bajpai, 2013); Lignin separation (Vakkilainen and Välimäki 2009; Hubbe et al., 2019); Emerging drying technologies (boost drying (Haase, 2005), microwave drying (Kumar et al., 1990), supercritical steam drying (Kiiskinen & Edelmann, 2002), supercritical CO_2 drying (Aggarwal & Hakovirta, 2021) and Deep Eutectiuc Solvent (DES) pulping (Fiskari et al., 2020). For example, CCS has been considered to be an important future option to control CO_2 emissions and according to Paltsev et al., (2021) the industrial CCS mitigation cap provide cost savings of 12 % by 2075 and 71 % by 2100 compared to the case without it. This is especially useful for sectors with limited possibility to control direct emissions. All these technologies are still in the development and piloting phase and are connected to new earnings models and offer value added if implemented successfully.

PPI towards carbon neutrality

Energy use in different industry sectors in EU vary and especially process temperature levels used are different (Madeddu et al., 2020). The energy use profiles of PPI in EU represent different sectors also globally. Fuels combustion accounts for 70 % of the final energy use in industry (excluding feedstock energy content), mostly to supply heat (Mantzos et al., 2018). The remaining use of 30 % was from electricity, which is primarily used for cooling and supplying mechanical power.

There are differences between sectors in the heat levels used. The largest energy use sectors in EU are chemicals, primary steel and paper sectors, followed by food, ceramic and glass sectors.

The sectors have differences in their energy demand. If the feedstock energy content is accounted for the chemicals sector feedstocks are the single largest energy user (Madeddu et al., 2020).

Electrically powered technologies are often considered as potential solution towards decarbonization of a particular the industry. PPI can be among the first ones to electrify, as heat levels required are often below 400 °C. The PPI can be electrified with mature and existing technologies. The technologies that are be used are compression heat pumps, electric boilers, mechanical vapor recompression, chillers, infrared, microwave, and radiofrequency heaters. Solid wood products are fully electrified with these technologies already while pulping process limestone calcination (3 % of energy use in pulp and paper sector) requires additional designs for electric kiln furnaces. (Madeddu et al., 2020). However, this is not the silver bullet, as the electrification requires large investments to energy infrastructure and other energy saving measures are also important to have CO_2 emissions reducing solutions in place to achieve emissions reduction targets on time.

The pulp and paper sector has faced challenges over the last two decades, especially seen by fast decline of newsprint and graphic papers consumptions as part of digitalization of our society. Overall, the consumption of products has still been in increasing slope (FAO, 2022). The trend in overall consumption may be also changing to decreasing slope, as the pandemic has had influence on the routines of people, both at home but especially at work (Chen et al., 2022; Jpmorgan.com, 2022; Xiong et al., 2022). Whether this effect be permanent or not, remains to be seen. Still the production of pulpwood (describing uses in pulp and paper) was 688 Mt in 2020, a decline from 2018 peak of 729 Mt.

Table 15. The changes in production of graphic papers, packaging paper and paperboard, paper and paperboard, excluding newsprint, pulp for paper, pulpwood, round and split, all species (production), total fibre furnish, wood pellets and other agglomerates, wood pulp and newsprint between 2000-2020, 2010-2020 and compound annual growth rate (CAGR) between 2010-2020.

	Change 2000-2020, %	Change 2010-2020, %	CAGR[2] 2010-2020
Graphic papers	-30 %	-32 %	-3,8 %
Packaging paper and paperboard	65 %	22 %	2,0 %
Paper and paperboard	24 %	2 %	0,2 %
Paper and paperboard, excluding newsprint	35 %	7 %	0,7 %
Pulp for paper	3 %	2 %	0,2 %
Pulpwood, round and split, all species (production)	37 %	14 %	1,3 %
Total fibre furnish	28 %	5 %	0,5 %
Wood pellets and other agglomerates (from 2012)		116 %	10,1 %
Wood pulp	28 %	5 %	0,5 %
Newsprint	-62 %	-55 %	-7,6 %

Wood binds carbon when it grows. The carbon is taken from the air's CO_2. Each cubic meter of wood binds approx. one tonne of CO_2, forest growing stock in EU-27 being around 7.4 Gt C (Eurostat, 2020). For example, current annual emissions of carbon from energy production are approx. 9 Gt C (33 Gt of CO_2, IEA, 2022), out of which forests absorb 3.4 Gt C and seas, 2.5 Gt C (Friedlingstein et al., 2020). To prevent imbalance between sinks and sources leading to increase in CO2 in atmosphere, the use of

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[2] CAGR=(EV/BV)^(1/n)−1×100, where: EV=Ending value, BV=Beginning value, n=Number of years

fossil fuels is a primary reduction target. One introduced solution is in EU, where a price on the emissions is put in the form of carbon trade (EU ETS, 2022). Its main limitation is that it is only limited to EU. Emissions outside EU are not included. Emissions in EU region are reduced but replaced by emissions outside EU (Kuusi & Wang, 2022). Other large CO_2 sources, like natural gas in EU, are likely to require shifting away from fossil-based, as suggested recently by EU-commission (European Commission, 2021).

Physical CO_2 emissions from wood arise from its principal components of cellulose, hemicelluloses and lignin during burning. Their influence on CO_2 emissions can be estimated using following molar masses: Cellulose $C_6H_{10}O_5$ with molar mass of 162 g/mol, hemicelluloses are sugars $C_6H_{12}O_6$ with molar mass 342 g/mol and lignin, e.g. $C_{81}H_{92}O_{28}$, organosolv, (Pubchem.ncbi.nlm.nih.gov., 2022), gives molar mass 1512 g/mol). CO_2 has a molar mass of 44 g/mol. Also, assuming average proportions (Keränen, 2011) of cellulose in wood, (A), hemicellulose (B) and lignin (C) 43,8 %, 23,8 % and 25,8 % respectively, we get that burning 1t of wood gives 1.5 tonnes of CO_2. Considering pulping process, where cellulose is not burned as part of process, but black liquor containing the hemicelluloses and lignin, the similar approach gives 1.6 tonnes of CO_2 from each hemicellulose- and lignin-tonne burned. Sugars in hemicellulose burn with least amount of emitted CO_2, so the utilization of lignin instead of burning it gives better reduction potential of CO_2 emissions from black liquor. The currently unaccounted emission from black liquor has a significant influence on real physical CO_2 emissions of the PPI (Figure 22). EU-28 PPI emissions from JRC-IDEES database (Mantzos et al., 2018) do not contain black liquor or other biomass-originated emissions.

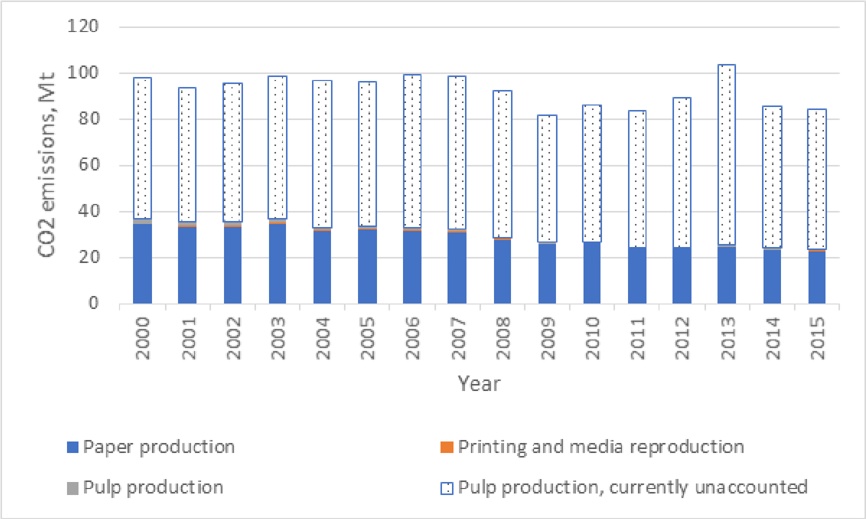

Figure 22. CO_2 emissions of EU-28 PPI between 2000-2015 (includes also UK). Drawn from Mantzos et al., (2018), and their currently unaccounted emissions from black liquor based on calculation above. Example of how this utilization could be done in practice is e.g. manufacturing of anode materials for li-ion batteries created from lignin (Stora Enso 2021), however other value added chemicals can also be produced from it (Yoo & Ragauskas, 2021).

If all CO_2 emissions would be required to be calculated as part of emission trading system (also from black liquor burned in pulping), the emissions of the industry would increase 240 % in EU from 2015. Current price (August 1, 2022) of carbon in the system is 81 €/t CO_2 (Ember, 2022). With this CO_2 emissions would bring additional annual cost of 4.9 billion € to the industry in EU (unaccounted 60.7 Mt CO_2). Calculating separately three large Finnish-based companies and using their annual financial statements in 2020, 58% of their EBITDA would be required to cover this cost or 8,7 % of their turnover. This example reveals the influence of CO_2 emissions and their economic and policy risks for the sector. The future CO_2-savings potential in pulp industry arises mainly from large-scale lignin utilization. If all lignin can be utilized, it can reduce 47 Mt CO_2 emissions annually in EU, while hemicelluloses full utilization offers 14 Mt CO_2 emission reduction potential (Figure 23). The current CO_2 emissions of the industry are mostly related to biomass, which already reduces the need to use fossil nonrenewable sources in energy production. The actual total emissions (Figure 23) coming from the utilization of renewable sources in PPI are about 84 Mt in EU. Comparing only the share of renewable wood usage for primary energy the total amount of wood is about 52 Mt. In total replacing 37 Mt of oil (264 million barrels or under 16 days of EU oil consumption). It should be noted that the absolute CO_2 emissions per GJ for wood is higher (wood/oil-ratio=1,57). To reduce land area required for the production of woody biomass, developments in short rotation crops, like eucalyptus, has improved productivity in regions where these crops can be grown (IEA bioenergy, 2011; Stape et al., 2010). Other options introduced that reduces use of primary raw materials and saves production costs are recycling and use of minerals and additives in the pulp and paper products. However, there are limits in recycling as utilization of recycled material in e.g. food contact packaging and each recycling step produces some losses. (Keränen & Ervasti, 2014).

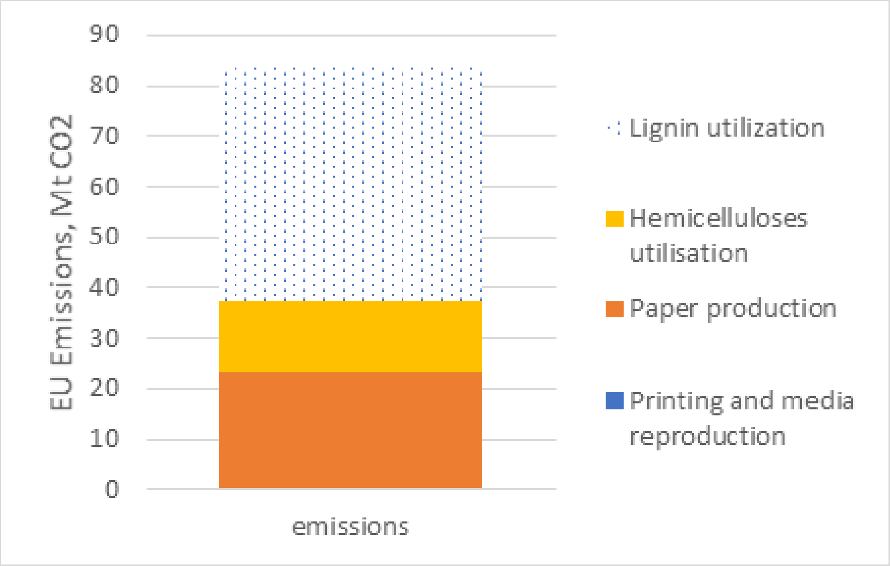

Figure 23. Emission reduction potential form pulp industry from lignin and hemicelluloses.

Technology timelines, reducing CO_2 emissions

In pulp mills the economic lifetime is important to understand. For example, sulfite pulp mill in Äänekoski (Arkistot.info, 2017) started production in 1938 and lasted until 1984 (46 years). New sulfate technology started production in 1961, that was replaced by new in 1985 (still sulfate), which was in production until 2017, when latest integrated bioproduct mill started (still using sulfate-process). Sulfite process itself was invented in 1867 (Fernández-Rodríguez et al., 2019). Lifetime of that technology has been quite long, as it still is in use, but its relative share of all pulp mills is decreasing. Sulfate process gained success from 1940's onwards with the invention of recovery boiler. Sulfite process was the main process technology for 60-70 years, replaced by sulfate process, which has now lasted over 70 years. With such slow adaptation cycle and long life-times of equipment this means decade-long technology adaptation process. E.g. if we use the sulfite case as an example, then if a new pulping manufacturing technology was invented in the 1950's, the adaptation of it for the sector would take approximately 70-80 years and would be considered to be mainstream today. Regardles of the fact is that the process and product development takes time. This can be speeded up for example by outsourcing laboratory and piloting phases (Tanthapanichakoon, 2013) and using more co-creation approach involving partners and the value chain. Innovation needs to be in one of the key strategic priorities in the industry and emphasiws needs to be made to improving the innovation culture not just stating over-ambitious goals, too high expectations, or treating innovations as a mere KPI (people know KPI and act accordingly). Short term goals are needed but also focusing on 3-5 year trends with a balanced approach is critical. The pulp and paper industry has recently made several progresses in creating novel products from pulp, including novel textile products that are developed with built-in sustainability and digitality (Kamppuri et al., 2021). The pulp and paper industry products are broadly used in our socielty and in many industrial sectors and product segments including energy, printing and publishing, packaging, food, electronics, pharmaceutical and medical, chemicals, textile, and other industries. The macroscopic structure of wood enables engineered products, while fiber-level enables many other cellulose products including paper, tissue and board products. The novel materials development for smaller scale utilizes parts of cell-wall structure or nanostructure or chemical components derived from it. Technologies that are important for the industry are fiberizing and separation, conversion, modification and processing via mechanical, chemical or enzymatic means. Recently, digitalization of industry has enabled improvements in sourcing of raw material (satellites, drones, harvesting IT), production and logistics (automation and integration of data to information) and products enabling seamless and simulataneously customized operation.

The role of products in carbon neutrality - light weighting

Environmental impacts of paper and board products can be estimated by life cycle analysis, LCA, that counts in all the inputs from wood harvesting to end-of-life stage, and by the ISO standard is defined as ‘the calculation and evaluation of the environmentally relevant inputs and outputs and the potential environmental impacts of the life cycle of a product, material or service’ (ISO, 2010). For assessing the impacts of paper and board products, CEPI has defined ten elements (10 toes of CEPI framework) (Cepi, 2017) to be included for describing the carbon footprint. While LCA is already well-established and widely used method in paper and board industry, there has been interest in looking at the timing of the emissions, making the calculation more complex. Carbon is stored in wood, or in products made of wood for as long as it is not biologically degraded or incinerated. Evidently, the storage time varies greatly depending on the use of the product. In their recent report, Finnish Environment Institute presented models for calculating the carbon storage times for wood-based products (Soimakallio et al., 2022). Further, related to carbon storage time, is the recycling of papers and boards. It is critical to know recycling emissions, with its collection system and recycling processes (sorting, cleaning, and screening) and how much of the material is eventually recycled. This information should then be compared to the virgin fiber production process (Keränen & Ervasti, 2014). An additional aspect to carbon balance of paper, tissue and board products is the substitution of alternative fossil-based materials (notably plastics). For substitution comparison, products of the same function are compared regarding GHG emissions. We have chosen a perspective that focuses on the impact of light-weighting paper and board products to carbon emissions. This general theme or topic of improving the material performance - increasing the strength to density ratio - has been on the agenda of the papermakers for a long time, mainly looking for production cost reduction by lower raw material and processing cost. Now, with attempts to reduce the carbon footprint of paper and board products, there is an additional strong driver to use less biomass carbon in the first place. The aim is to have a general and qualitative understanding of the proportions of selected means to reduce the GHG emissions of a product. A simple comparison between the impacts of reducing the fossil fuel to zero and a basis weight reduction will help to point out the most potential focus areas in the reduction of carbon footprint. Folding box board was selected as an example product for calculating the lightweighting. It belongs to the packaging grade category that has been a steadily growing segment, representing 58.7 % of the total paper and board production in the CEPI member countries in 2021 (58.2 % in 2020) (Cepi, 2022).

Basic assumption used for light-weighting calculation:

- European level, based on CEPI statistics of the pulp and paper products
- Coated folding box board of 240 gsm, with 40 gsm HW+SW top and backing plies and 140 gsm CTMP middle ply and 10+10 gsm double pigment coating on the top ply
- Carbon (eCO_2) emission kg/per ton produced
- Include only the initial sequestration effect: reduced harvesting due reduced need of fibre per ton FBB.
- Exclude the effects of light weighting on the other factors such as the process and transport
- Consider qualitatively technical solutions to offset the impaired mechanical properties, such as use of CNF or MFC.
- CO_2 emissions of MFC production vs. kraft/CTMP production
- According to Cepi, the total paper&board production in 2021 reached 90.2 million tonnes in Europe (Cepi, 2022). Intensity of emissions were 0.29 $ktCO_2$/kt of product.

This direct estimation gives 2.6 $MtCO_2$ (90.2 Mt * 10 % * 0.29 $ktCO_2$/kt product) as minimum CO_2 savings. This does not consider the emissions from burning black liquor containing the hemicelluloses and lignin, giving 1.6 t of CO_2 from each hemicellulose- and lignin-tonne burned, which increases the emissions related to pulp manufacturing. Deducting the non-fibrous materials from products, and adding all pulp manufacturing CO_2 emissions, additional savings of 11.7 $MtCO_2$ are obtained. There are also savings in manufacturing of filler materials (although manufacturing of PCC binds CO_2, if all filler material would be PCC, the savings would be in the order of 0.2-0.5 $MtCO_2$ in European level). In total, the CO_2 emission reduction is approximately 14 $MtCO_2$ (with -10 % basis weight reduction in European level). If reduction of basis weight is an impactful way to reduce carbon footprint, the evident way forward would be to continue the material development aiming to reach the technical product specifications with less wood fibre. At the same time, the possibilities to downgrade the material specifications should be looked at, both from the point of view of technical performance of both products and the consumer acceptance of new, more environmentally friendly products.

Conclusions

There are several decarbonization technologies that can be utilized for PPI carbon zero strategies. Carbon Capture and Storage technologies are one of the promising alternatives. Costs of this approach ranges between 62-92 €/tCO_2 (Onarheim et al., 2016), which can be feasible looking at the current ETS price of 81 €/tCO_2. Electrification of many manufacturing processes in PPI has high potential as heat levels required are often below 400 °C. There are various available and mature technologies that can already be used to rapidly advance electrification in PPI manufacturing needs for heating, drying, and cooling. The utilization of lignin in various new products instead of burning is an attractive approach for CO_2 reduction potential. This is critical also for risk mitigation in case policy changes will drive related carbon trading costs. The life cycle of manufacturing technologies in the PPI is long and due to its nature of the industry's maturity means that no silver bullet manufacturing innovation can be expected for decarbonization. The solution will need to be composed of several innovations in supply chain, own manufacturing operations and new sustainable products. One of the major flagship CO_2 reducing technologies has been light weighting. It continues in PPI in various forms and therefore continuous investments in material development continues to be needed. Also, consumer acceptance and product performance knowhow are needed for possible downgrading material specifications to a level of "good enough". This will be imperative in making advances in developing new more sustainable low carbon products.

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Preparation of Dialdehyde Cellulose (DAC) from Cellulose Pulp and its Applications as Reversible Wet Strength Additive

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Abstract

Dialdehyde cellulose (DAC) with a high degree of oxidation was obtained from NBSK pulp via Malaprade oxidation. The obtained polymer was cationized using Girard's reagent T and its application as a temporary wet strength agent was investigated.

Introduction

For many paper products including, among others, paper towels, tissue paper, bank note and packaging paper, wet strength is a necessary property, required for their respective application. (Ek et al., 2009) Temporary wet strength agents, like the commercially available glyoxalated polyacrylamides (g-PAM), contain reactive aldehyde functionality, forming hemiacetals with the cellulose fibers, providing the necessary cross linkage required for wet strength, yet can be easily hydrolyzed during the paper recycling process. (Chen et al., 2002; Ek et al., 2009) However, those polymers build on a fossil raw materials basis and their relatively short shelf life in addition to the toxicity of glyoxal prove to be problematic for paper manufacturers.

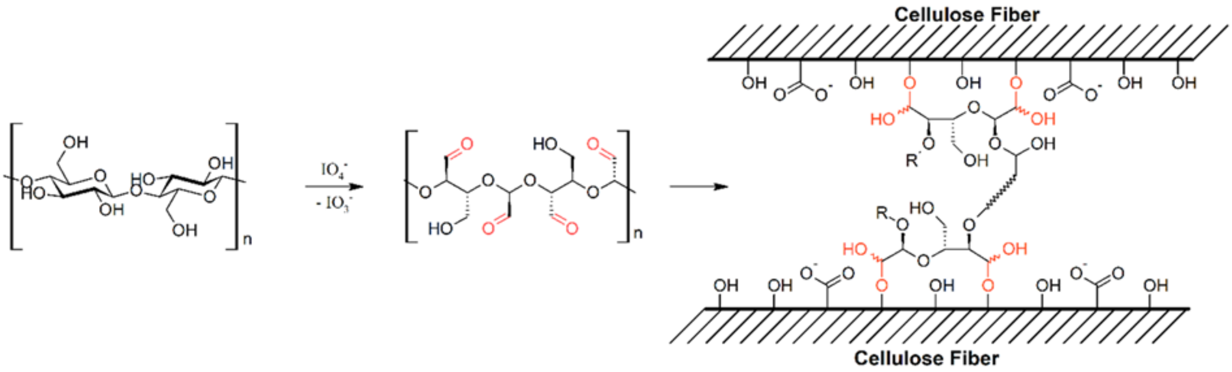

Figure 24. Formation of DAC via periodate oxidation of cellulose and application as a wet strength agent by binding to cellulose fibres.

Following the same wet strengthening mechanism as g-PAM, dialdehyde celluloses (DAC) are eligible as new and biobased wet strength agents in paper manufacturing and can easily be produced by a one-step Malaprade-reaction of cellulose pulp (see Figure 24). Thus, in this report we produced biobased DAC with a high degree of oxidation according to modified literature procedure (Dang et al., 2019) and subsequently cationic DAC using Girard's reagent T. Laboratory handsheets with cellulose pulp utilizing the produced DAC were formed and the tensile strength and relative wet strength properties were measured.

Experimental

Chemicals: NBSK pulp (80 % pine, 20 % spruce) was provided by Mercer LLC, $NaIO_4$ (>99 %) was obtained from Carl Roth, hydroxylammonium chloride (99 %) and Girard's reagent T (98 %) were obtained from Sigma-Aldrich, the biocide Precid MV was obtained from Prechel GmbH, iso- propanol (99.9 %), HCl (0.1 M) and NaOH solution (0.1 M) were obtained from Chemsolute.

Instrumentation: Pulp was disintegrated in a Messmer Disintegrator MK IIIC. Titrations were carried out utilizing a Metrohm Titrando 888 equipped with a Metrohm Electrode Plus pH- electrode. When stated, samples were milled using a Retsch MM400 vibrating ball mill. IR-spectra were recorded using a Bruker Tensor 27 FT-IR spectrometer. Elemental analyses were recorded on a HEKAtech Eura EA Elemental Analyser. Laboratory handsheets were prepared on a Rapid-Köthen sheet former. The wet and dry breaking loads were determined using a Hegewald & Peschke MPT GmbH inspekt 20 universal testing machine.

Preparation of DAC: NBSK pulp was disintegrated in water for 10 min and diluted in water:iso-propanol (93.7:6.3) solution to a final consistency of 1.5 %. Sodium periodate (1.9 eq.) was added, the reaction vessel shaded and the reaction mixture was stirred at 47 °C for up to 8.5 h. The mixture was filtered and the residue was washed multiple times with water. Biocide (0.5 g/g(DAC)) was added in the last washing step.

Preparation of cationic DAC: DAC (10 g, DO = 77 %) was suspended in water (500 ml) and disintegrated until the suspension becomes homogeneous. The suspension was diluted to 1 l, heated to 80 °C and acidified to pH = 3-5. Girard's reagent T (varying amounts: 0.28 to 20.3 g, 0.01 eq. to 1.26 eq.) was added and the reaction mixture was stirred at 80 °C for 7 h, after which remaining solids were filtered off. The filtrate was slowly reduced to dryness at 45 °C over 10 d. The obtained cationic DAC were milled in a vibrating ball mill at 30 Hz for 60 s.

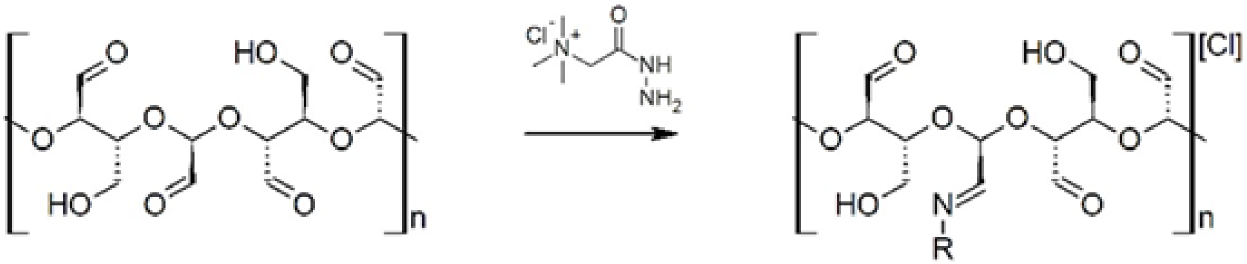

Figure 25. Preparation of cationic DAC using Girard's reagent T.

Determination of the degree of oxidation (DO): The DO was determined via hydroxylammonium chloride titration in two-point measurement, via modified literature procedure (Zhao & Heindel, 1991). DAC (about 0.2 g per determination) was suspended in water (200 ml) the pH was adjusted to 4 and the solid was filtered off. The obtained residue was halved and each half was suspended in an aqueous solution of hydroxylammonium chloride (0.25 M, 100 ml, pH = 4). The reaction mixtures were stirred at room temperature for 2 h, after which the mixtures were filtered and the residues dried at 105 °C for 16 h. Aliquots of the filtrates (75 ml each) were titrated back to pH = 4 with NaOH solution (0.1 M). The DO was determined according to eq. (1). (AGU = anhydrous glucose unit)

$$DO = \frac{c_{NaOH} \cdot V_{NaOH} \cdot M_{AGU}}{2 \cdot m_{DAC,oven\ dried}} \tag{1}$$

Determination of the degree of substitution (DS): The DS for cationic DAC was calculated via the nitrogen content obtained by elemental analysis according to eq. (2).

$$\%N = \frac{3 \cdot DS \cdot M_N}{(1 - DS) \cdot M_{AGU} + DS \cdot (M_{DAC} + M_{Girard} - M_{H_2O})} \tag{2}$$

Handsheet preparation: Sheets of 80 g/m² were produced according to Rapid-Köthen method (DIN EN ISO 5269-2:2005-03, 2005). Varying amounts of cationic DAC were added to the pulp suspension during paper production.

Tensile strength and relative wet strength: The wet breaking load of the produced papers was determined according to (DIN ISO 3781:2012-07, 2012). Relative wet strength values are given as the ratio of the average breaking load of fully saturated wet samples and samples conditioned in standard atmosphere (ISO 187:1990-12, 1990).

Results and discussion

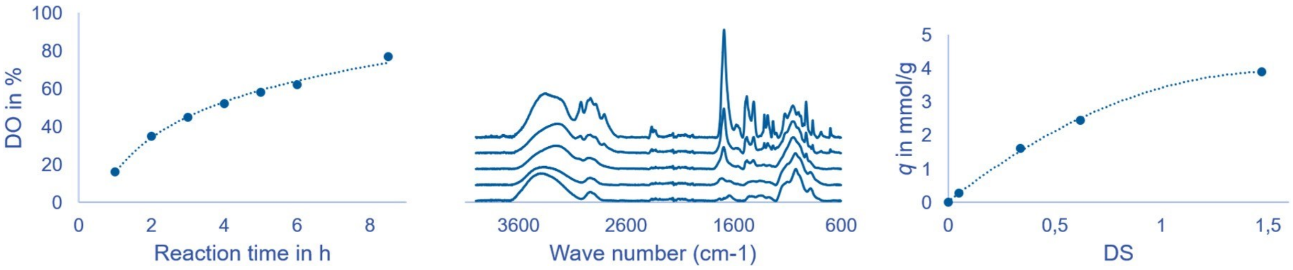

Figure 26. a) DO of produced DAC dependent on reaction time, b) IR spectra of DAC (DO = 77 %) and cationic DAC (with increasing DS). c) charge of cationic DAC dependent on DS.

As the ability of a polymer to act as a temporary wet strength agent heavily relies on the amount of available aldehyde groups, the DO of the produced DAC is of great importance. Figure 26 a) shows the increase of DO of the produced DACs dependent on the reaction time. It clearly shows asymptotic approach of the DO towards full oxidation, yielding a DO of 77 % after 8.5 h of reaction time, which was deemed sufficient for the desired application as a wet strength agent.

Furthermore, for a wet strength agent to work properly, a good interaction between the polymer and the fiber surface is required. Since fibers are slightly negatively charged, due to the presence of carboxyl groups on the fiber surface, wet strength agents are usually positively charged. However, as DAC is also produced from cellulose fibers, it also carries a slight negative charge natively. To facilitate proper fiber interaction, previous groups, investigating dialdehyde starch in a similar fashion, utilized alum as a retention aid under acidic conditions (Young, 1978). Since acidic conditions for paper production have fallen out-of-favor, we investigated cationic DAC obtained via the reaction of DAC and Girard's reagent T. Figure 26 c) shows the increase of the observed charge of the cationic DAC with increasing DS. While a highly charged polymer can be obtained in this matter, the cationization derivatizes available aldehyde groups and is thus in competition with the application of the polymer as a wet strength agent. Hence sample 2 (DS = 0.34, q = 1.61 mmol/g), showing a good compromise between remaining aldehyde groups and charge density, was deemed most promising as a possible wet strength agent.

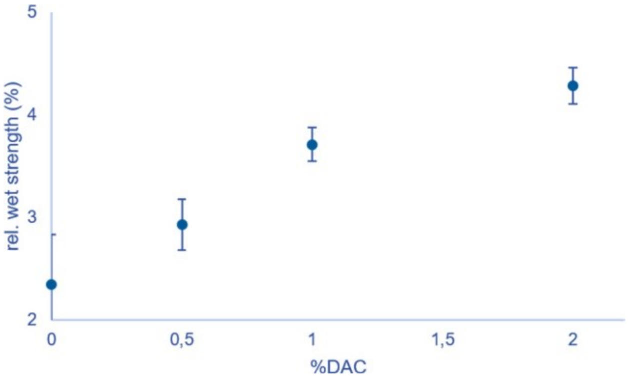

Figure 27. Relative wet strength of produced handsheets with varying amount of added DAC.

Figure 27 shows the relative wet strength of the produced handsheets with varying amount of cationic DAC added during the production process. It clearly shows an increase in the relative wet strength with an increase in added DAC (from 2.3 % without additives to 4.3 % with 2 % DAC added). While this demonstrates the general wet strengthening effect of cationic DAC, the obtained rel. wet strength values are below required values for commercial wet strength paper. The lack of performance may stem from a multitude of factors, which are currently being investigated. Foremost we believe the high water solubility of cationized DAC to be an issue, resulting in an incomplete adsorption of the wet strength agent to the fiber or rather a flushing out during the filtration step of the paper making process. Hence, we currently investigate alternative methods of introducing DAC into paper.

Conclusions

We were able to produce DAC with varying DO via Malaprade oxidation of cellulose pulp. Further the obtained DAC was cationized via the reaction of DAC with Girard's reagent T in varying stoichiometric ratios. First investigations into the application of cationized, water soluble DAC as a temporary wet strength agent showed an increase in the relative wet strength with increasing DAC content, proofing a general wet strengthening effect of DAC on paper. However, since the observed effect is currently below required benchmarks for wet strength papers, further research is required to substitute current wet strength agents with biobased DAC.

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Nanocellulose-Based Antimicrobial Microparticles as an Alternative to Toxic Nano-Biocides

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Abstract

Dialdehyde cellulose nanofibrils (CNF) and nanocrystals (CNC) were prepared via periodate oxidation (CNF/CNC-ox) and subsequently functionalized with hexamethylenediamino (HMDA) via the Schiff-base reaction. This resulted n porous and micro-sized (0.5-10 µm) particles (CNF/CNC-ox-HMDA) that can catch bacteria by multi-targeted (ionic and hydrophobic) non-specific modes of action, and prevent them from growing at minimum nontoxic (both in vitro to human lung cells and in vivo to Daphnia magna) concentrations (<0.2 wt.-%). The hydrodynamically smaller (0.5-1 µm) CNC-ox-HMDA decorated with aldehyde, anionic, amino and hydrophobic surface groups was found to be the most effective, with up to log 9 of bacteria reduction at >0.4 wt.-% and a bactericidal effect. While the antimicrobial less- active CNF/CNC-ox were fully biodegradable in composting soil within 24 weeks, this process was inhibited considerably for CNF/CNC-ox-HMDA, indicating their different stability and disposal after use (e.g. composting vs. recycling). As such, however, they can serve as an alternative to nano-biocides (such as metal nanoparticles), which are limited by their toxicity for humans and the environment.

Introduction

Research focusing on naturally-occurring biocides with a low-risk of toxicity for humans and the environment is becoming increasingly urgent. The use of nanocellulose (NC) in this context is also increasing (Norrahim et al., 2021), due to Its low cost and unique properties, which are potentially useful in many applications, such as wound dressings, composites, packaging materials, filters/adsorbents, textiles and paints. However, NC needs to be surface modified to gain an antimicrobial potential. Chemical modifications with non-leaching properties and prolonged biocidal activity are of the highest interest (Alavi et al., 2019; Norrahim et al., 2021). Surface modification of NC has been proposed with aldehyde, amino or quaternary ammonium groups, as well as conjugation with metal/metal oxide nanoparticles (e.g. Au, Ag, CuO, ZnO, and TiO_2), biocidal agents (e.g. gentamicin) or antimicrobial polymers (e.g. ε-poly-L-lysine). Dialdehyde modified NC (i.e. oxidized by sodium periodate to yield aldehyde groups at the corresponding C2 and C3 positions) has garnered substantial interest recently (Dalei et al., 2022), due to a good antimicrobial efficacy against both Gram-negative and Gram-positive bacteria, as well as possible follow-up modification chemistry (above all, Schiff-base reaction and oxidation to dicarboxylic acid or reduction to dialcohols). Functionalizations with amino or quarternary ammonium-bearing hydrophobic molecules are of particular interest, as they can, additionally, promote interactions with a negatively charged and hydrophobic bacterial cell membrane, compromising its integrity and leading to leakage of cytoplasmic content and, ultimately, cell lysis (Timofeeva and Kleshcheva, 2011; Tavakolian et al., 2020), thereby resulting in a bactericidal effect. However, despite the chemical similarity of dialdehyde-modified NC to the potentially (acute, eco, and cyto) toxic glutaraldehyde, such modifications are still generally considered as biocompatible, and low or non-toxic for the environment and human health, although rare studies can be found to support these claims.

The aim of this study was, thus, to determine the relative influence that NC aspect ratios (fibrillated CNF vs. rod-shaped CNC) and their surface chemical modifications (periodate oxidation to aldehydes and further conjugation with HMDA by the Schiff-base reaction), which alter their morphology and physicochemical properties, have on their antibacterial activity, aquatic (in vivo) and human cells (in vitro) toxicity, and ecotoxicology (biodegradability in composting soil). By performing an in vivo study on rabbits, it was already proven that HMDA- functionalized CNF can be classified as skin non-irritating (Kokol et al., 2021).

Experimental

The wood-based chain-like cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC), purchased from the University of Maine, USA, were modified by a two-step procedure (Kokol et al., 2021), i.e. the site-selective periodate oxidation in the first stage to form aldehyde groups (CNF/CNC-ox), and their functionalization with HMDA in the second according to a Schiff- based coupling reaction between the amine of the HMDA and CNF/CNC aldehyde groups, yielding CNF/CNC-ox-HMDA. The content of aldehyde groups of milli-Q suspended samples was determined by the modified spectrophotometric method using a 2,3,5-triphenylterazolium chloride (TTC)/KOH solution. Potentiometric titration was performed for quantifying the surface charge contribution using a dual-burette instrument (Mettler Toledo T-70), equipped with a combined glass electrode (Mettler TDG 117). The hydrodynamic size and the zeta-potential of the samples were assessed by Dynamic Light Scattering (Zetasizer, Nano ZS ZEN360, Malvern Instruments Ltd., UK) at 25±0.1 °C. The high resolution images of the sample were performed using a Sirion 400NC (FEI, USA) Scanning Electron Microscope. The standard dilution antibiogram, using the Gram-negative (G-) bacterium E. coli (EXB-V127) and Gram- positive (G+) bacterium S. aureus (EXB-V54), obtained from the Microbial Culture Collection Ex, which is operated within the Infrastructural Center Mycosmo, University of Ljubljana, Slovenia, was performed to evaluate the antibacterial properties. The acute toxicity tests were carried out in vivo according to modified ISO Standard (ISO 16197:2014) with Daphnia magna ephippia purchased from Microbiotests Inc., Belgium. The in vitro cytotoxicity of samples with A549 human lung adenocarcinoma cells was evaluated by three different cytotoxicity assays (Resazurin, Coomassie Blue, and Neutral Red Uptake). The biodegradation of approx. 0.1 g of each sample (prepared by solvent-casting as films, or by freeze-drying them as sponges) was analyzed in a composting soil obtained from the company Javne službe Ptuj LLC, Slovenia, according to the Standard ISO 11721-1: 2001.

Results and discussion

The attachment of HMDA on aldehyde groups was confirmed by reduction of the aldehyde content for CNF/CNC-ox after functionalization with HMDA (Table 16). The non-stoichiometrical attachment of

HMDA to CNF-ox might be related preferentially to a both-sides (crosslinking) rather than one-side (grafting) reaction, being supported by the formation of larger CNF-ox- HMDA micro-sized forms, as revealed from the hydrodynamic size analysis and SEM images (Figure 28). In the case of CNC-ox, an even higher amount of positively charged CNC-ox-HMDA was detected, despite the relatively smaller quantity of aldehyde groups, due to the preferential one-side conjugation of HMDA also associated to the contribution of the negatively repulsive groups. This wasmalso supported by the relative better dispersibility of all forms of CNC in aqueous media.

Table 16. The average content of surface groups and hydrodynamic-size for different forms of CNF/CNC with their minimum inhibitory (MIC) and bactericidal (MBC) concentrations against (G-) E. coli and (G+) S. aureus after 24 h of exposure.

Sample	Surface groups (mmol/g)			Hydrodynamic size (nm)	MIC (wt %)		MBC (wt %)	
	Aldehyde	Positive, amino	Negative, carbo-xylic/ sulfonate		*E. coli*	*S. aureus*	*E. coli*	*S. aureus*
CNF-ox	1.32±0.02	0.09	0.12	117±2	0.78±0.2	0.33±0	1.34±0.6	0.44±0
CNF-ox-HMDA	0.05±0.001	5.64	0.09	515±92	0.8±0	0.3±0	1.6±0	0.4±0
CNC-ox	1.04±0.06	/	3.59	11266±4197	0.98±0	0.49±0.23	1.3±0	0.65±0
CNC-ox-HMDA	0.35±0.02	1.80	3.56	6761±8427	0.43±0	0.26±0.08	0.85±0	0.43±0

The native CNF/CNCs cannot target and disturb the cell wall, cell membrane, or active enzymes of bacterial strains, so did not show any antibacterial activity (MIC and MBC could not be determined) against both tested bacteria. However, both oxides (CNF/CNC-ox) and HDMA-functionalized (CNF/CNC-ox-HMDA) forms exhibited good, but also quite different, concentration-dependent response to both bacteria. While CNF/CNC-ox gave generally higher (in the case of CNC) or similar (in the case of CNF) MIC values than CNF/CNC-ox-HMDA, and lower against (G+) *S. aureus*, such a difference might be related to both the presence and accessibility of aldehyde groups, as well as hydrophobic tails bearing amino groups to interact with the bacteria cell wall (Saini et al., 2016; Li et al., 2018). On the other hand, a significant reduction in (G-) *E. coli* bacteria in the presence of CNC-ox-HMDA, as compared to the CNF- ox-HMDA, can be interpreted by the even stronger and diverse (electrostatic, hydrophobic and unspecific) adsorption of hydrodynamically smaller particles to such a cytoplasmic membrane with hydrophobic, negative and unprotonated surface charge properties.

Among all the tested suspensions, the highest immobility of D. magna (85 %) was reached for CNC-ox-HMDA, followed by CNF-ox-HMDA with 56 %, after exposure to the highest tested concentration (20 mg/l), while it was much lower for CNF/CNC-ox (25 %) and native CNF/CNC (13-14 %). The immobility of HMDA alone was much more concentration dependent, resulting to only 38 % of animals immobile at 20 mg/l.

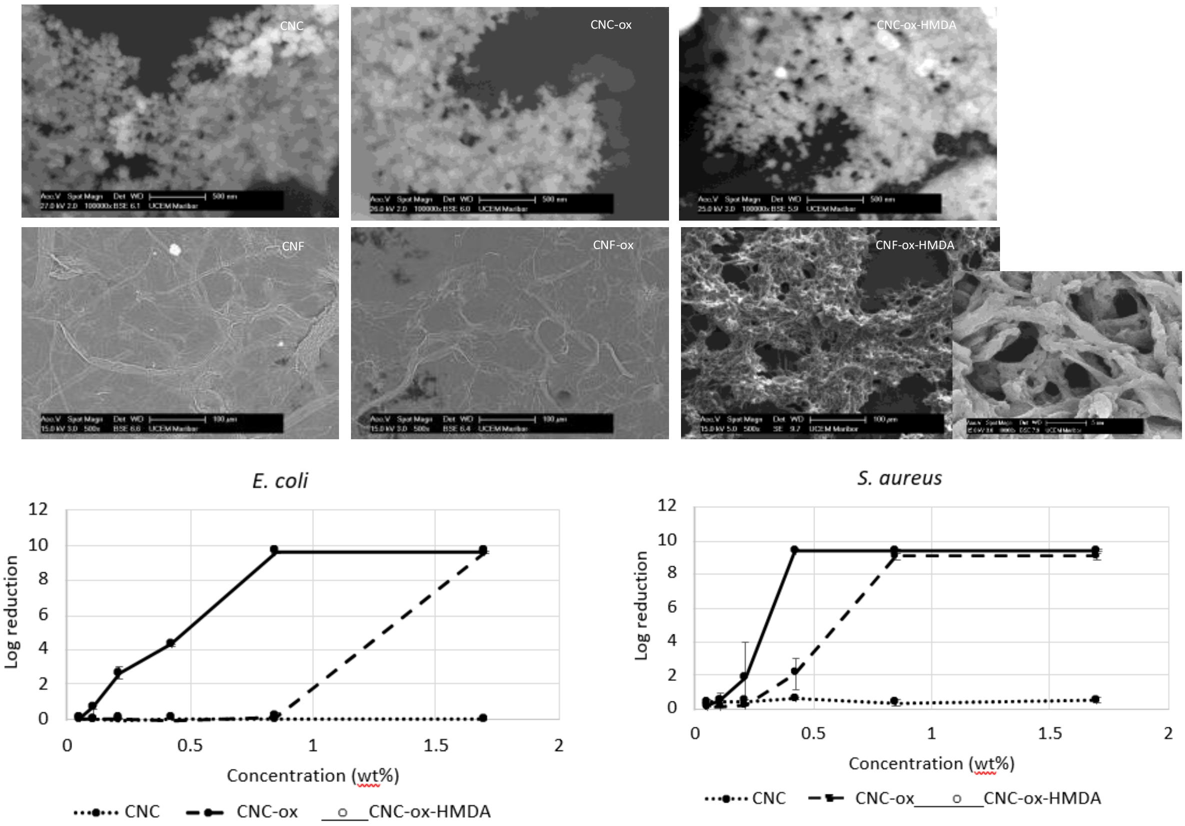

Figure 28. SEM images of native (CNF/CNC), oxidized (CNF/CNC-ox) and HMDA-functionalized

The results from the cytotoxicity assays revealed no (for native CNF/CNC, as well as CNC- ox) or low (at ≥ 75 mg/l for native CNF/CNC, and at ≥ 50 mg/l for CNCF/CNC-ox-HMDA) cytotoxicity, including the HMDA alone, while CNF-ox was not cytotoxic in all the used concentrations (up to 100 mg/l)

The degradation in composting soil was faster for CNF film than CNC film, followed by CNF and CNC sponges, confirming the effect of both samples` crystallinity (highly crystalline CNC vs. semi-crystalline CNF, and the presence of surface acid groups, as well as the accessibility of microbial species / specific enzymes) for prerequisite interaction with the sample surface and its bulk, necessary to achieve time-comparable dynamics of biodegradation (Vikman et al., 2015). The antimicrobially active CNF/CNC-ox films did not hinder samples` degradation, but rather delayed it considerably, following the same trend, although both tested samples were biodegraded up to >80 % over 24 weeks (168 days). On the contrary, all CNF/CNC-ox-HMDA samples were not, or slowly susceptible to biodegradation, which indicated that the aminated and hydrophobic nature of the samples hindered their biodegradation in such a microbiological environment, which was reflected in their weight gains. The biodegradation is, namely, inhibited primarily by the degree of functionalization on its surface, which involves the adsorption and colonization of microorganisms in the first stage; this process was more evidenced for the sample prepared as a film than a sponge, which further confirms their better accessibility and maintaining of microbial populations.

Conclusions

The antibacterial efficacy, aquatic in vivo (to Daphnia magna) and human in vitro (to human lung cells) toxicities, and degradation profiles in composting soil of differently modified CNF/CNCs were assessed, in order to define their safety profile. CNF/CNC-ox-HMDA exhibited higher antibacterial activity than CNF/CNC-ox, and higher against Gram-positive *S. aureus* already at minimum nontoxic (both in vitro and in vivo) concentrations (<0.2 wt.-%). Hydrodynamically smaller CNC-ox-HMDA increased the reduction of both bacteria to log 9 at >0.4 wt.-% and their bactericidal effect, although showing noticeable toxicity. While CNF/CNC- ox are fully biodegradable within 24 weeks, this process was inhibited considerably for CNF/CNC-ox-HMDA.

Acknowledgements

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Efficient New Extraction Method for Highly Charged Phosphorylated CNC

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Abstract

Phosphorylated cellulose nanofibrils (CNF) have been shown to have tremendous potential in a broad range of applications including flame-retardant materials, high-capacity renewable ion exchange materials or substrates exhibiting controlled biomineralization as well as biocompatibility. Compared to CNF, cellulose nanocrystals (CNC) have exhibited improved colloidal stability and higher potential for controlled assembly applications. Yet harnessing these properties for phosphorylated CNC has been impossible thus far due to laborious extraction procedures that suffer from low degrees of substitution, poor reproducibility and inadequate yields. We can overcome these drawbacks by combining the modification routines for phosphorylated CNF with hydrolysis by gaseous HCl to liberate CNC. This allows us to reliably and reproducibly isolate phosphorylated CNC with exceptionally high surface charges at high yields and minimal water consumption.

Introduction

Rod-like cellulose nanocrystals (CNCs) are gaining prominence given their sustainability and broad range of applications, which include rheological modifiers, water treatment membranes, functional coatings and biomedical templates (Klemm et al., 2018; Thakur et al., 2021; Vanderfleet & Cranston, 2021).

Phosphorylated cellulose derivatives come with additional functional benefits such as their increased biocompatibility, flame-retardant behavior and potentially higher surface charges (Li et al., 2012; Sionkowska et al., 2019). Unfortunately, conventional phosphoric acid hydrolysis fails in delivering such particles. Instead, the obtained particles showed low degrees of substitution and poor reproducibility (Martin & Annamalai, 2021; Vanderfleet et al., 2018).

High-charge phosphorylated cellulose derivatives including cellulose nanofibers (CNFs) however, have routinely been obtained by a solvent-free urea-mediated reaction between cellulose and phosphate salts (Ghanadpour et al., 2015; Little, 1947; Liu et al., 2015; Rol et al., 2020). The crucial difference between this approach and the conventional phosphoric acid hydrolysis seems to be the absence of water.

Therefore, we propose a new route towards high-charge pCNC which combines the urea/phosphate modification protocols with HCl gas hydrolysis (Kontturi et al., 2016; Lorenz et al., 2017; Pääkkönen et al., 2018) of the obtained substrates in the dry state (Figure 29). Thereby, water consumption is reduced significantly and potential drying steps in between hydrolysis and cellulose modification can be avoided, facilitating the process and reducing resource consumption and energy demand. Stable pCNC dispersions in water were obtained by a means of scalable microfluidization of the modified and dispersed pulp.

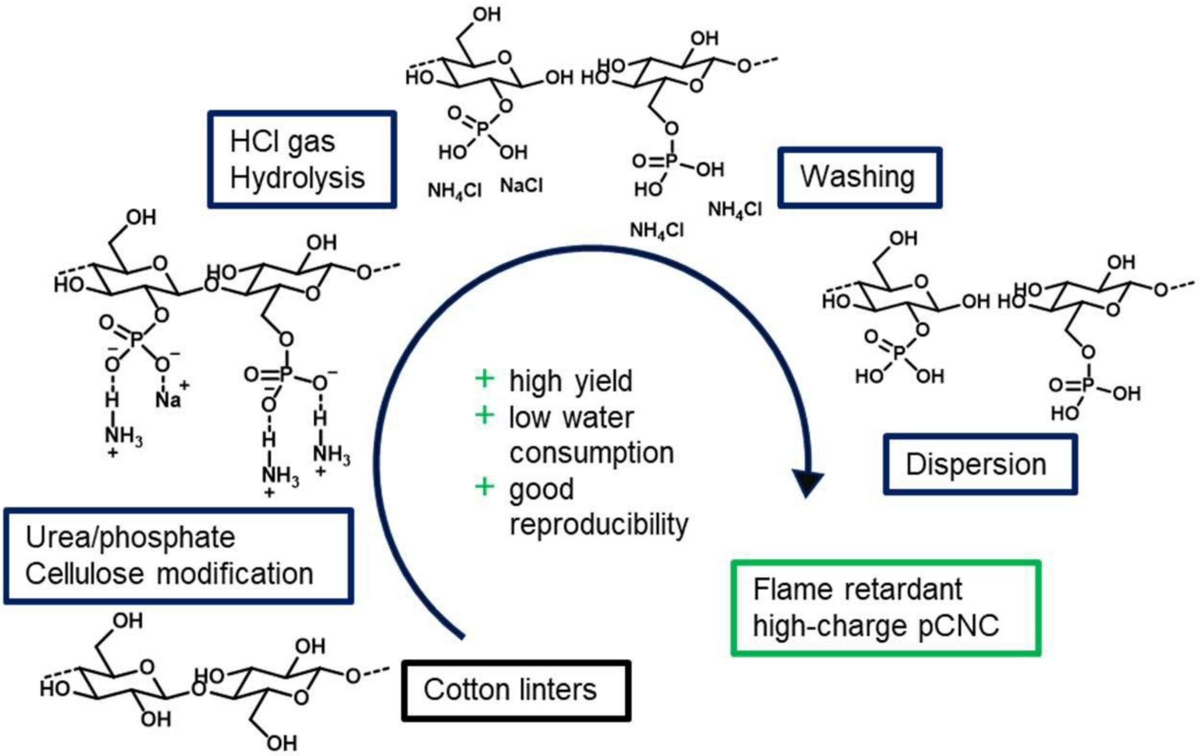

Figure 29. Reaction scheme

Experimental

Cotton fiber modification

For the modification of the fibers, we adapted the procedure used by Rol et al. (2020) to produce phosphated CNF. In a typical experiment, 1.10 g phosphoric acid (85 %, VWR Chemicals), 1.49 g monosodium phosphate dihydrate (98 %, Supelco) and 5.5 g urea (Sigma Aldrich) were added to the wet and blended Whatman 1 filter paper ($AGU:H_3PO_4:NaH_2PO_4:urea$ 1:0.5:0.5:4.7), along with deionized water to bring the total weight to 40 g. The modified and dried pulp was blended again in the dry state to increase the surface area. Subsequently, HCl gas hydrolysis was conducted at 1.1 bar pressure for 4 h in the custom-built reactor as described earlier (Pääkkönen et al., 2018) After wetting by stirring overnight at pH 6.5, centrifuging and decanting, the pulp was redispersed in 300mL 1 M HCl to protonate the phosphate groups. Further washing was conducted following renewed dispersion, centrifuging, decanting and redispersion in water until conductivities below 50 µS/cm and a pH of 4.5 was reached. The produced CNC were dispersed using a

Microfluidics M-110P microfluidizer at 1 wt.-% consistency. The fluidizing was performed in three passes at 1500 bar through a pair of Z-type collision chambers with dimensions of 400 µm and 200 µm, respectively. The obtained dispersion was filtered through a 10 µm mesh to exclude large aggregates. A CNC yield of 70 % was achieved based on the mass of cellulose in the modification step and in the obtained CNC (92.2 wt.-% cellulose, 7.8 wt.-% phosphate groups).

Analytics

Conductometric titrations were carried out on the washed pulp according to the protocol described by Ghanadpour et al. (2015). Zeta potentials were measured in triplicates using a Malvern Zetasizer ZS90. For AFM analyses, 0.01 wt.-% pCNC dispersions were spin-coated at 4000 rpm on poly(ethyleneimine) coated silicon wafers. The substrates were imaged using a Bruker Multimode 8 AFM in tapping mode. Cantilevers of the model NCHV-A by Bruker with force constants of 42 N/m and 320 kHz resonance frequency were used.

Analyses for carbon, hydrogen and nitrogen contents were carried out on a Thermo Scientific FlashSmart CHNS/O elemental analyzer equipped with a copper reduction phase on moisture- free samples. Phosphorus was determined by digesting the pCNC both in HNO_3/HCl/H_2O_2/HF, $B(OH)_3$ and H_2O_2/HNO_3 and analyzing the digestate by ICP-OES using an Agilent 5900 SVDV system. The thermal decomposition of the produced samples was analyzed using a Netzsch STA 449 F3 Jupiter analyzer. The samples were burned in air.

Results and discussion

As shown in, our pCNC carry significantly higher charge than the pCNC produced by phosphoric acid hydrolysis. Instead, the charges and zeta potentials are in the same range as pCNF produced with urea/phosphate modifications. This shows that the phosphate surface esters are formed successfully and can be retained during hydrolysis and the single washing step.

It should be noted, however, that while the zeta potentials, surface charges and phosphate contents in *Table 17* are adapted from literature based on the information available the data is not unequivocally comparable. Firstly, for zeta potentials reported in literature, there seems to be an ambivalence as to whether to adjust the ionic strength of the analytes (Foster et al., 2018; Vanderfleet et al., 2018) or not (Kassab et al., 2020; Kokol et al., 2015; Martin & Annamalai, 2021). Increasing the ionic strength invariably lowers the measured mobilities and zeta potentials as the more mobile co-ions effectively slow down the mobility of the analyte particles. Secondly, the data acquired by conductometric titrations does not genuinely reflect a surface charge. Rather, it is the sum of deprotonated phosphate groups and sodium ions bound to the particle surface through counterion condensation. Separating both phenomena is not trivial and currently under investigation.

Table 17. Zeta potential, surface charge and phosphate content reported for phosphorylated CNC and CNF compared to this work.

Product	Synthesis method	Zeta potential (mV)	Surface charge (mmol/kg)	Phosphate content (mmol/kg)	Ref.
pCNC	Cotton linters treated with urea/ NaH_2PO_4/H_3PO_4	-35 to -45	1920$^{(a)}$	1000$^{(c)}$	This work
pCNC	Phosphoric acid hydrolysis of cotton linters	-9.8 to -36.9	10.8 to 79.2$^{(a)}$	3.95 to 44.5$^{(b)}$	(Frost. & Foster, J. 2020; Camarero Espinosa et al., 2013; Kassab et al., 2020; Vanderfleet & Cranston, 2021)
pCNF	Kraft pulp treated with Urea/ ammonium phosphate		1840 to 2560$^{(a)}$	230 to 2200$^{(b)}$	(Ghanadpour et al., 2015; Messa et al., 2021; Noguchi et al., 2017)

a) Determined by conductometric titration; b) Determined by molybdate colorimetric essay;
c) Determined by elemental analysis. * calculated from reported values for degrees of substitution

The successful dispersion of nanoparticles could be proven by AFM as shown in Figure 30a. We found the average length of the particles to be 116 nm, which is to be expected from HCl hydrolysis of cotton linters (Kontturi et al., 2016; Lorenz et al., 2017). Figure 30b shows the thermal decomposition behavior during TGA. It is evident that the initial degradation of the pCNC occurs at significantly lower temperatures than the unmodified cotton linters. However, the pCNC show significantly increased stability between 250 °C and 500 °C, which has been linked to flame- retardant behavior, and a significant amount of ash at 900 °C which is due to non-volatile polyphosphates formed during pyrolysis. For sulfated and TEMPO-oxidized CNC, the same degradation behavior at low temperatures has previously been attributed to the imparted surface functionality, that facilitates surface dehydration (Lin & Dufresne, 2014; Vanderfleet et al., 2019). While the same degradation behavior has been established for pCNF, (Ghanadpour et al., 2015) however, no similar decrease in the initial thermal stability has been observed for pCNC (A. Frost & Johan Foster, 2020; Camarero Espinosa et al., 2013; Vanderfleet et al., 2018). This is most likely due to the significantly increased degree of substitution (Lin & Dufresne, 2014), which would also account for the lack of ash for the reported pCNC.

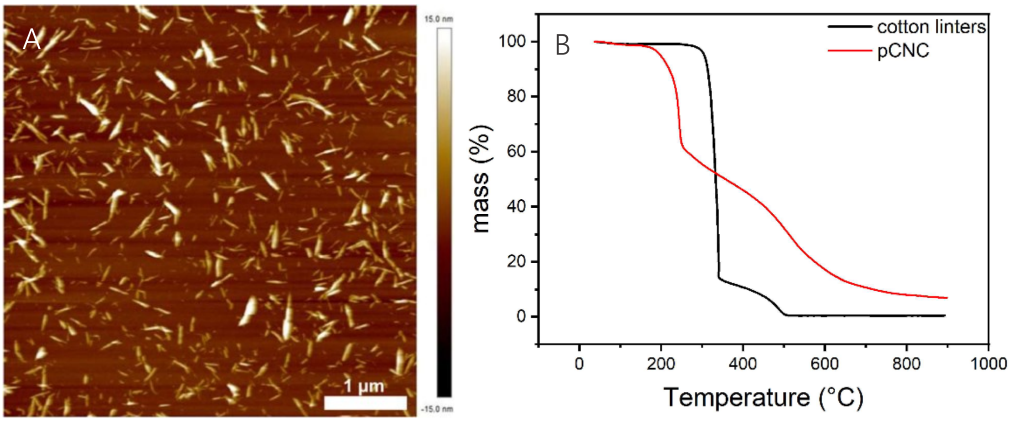

Figure 30. AFM image of the produced pCNC (5 µm x 5 µm) (A) and thermal degradation behavior of cotton linters and pCNC (B). The sample mass decreases to 95 % at 207 °C (pCNC) and 308 °C (cotton), with the strongest decline in mass occurring at 244 °C, and 337°

Conclusions

We have presented a robust method to produce highly-charged pCNC at high yields. Compared to the previously reported protocols, we managed to significantly reduce water consumption and improve yields, reproducibility, dispersibility and the performance of the produced pCNC with the presented approach, which, unlike the phosphoric acid hydrolysis, has

the potential to be scaled up. As a consequence, we have obtained pCNC that have comparable surface charges and thermal degradation behavior as pCNF produced with the same method and will be suitable for a variety of anticipated applications.

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Novel Cellulose Modifications

Progress on Cellulose Esterification – Control Over Surface to Bulk Modification

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Abstract

The industrial acetylation of high-purity technical cellulosics is well studied mechanistically and known to involve elementary fibril chain exfoliation, leading to cellulose triacetate (CTA) for-mation Sassi, & Chanzy, 1995). The biodegradability of such materials, in the context of the single-use plastics di-rective, are justifiably under scrutiny, which is very much related to the increased hydrophobicity of high DS cellulose acetates (Yadav, & Hakkarainen, 2021).

Recently we developed two methods that allow for fine control over the regioselectivity of sur-face acetylation of different cellulose substrates (Koso et al., 2022, Beaumont et al., 2021). One method involves the controlled sur-face modification of dried cellulose substrates, e.g. nanocelluloses, pulps & regenerated fibres (Koso et al., 2022). Another, takes advantage of the novel properties of surface-bound water and mechanical ac-tivation to yield a thorough penetration of the fibre network, yet, still maintaining high regiose-lectivity (confinement of reaction to fibril surfaces). These methods are especially illustrated through the combined application of a novel solution-state NMR method, high resolution AFM and WAXS. The regioselectivity results are also supported by DFT-based transition-state model-ling on a cellulose surface fragment.

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Structure – Function – Performance Interrelations in Materials Engineering

Multifunctional and Biobased Coating Aided by Digital Material Design

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Abstract

Lignocellulosic biomass is considered one of the most viable alternatives to replace fossil-based raw materials for carbon-neutral advanced materials. While there are many promising methods to produce sustainable cellulosic packaging and textile materials, there is a clear need for sustainable and scalable surface functionalization methods. Many of the modification methods are either toxic or they hamper the biodegradability of the material. Although we strive for recyclable and long lasting materials, they should degrade if ending up in soil or waters, not to form microplastic pollution. Our research addresses this problem by developing green, enzymatic methods to functionalize cellulosic surfaces. Purely natural lipids and lignin nanoparticles are used to produce superhydrophobic, UV-resistant and antimicrobial activity. We aim at developing robust and rough coatings mimicking nature's superhydrophobic materials (Figure 31). An environmental impact estimate will guide the coating development to find the most scalable and sustainable approaches. We use enzymes both to attach and detach the lipophilic materials to the substrate consequently improving both durability of coating and the recyclability of the materials. Using cellulose, we target to biobased, durable yet easy to remove, hydrophobic coatings and a coating technology that is applicable in textiles and packaging.

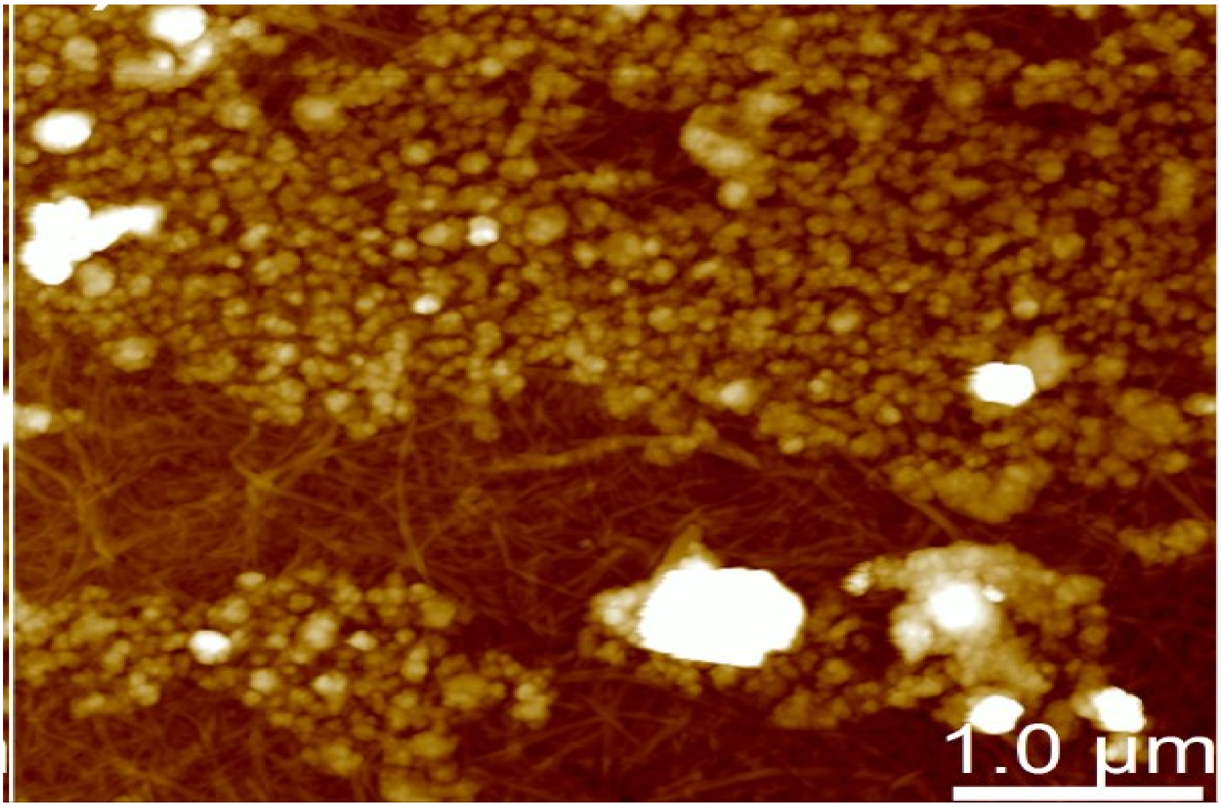
1.0 µm

Figure 31. AFM height image of wax particles on cellulosic thin film (upper image) and water droplets on a wax particle treated cotton fabric illustrating the waer repellance achieved by combining roughness and low surface energy (Forsman et al., 2020).

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Structure – Function – Performance Interrelations in Materials Engineering

Simulating the Impact of Nozzle Hole Locations and Diameters on Film Thickness in Spinning Process

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Abstract

In the film spinning process, pressure applied on the cellulose solution in an extruder forces the polymer through a narrow slit. Subsequently, a rotating chill roll stretches the emerging film in an air gap. As a desired result, the film becomes thinner, but as an undesired side effect the width of the film also decreases. Furthermore, the thickness variation in the lateral direction is another perturbation. To improve the control over the film properties, we experimented with two distribution plates having different locations and sizes of the holes through which the dope entered the nozzle. As a support for the experimental study, we also conduct a finite element simulation for both the viscous flow of the polymer through the nozzle and the mechanical balance in the film passing through the air gap. For the flow in the nozzle, we apply the cross model for a description of the dependence of the viscosity on the shear rate, employing experimentally obtained values for the parameters in the model. The connection between the flow in the nozzle and the sheet stretching in the air gap is the velocity profile in the slit.

Because the thickness dimension of the film is much smaller than the film width and stretching length, we can approximate the situation in the air gap with a 2D membrane model, where the velocity and stress assume constant values in the thickness direction. In addition, we model the convective and radiative heat transfer in the air gap. We carry out the simulation in the COMSOL Multiphysics software comparing the simulated thickness profiles generated by the two different plates with each other as well as with the experimentally obtained measurements.

Introduction

Necking and the edge bead effect are two common geometrical defects hampering the industrial film extrusion process (Dobroth, 1986), (Sollogoub et al., 2006). The former consists of a reduction in width as the extruded film approaches the collecting roll that stretches the film and the latter manifests itself as non-smooth thickness of the final cross section of the film with the edges being thicker than the center. Early mathematical models of the film spinning process were essentially monodimensional accounting for the width of the film as a function of the length coordinate. This kind of models were able to address the necking phenomenon but obviously not the edge bead effect. Consecutive models included the width coordinate and dealt with the thickness ass a membrane approximation, the thickness of the membrane being a function of the distances from the outlet slit of the spinneret and the center line of the film. Usually, computational

models assume the exit velocity being constant across the width of the slit, but in this study, we consider the prospects of adjusting the spinneret to generate a variable flow velocity that may affect the formation of the film.

Experimental

The study employed three laboratory spinnerets of different geometries combined with two distribution plates with different hole sizes. *Table 18* and *Table 19* summarize the geometric features of the three spinnerets and the diameters of the holes in the two distribution plates respectively. Furthermore, Figure 32 shows the locations of the holes on the distribution plate. We note that the spinnerets differ in their cone angles and slit depths, whereas for the two distribution plates, the contrast lies in plate 2 having smaller central holes than plate 1, to induce a faster flow at the ends of the spinneret outlet, aiming to affect the necking of the film.

Table 18. Geometric features of the spinnerets

	Spinneret 1	Spinneret 2	Spinneret 3
Cone angle	13°	8°	4°
Slit width	0.25 mm	0.25 mm	0.25 mm
Slit length	70 mm	70 mm	70 mm
Slit depth	0.3 mm	1.2 mm	2.4 mm

Figure 32. Locations of distribution plate holes

Table 19. Diameters of distribution plate holes

	Plate 1	Plate 2
Holes a and g	1.95±0.05 mm	1.95±0.05 mm
Holes b and f	1.45±0.05 mm	1.45±0.05 mm
Holes c and e	0.95±0.05 mm	1.45±0.05 mm
Hole d	0.7±0.05 mm	1.45±0.05 mm

For the simulation we employ the CFD module of the Comsol Multiphysics software to model the dope in the spinneret as a generalized Newtonian fluid, with the viscosity depending on the shear rate according to the cross model.

$$\mu(\dot{\gamma}) = \mu_\infty + \frac{\mu_0 - \mu_\infty}{1 - (k \cdot \dot{\gamma})^n}$$

Here $\mu(\dot{\gamma})$ is the viscosity as a function of the shear rate $\dot{\gamma}$. Furthermore, $\mu 0$ and $\mu\infty$ are the first and second plateaus respectively. Finally, k and n are experimental constants. Fitting the cross model to experimental data rendered the estimates of the parameters in the model. (Moriam et al, 2021)

Results and discussion

Figure 33 shows the simulated flow field for spinneret geometry 1 and distribution plate 1. Generally, the simulation, for all the combinations of spinneret geometry and plate hole distributions, results in a flow field increasing in magnitude towards the edges. This is not surprising given the sparser density of the inlet holes in the center. Furthermore, the effects on the flow from modifying the spinneret are coherent, in the sense that distribution plate 1 promotes a stronger flow near the edges as compared plate 2 as does the spinnerets with narrower cone and deeper slits when compared to their counterpart. In addition, the effect of the spinneret geometry dominates that of the distribution plate. Figure 34 shows the simulated outflow velocities. Obviously, decreasing the hole diameters enhances the flow near the edges. Perhaps a bit more surprisingly, the slimness of the cone, hampering the redistribution of the fluid, seems to be the more important factor in increasing the flow near the edges.

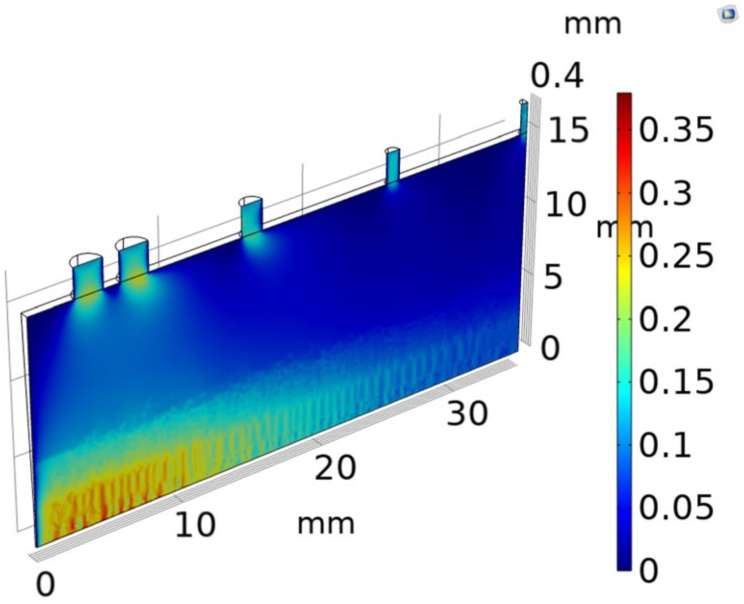

Figure 33. Simulated flow magnitude in spinneret 1 having distribution plate 1

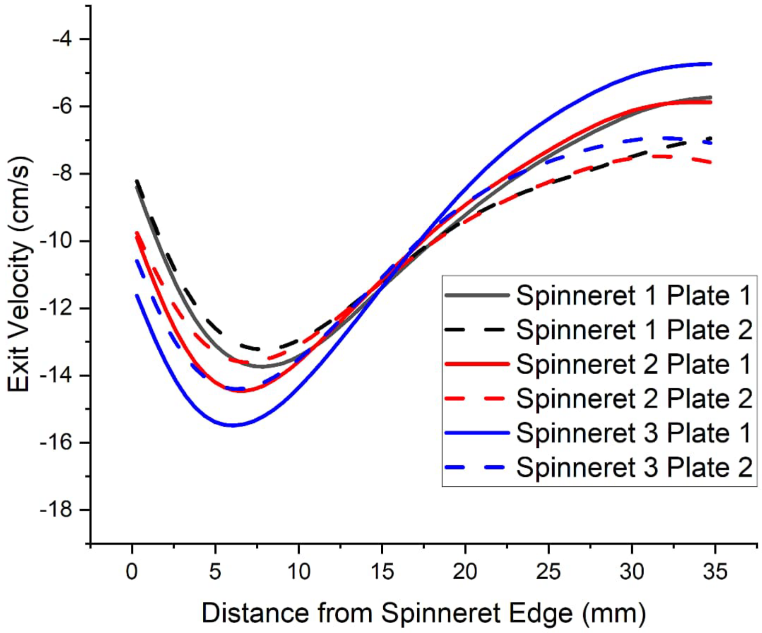

Figure 34. Smoothed simulated velocities at spinneret exit for different spinneret geometries and plate distributions

Conclusions

Smaller cone angle in the spinneret and prevalence of the lateral holes in the distribution plate promote the flow near the edges of the spinneret exit.

Acknowledgements

An academic license of COMSOL Multiphysics enabled the fluid dynamics calculations.

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Structure – Function – Performance Interrelations in Materials Engineering

Capturing Colloidal Nano- and Microplastics with Plant-Based Nanocellulose Networks

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Asbtract

Microplastics is one of the most pressing environmental concerns. They accumulate in various aquatic organisms causing serious health issues, and they have raised concerns about human health by entering our food chain. Especially nanosized plastics are considered harmful to the environment due to their colloidal size and large surface area.

Currently, there are no means to recover or investigate nanoplastics since existing methods are suited only for larger microplastic particles. This study shows how an extremely hygroscopic and nanoporous network formed by cellulose nanofibrils can bridge this significant methodological gap related to efficient entrapment and filtration of the most harmful fraction of nanosized plastics. Nanocellulose acts as an ideal capturing element since in aqueous environment, capillary forces are present transporting water into the hygroscopic nanocellulose network. The formed water flux conveys the particles inside the network structure, which in turn, provides additional sites that can be tuned to enhance the attractive forces between microplastics and nanofibrils.

To demonstrate the viability of nanocellulosic networks in microplastic recovery and capturing, we utilized polystyrene beads with defined properties. Nanocellulose hydrogels and self-standing films were used as capturing substrates, and the accumulation of polystyrene particles was qualitatively and quantitatively followed using fluorescence methods. In addition, the adsorption of nanoplastics was monitored by quartz crystal microbalance with dissipation monitoring (QCM-D) verifying the specific and quantitative binding of the nanoplastics on CNF. In our interfacial approach, we coupled the adsorption data from QCM-D with image analysis and a random sequential adsorption (RSA) model and thus we were able to not only quantify the nanoplastic uptake but also provide kinetic information on the particle update and provide novel methods for nanoparticle detection.

Structure – Function – Performance Interrelations in Materials Engineering

High Performance Cellulose-Based Substrates for Flexible Printed Electronics

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Abstract

Nanocellulose films with their renewable and biodegradable nature can be an excellent alternative to plastic substrates in printed electronics applications. However, these films are inherently brittle and possess low tear resistance. They are also sensitive to moisture and lack stretchability which is an important criterion for wearable skin-mounted electronic applications.

In this work, we improved various performance aspects of nanocellulose films through combining novel approaches based on structure function optimization. Cellulose fibers with varying lengths and cellulose derivatives with varying viscosity and molecular weights were explored as additives to nanocellulose, and their impact on film flexibility, tear resistance, and stretchability were studied. Furthermore, antimicrobial performance was introduced into the films through use of a wood-based additive, tannin.

Introduction

The demand for smart wearables, such as sensors in personal health, monitoring, and diagnostic medical gadgets, is increasing, which is driving the demand for flexible printed electronics (Corzo et al., 2020). These applications currently use fossil-derived flexible plastic substrates. The increasing usage and disposal of such devices will add further to the accumulation of plastic waste, which is already an enormous burden on the environment. Nanocellulose films with their renewable and biodegradable nature can be an excellent sustainable alternative to plastics in these applications (Vasara et al., 2021). However, nanocellulose films have a highly brittle nature and they possess very low tear resistance. In addition, their sensitivity to moisture and lack of stretchability makes it challenging to use them for wearable skin-mounted electronic applications. Hence, these films need significant improvements before they become suitable for such demanding applications.

In this work, we explored the use of cellulose fibers and derivatives to impart the missing performance attributes to nanocellulose films. Sorbitol and alkyl ketene dimer (AKD) were used to provide plasticizing effect and hydrophobic character to the films, respectively.

Experimental

Materials

Nanocellulose or cellulose nanofibers (CNF) with a solids content of 1.7 % was prepared from bleached never-dried Nordic hardwood kraft pulp using mechanical grinder (Masuko), followed by a total of 6 passes through a microfluidizer (M-7115-30, Microfluidictics, USA). Unbleached CNF was produced from hardwood pulp in the same manner. The cellulose derivates hydroxyethyl cellulose (HEC; viscosities 80-125 cP (2 %), 145 cP (1 %), and 3400-5000 cP (1 %) and (Hydroxypropyl)methyl cellulose (HPMC; viscosities 15 cP (2 %), 15000 cP (2 %), and 75000-140000 cP (2 %)) were purchased from Sigma-Aldrich. Lyocell (length 6-8 mm), softwood pulp (length 2- 3 mm), and microfibrillated cellulose (MFC; length <1 mm) were used as physical fiber additives. Microfibrillated cellulose (MFC) with a solids content of 1.8 % was prepared from bleached kraft pulp using Masuko grinder followed by fluidizing once. The softwood pulp was diluted to 1 % consistency and dispersed with a high-shear Dispermixer (Ystral GmbH, Germany) at 1800 rpm for 20 minutes. 1.5 denier lyocell short-cut fibres with a 6 mm length were obtained from Engineered fibres technology LCC, Shelton, USA. D-Sorbitol (Sigma-Aldrich GmbH, Germany) was used as a plasticizer and alkyl ketene dimer (AKD; Aquapel™ 320, Solenis LLC, USA) to increase hydrophobicity. Chestnut tannin was purchased from Christian Markmann GmbH (Chestnut Extract Type N, Hamburg, Germany) consisting of a 93.8 % of dry matter content and a 0.11 % of nitrogen content.

Preparation of films

The small-scale films were prepared through solvent casting. Prior to casting, CNF, cellulose derivative or physical fibers, sorbitol, and AKD were homogenized using a disperser (Dispermat, VMA-Getzmann GmbH, Germany) over 20 minutes. After mixing the suspensions were deaerated in an asymmetric vacuum centrifuge (SpeedMixer DAC 600, Synergy Devices Ltd., UK). The suspensions with varying consistencies of 1-1.5 % were cast on polystyrene Petri dishes and dried at 23 °C and 50 % relative humidity until the film was fully dry. Based on the performance of small- scale films, the best performing film formulations were produced on a pilot scale using VTT’s roll- to-roll water-based casting process (SutCo). The dispersion with consistencies of 1.5-1.8 % was gap cast on plasma-treated polypropylene film and dried at room temperature to obtain the film.

Mechanical properties

The mechanical properties of the films were studied with a tensile tester (Lloyd LS5, Ametek Inc., USA) using 1 kN load cell, 5 cm gauge length, and 5 mm min-1 elongation rate. The thickness of films was measured using a L&W micrometer 051 (Lorentzen & Wettre AB, Sweden) and films were cut into 5 cm x 10 cm specimens. Samples were equilibrated at 21 °C and 50 % relative humidity at least for 1 day. The mean tensile strength and strain were determined from five parallel samples. The tear resistance of films was assessed qualitatively by hand testing, and it was done by four different researchers to avoid bias.

Antimicrobial properties

Antimicrobial properties of the CNF films were examined against Staphylococcus aureus (E- 70045 strain) which was obtained from VTT Culture Collection and used as a target microbe. Diluted test samples were prepared into the media. Inoculation was carried out in a constant concentration of the microbe, and the samples were in the incubator over night at 37 °C. Growth of colony in the samples was monitored with automated turbidometer, Bioscreen CTM (Thermo Scientific, Finland) and Research Express software (Transgalactic Ltd, Finland) for 48 h. More detailed procedure is described by Alakomi et al., (2006).

Results and discussion

Mechanical performance of films

The conflict of strength and ductility is a well-acknowledged challenge, as strong materials tend to be fragile while ductile materials tend to be weak, and when either of these properties is improved it is usually done at the expense of the other. Keeping this in mind, the target film performance for this application was set to a reasonable level: 50 MPa (tensile strength) and 20 % (strain at break). As seen in Figure 35A, CNF concentration in CNF-HEC films was found to be proportional to the obtained film strength, and all the concentrations led to sufficient tensile strength (>50 MPa). The relationship between strain and HEC concentration was not as clear since the largest ductility was achieved with the middle concentration and not with the highest HEC concentration, as expected. The best performing ratio of 60:40 was further investigated with the other cellulose derivative, hydroxypropyl methylcellulose (HPMC), to screen the best performing additive and viscosity in terms of strength and ductility (Figure 35B). Both HEC and HPMC (the medium viscosity grades) provided the film with the best combination of tensile strength and strain. However, only HEC with medium and low viscosity grades were near the strain target of 20 %. Tear resistance was better in HEC than HPMC (which had better strain values), as seen in Figure 35C. The tear resistance was observed to be improved in the film along with the improvement in strain.

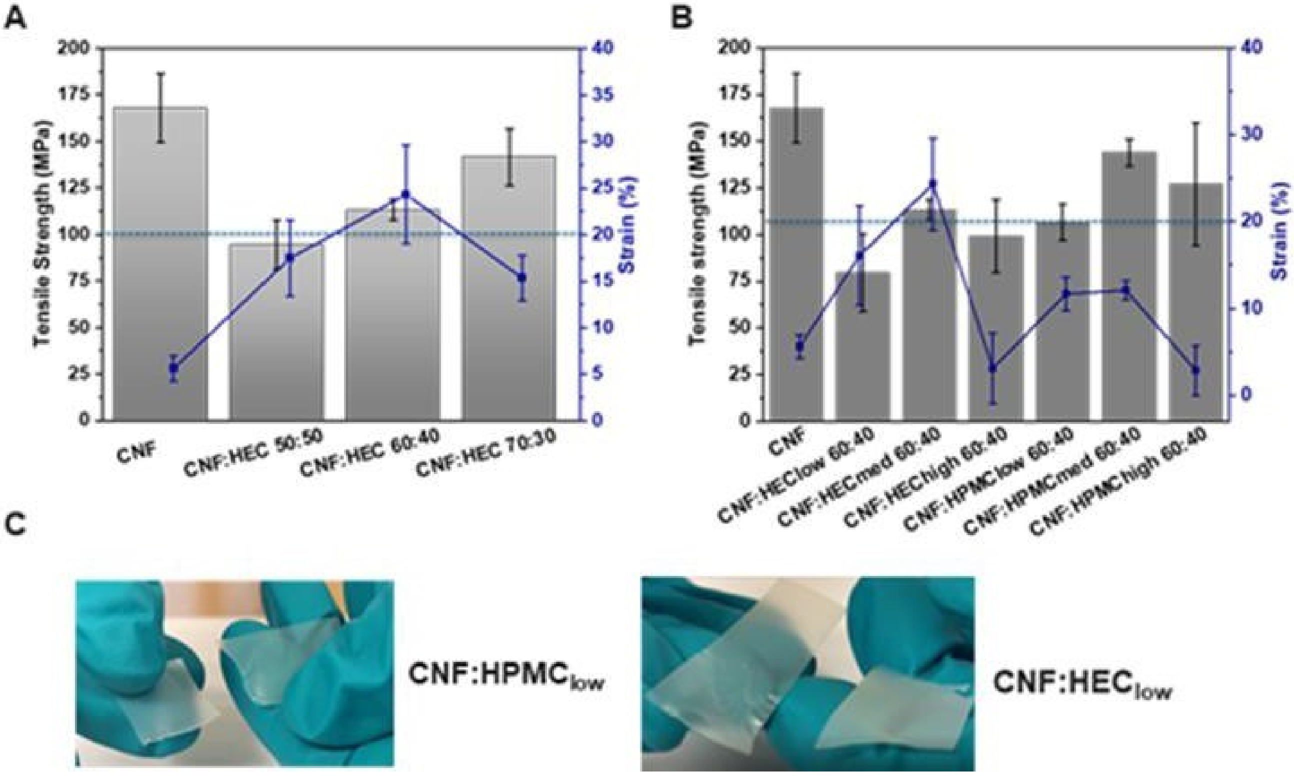

Figure 35. A. The effect of CNF to HEC medium viscosity on mechanical properties., B. the effect of HEC and HPMC at low, medium, and high viscosities with the ratio of 60:40 (CNF:additive) on the mechanical properties, and C. Images of films with poor tear resistance (left panel) and improved tear resistance (right panel).

Typically, once the crack is formed, the tear propagates through the film. Therefore, three different physical fibers were tested as additives in films to prevent crack propagation (Figure 36A). The addition of physical fibers however made the films even weaker and less ductile than neat CNF film Figure 35C). Increased shrinkage during drying was another challenge observed with the addition of fibers. The higher fiber length additive led to a higher shrinking during drying and thus produced a wavier film (Figure 36B).

The influence of the film thickness on the mechanical properties of the films is shown in Figure 37A. The strength of the film remained at a similar order of magnitude regardless of the thickness of the film, but the strain exceeded the critical 20 % target in thicker films. The thicker films also showed better tear resistance than thinner films (Figure 37B). Tear resistance was at its highest when the film had sufficient ductility and a higher thickness.

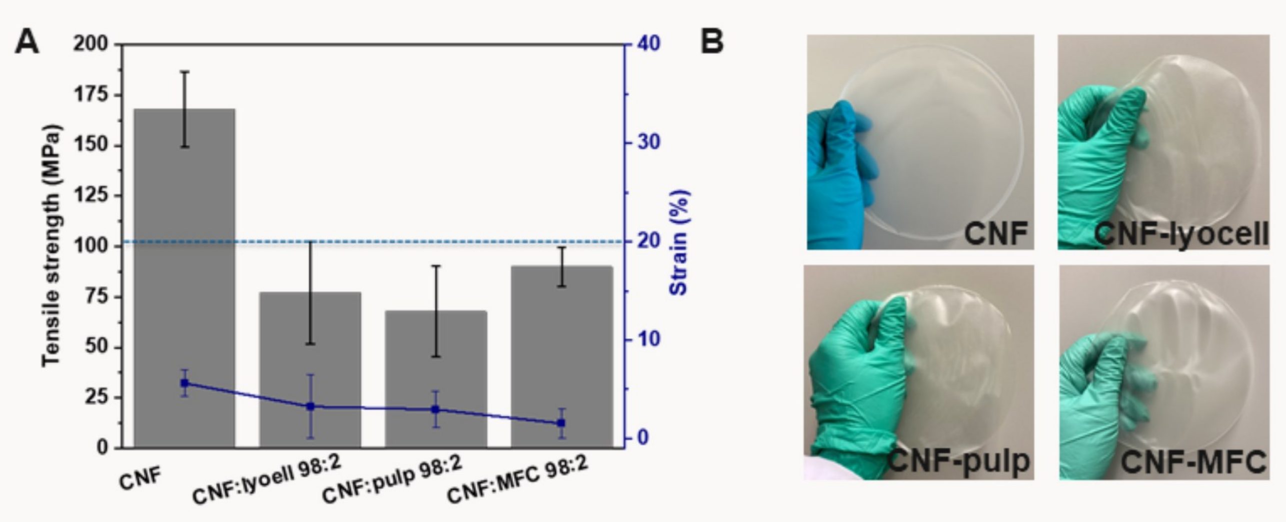

Figure 36. A. Mechanical properties of films with fiber additives B. Pictures of native CNF film in comparison to films with lyocell, pulp, and MFC as additives.

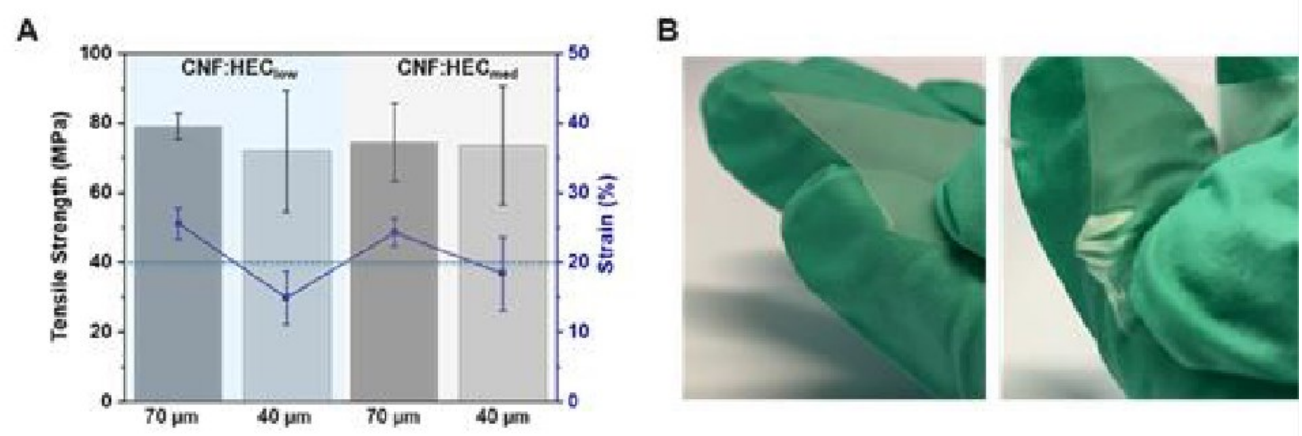

Figure 37. A. The effect of film thickness to mechanical properties of films prepared from CNF:HEC with a ratio of 60:40 using low and high viscosity HEC. B. The tear difference between easily tearing film (left panel) and film with improved tearing resistance (right panel).

Effect of chestnut tannin and unbleached CNF on the mechanical performance

Determination of mechanical properties of films containing chestnut tannin and unbleached CNF showed that the addition of tannin led to a reduction in tensile strength and strain at break. However, the mechanical performance was maintained at 1 part tannin addition level (Figure 38). On the other hand, mixtures with unbleached CNF had a clear correlation of the mechanical properties and addition levels. Although excess ratio of unbleached CNF would deteriorate the mechanical properties, unbleached CNF showed potential to improve the properties when used at less than 50 % of total CNF. Comparison of these findings with those of other studies showed that lignin has potential to reinforce the tensile strength of CNF film (Farooq et al., 2019), moreover addition of lignin to CNF in nano particle form might be more effective for the purpose than utilizing lignin as unbleached CNF. This is an important next step for future research.

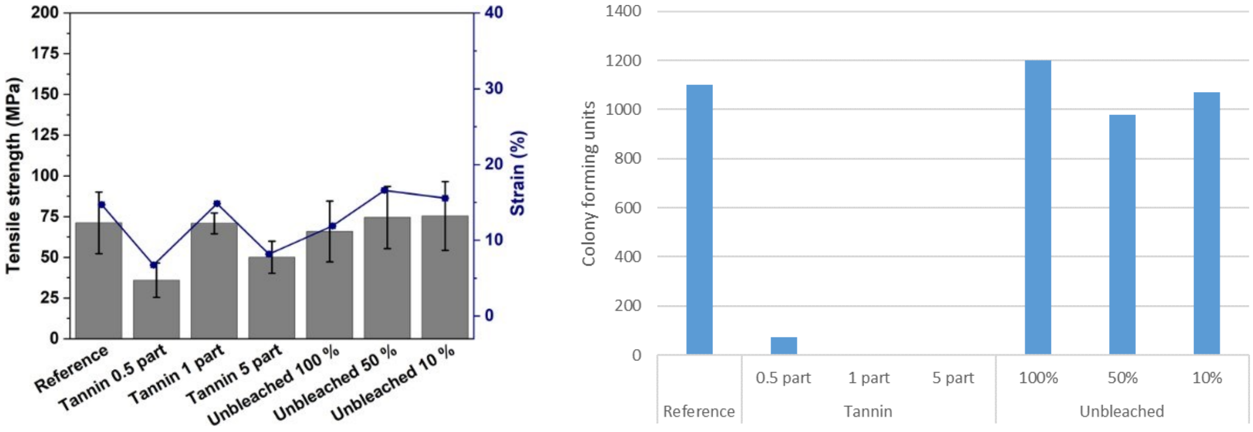

Figure 38. Comparison of mechanical properties of CNF films containing chestnut tannin and unbleached CNF in different ratios. B. Antimicrobial effect of the CNF films containing chestnut tannin and unbleached CNF against S. aureus.

Antimicrobial effect of chestnut tannin and unbleached CNF

To evaluate antimicrobial effect of chestnut tannin and unbleached CNF, the test was conducted against S. aureus, which is a Gram-positive bacterium frequently found in skin infections. Figure 38 compares the results obtained from the antimicrobial tests. There was a significant reduction in colony forming units in the CNF films containing chestnut tannin compared to the reference sample. This is indicative of antioxidant effects provided by a polyphenolic substance like tannin (Missio et al., 2020). In contrast, no significant difference was found between the group of CNF films containing unbleached CNF and reference, suggesting no antimicrobial effect of the unbleached CNF.

Conclusions

Films based on cellulose nanofibrils (CNF), cellulose fibers of varying lengths and cellulose derivatives of varying molecular weight and viscosities were prepared and characterized for their mechanical performance. The addition of cellulose derivatives was found to improve the flexibility, stretchability, and tear resistance of the films. However, the addition of cellulose fibers led to a significant drying shrinkage resulting into very poor-quality films. The addition of chestnut tannin improved the antimicrobial performance without significantly deteriorating the mechanical performance of the films. The ultimate goal of this work is to combine the best of all these performances to achieve a high-performance substrate for printed flexible electronics.

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Low Emission Biorefineries and Side-Stream Valorization

When Historical Partners, METSA and FIRMENICH, Combine Technical Expertise to Improve both Recovery Yields and Quality of Crude Sulfate Turpentine

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Abstract

Turpentine, constituted by monoterpenes such as alpha-pinene, beta-pinene and/or delta-3-carene, play an important role as fragrances in perfumes, cosmetics, detergents, as flavors for spicing foods and are predicted to be more important in the future to compete and replace some of the current fossil-based products.

Originally recovered from tapping industry, turpentine is nowadays mostly produced from softwood kraft pulping industry, so-called crude sulfate turpentine (CST). Being by far the most important chemical conversion industry of wood, kraft pulping is also considered as the largest biorefinery industry. Aiming first at producing pulp from carbohydrates and recovering energy from lignin, more and more attention is given on upcycling some by-products such as Tall Oil, CST and Methanol.

Sharing similar values and targets regarding sustainable growth, and being historical commercial partners, Metsä – leading global BSK market pulp producer, and FIRMENICH – biggest consumer of CST in the World, decided to launch a technical win-win collaboration with the goal of improving both CST qualities and recovery yields in kraft mills, allowing then to lower environmental and safety concerns and generate additional volumes of CST for FIRMENICH and so additional revenues for Metsä.

Specific LEAN methodology was developed and implemented with the involvement of both expertise team.

Rauma Mill CTS recovery needs to be optimized as the integrated pine saw mill is coming into operation in Q3/2022. With the fresh saw mill chips an increased potential to recover more CST will be present. Evaluating the CST potential in different streams will be of most importance for the further work

Consequently, combining technical expertise and drafting specific methodology are key to succeed, to strongly reinforce win-win partnerships and reduce environmental impact.

Low Emission Biorefineries and Side-Stream Valorization

Size Based Monitoring of Cellulose Hydrolysis Reaction for the Cellulose Nanocrystal (CNC) Production

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Abstract

A new size-based monitoring of cellulose hydrolysis reaction for CNC production has been explored by using CrillEye technique. Two different starting materials (bleached pulp and rejected fibers) were used for this study. Initial rate of the reaction was faster for both type of pulp material. However, after 2.5 h of reaction, produced CNC particles are smaller for bleached pulp compared to rejected fibers.

Introduction

Cellulose is renewable, biodegradable, as well as non-toxic and one of the most abundant biopolymer found on Earth. In plant cell walls cellulose is organized into microfibrils, which consist of the organized or crystalline as well as less organized or amorphous form. The amorphous parts can be removed preferentially by a chemical reaction, i.e., selective acid hydrolysis, after which only the organized or crystalline parts of the cellulose remain (Dufresne 2013). Which is either nanocrystalline cellulose or microcrystalline cellulose, depending on the reaction conditions and application demands.

With increasing demand for high-performance renewable materials with tailormade mechanical and physical properties makes cellulose nanocrystals or nanocrystalline cellulose (CNC/NCCs) the most attractive material for diverse applications. CNCs have many different interesting properties which includes high specific Young’s modulus similar to Kevlar and steel, non-toxicity, ability to form lyotropic liquid crystals, promising reinforcing properties due to their amphiphilic nature and high aspect ratio (Trache et al., 2020). CNCs can also act as rheological modifiers and interface stabilizers (e.g., in emulsions, gels and foams) (Xie et al., 2018; Grishkewich et al., 2017). Another interesting property of CNCs is the high colloidal stability due to presence of highly charged functional groups that are adsorbed on the surface of CNCs during its production.

Chemically induced longitudinal de-structuring of cellulose microfibril is the most efficient and classical way to dissolve amorphous or less organized region which leads to formation of CNCs as an aqueous suspension. Various strong acids e.g., phosphoric acid, hydrochloric acid, nitric acid, sulfuric acid has been used for production of CNCs although sulfuric acid is always remained as preferential choice for acid selection (Nasir et al., 2017). One of the key reasons for selecting sulfuric acid is, its bisulfate anion (HSO 4-) adsorbed on the surface hydroxyl groups of cellulose. Which renders very high negatively charge CNCs with superior colloidal stability (Ioelovich, 2012 and Kobayashi, 1960).

However, the quality of CNCs by acid hydrolysis method is strictly depends on various parameters e.g., type of cellulose raw materials, acid strength and amount of acid, reaction time and temperature, size, or type of reaction vessel. Therefore, monitoring acid hydrolysis reaction of cellulose based raw material for the production of CNCs is very important and specially when various type of raw materials are subjected to hydrolyzed. However, there is no direct size based method is available for monitoring cellulose hydrolysis reaction to produce CNCs. Although, indirect UV based method available which is solely measurement of sugars, humins, HMF and other acid soluble compounds content but no size-based information possible to extract from the reaction (Becker et al., 2021).

In this regard CrillEye (Figure 39) can contribute significantly to measure and monitor size-based information from long chain cellulose unit to CNCs during hydrolysis reaction. CrillEye has been used extensively for measuring and characterizing pulp quality in pulp and paper industries (Paper FIRST 30 Nov 2020; Hansen et al., 2012). The term "Crill" was derived from the Norwegian term denoting pelagic organism was first reported by Steenberg et al., in 1960 as loose particles (Figure 41) (Steenberg et al., 1960). Historically, PulpEye AB develop the online crill measurement technique by using OptoCrill method from STFI (now RISE Innventia) which was first reported by Thorulf Pattersson and his coworkers in 1982 (Pattersson et al., 1982). Crill measurement is very straightforward techniques where sample suspension is passed through a transparent glass cell which is connected with two different wavelengths of light sources (UV and NIR) perpendicularly. Particles interacts with lights of different wavelengths (UV and NIR) according to their size and signals are collected and measurement results are presented as the ratio of signals of two different wavelengths (Figure 40). We envisioned that by using CrillEye's technology, direct size-based monitoring of cellulose hydrolysis will be possible. This will further open new door of CNCs process development where it will be possible to produce CNCs with desired quality irrespective of cellulose source.

In this work we are aiming to use two different cellulose sources from Domsjö Fabriker AB. Initial hydrolysis reaction trial will be done with Domsjö Fabriker's standard bleached pulp and later hydrolysis trials will be done with cellulose-based side-stream (rejected fibers). This project will further give us opportunities and knowledge of CrillEye's application into nanomaterials as well as use of cellulose-based side-streams from regional pulp and paper industries for CNCs production. By using cellulose-based side stream from pulp and paper industries, we can further lower the production costs of CNCs.

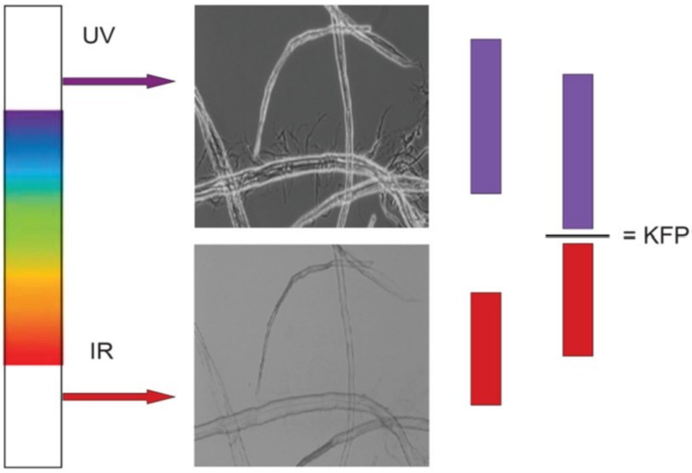

Figure 39. The CrillEye module

Figure 40. Principle of Crill measurement

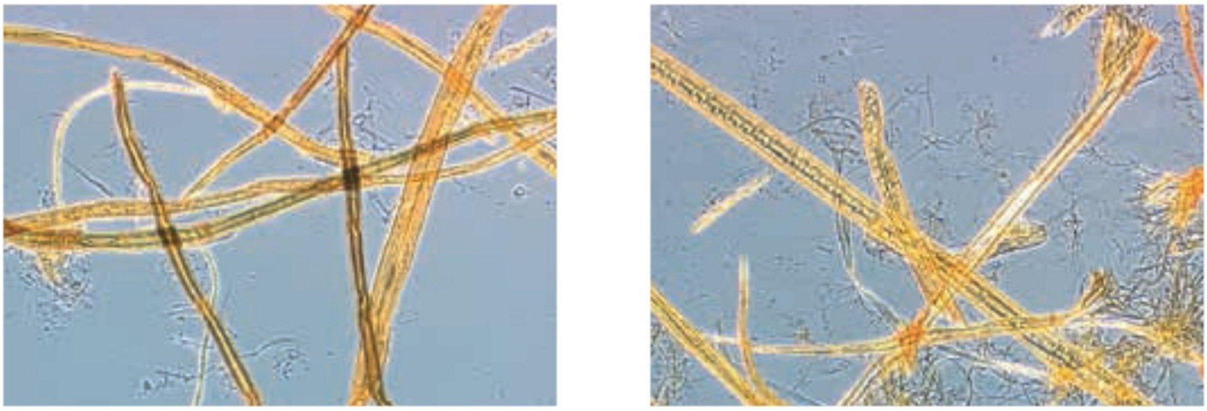

Figure 41. Refined fibres (left) and fibres with thin fibrils (crill) (right)

Experimental

In this work we performed experiment in two parts. In part 1 we have monitored hydrolysis reaction for Domsjö fabrik's standard bleached pulp and in part 2 we have monitored hydrolysis reaction of Domsjö fabrik's rejected fibers.

In our first part of the work, bleached pulp sheets were shredded by paper shredder (dokumentförstörare) to get small pulp pieces (Figure 42). 50 % H_2SO_4 was prepared by dilution of concentrated (VWR 95 %) sulfuric acid. The hydrolysis reaction was performed in 1L jacketed glass reactor. First, 1000 mL 50 % sulfuric acid solution was placed in 1L glass reactor, and the acid solution was heated to 45 °C with continuous stirring. After 30 minutes when the temperature of the oil bath and acid solution becomes under equilibrium, 100gm (~95 % dry matter content) shredded pulp was added to start hydrolysis reaction. Total 5 samples with approximately 100ml volume of each were taken out in every 30 minutes from the hydrolysis reaction. Samples were prepared for Crill analysis. During the sample preparation step we were aiming to prepare 3L solution with 1 % cellulose concentration for Crill measurement. Although Crill analysis is concentration independent but in our preliminary work we were intended keep sample concentration constant in order to verify application of Crill measurement for CNCs production. However, it was difficult to prepare 1 % sample solution without removing the remaining acids from samples. Therefore, we washed the samples via centrifugation until acid content becomes <0.5 %. Then we take small amount washed sample with accurate weight for freeze drying to get dry matter content of the wet samples. After obtaning the dry matter content, the samples were diluted with deionized water to make 1 % 3L solution for Crill measurement analysis.

In our second part, the rejected fiber was received from Domsjö Fabriker as wet lumps with 37 % dry matter content. Our initial attempt was to use the fiber directly without drying and perform reaction according to previous reaction conditions (~1:10 pulp to acid ratio). Unfortunately, it was very difficult to mix the suspension. Most of the cases we observed that the small lumps were hydrolyzing very quickly whereas the bigger pulp lumps remain unreacted. Thus, we decided to dry the rejected fiber before proceeding hydrolysis reaction. The rejected fibers were heated in a drying oven with temperature 100 °C for 4-5 hours to get stable weight. We observed that after reaching 80 % dry matter content the weight of fiber becomes almost constant although rejected fibers becomes very hard lumps (Figure 43). We decided to continue the hydrolysis reaction with rejected fiber containing 80 % dry matter content. Hydrolysis reaction was performed in same 1L reactor which was used previously and 100 gm of rejected fiber with dry matter content 80 % was used for hydrolysis reaction. The temperature (45 °C) and sulfuric acid concentration (50 %) kept same as previous experiment. Every 30 minutes samples were collected from reaction mixture for Crill measurements. In this experiment sample preparation process for Crill analysis was modified compared to previous experiment. The samples were washed with water in centrifuge until acid content becomes <0.5 % then samples were neutralized to pH ~5 with 1M NaOH. Dry matter content of neutralized samples were measured and samples were diluted to get 3L of 1 % cellulose solution. The neutralized 1 % sample solutions were analyzed via CrillEye for Crill measurements.

Figure 42. Bleached pulp

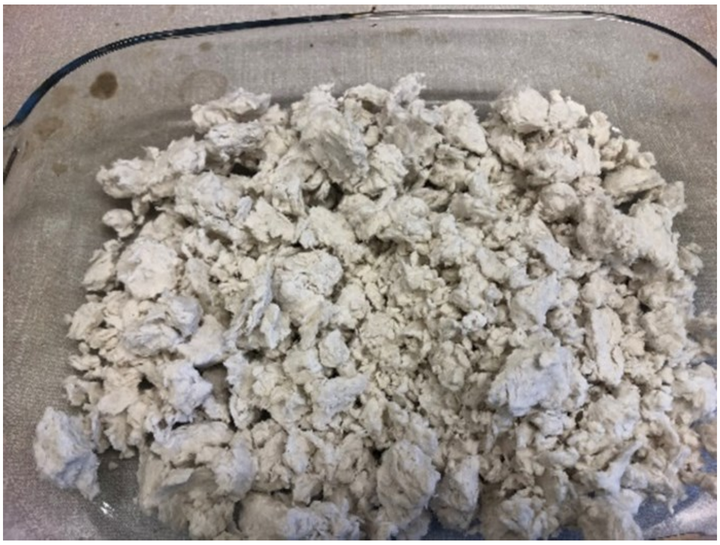

Figure 43. Fibre reject

Results and discussion

Crill value Data of bleached pulp were plotted (Figure 44a) with respect to reaction time and starting material taken as reference sample at time 0 minute. Initial Crill values for starting material was 108 whereas after 30 minutes it becomes 193 approximatly 78 % increment. After one hour the Crill values reaches to 244 which is 26 % increase in Crill value from previous sample. Although after 1.5 and 2 hours, only 9 % increase of Crill value was observed. However, with prolongation of reaction for further 30 minutes, there was only 7 % increase in Crill value was observed. From the Crill value plot we can see that the reaction was very fast at the beginning and becomes sluggish after 90 minutes. Although overall rate of hydrolysis reaction was comparatively faster than rejected fiber.

Crill value Data of rejected fiber were plotted (Figure 44b) with respect to reaction time and similarly starting material taken as reference sample at time 0 minute. The Crill plot of rejected fiber show slightly different results at the beginning compared to bleached pulp. Initial Crill values for rejected fiber was 140 whereas after 30 minutes it decreases to 133 whereas after 60 minutes Crill value increases to 181 with 36 % increment. However, after two hours only 8 % increment in Crill values was observed. The values became stable at 223 after 2.5 and 3 hours of reaction.

From the Crill plot it is very clear that the rate of hydrolysis reaction of rejected fiber was slower compared to bleached pulp and requires longer time or probably higher temperature. The rejected fibers were very inhomogeneous and some bigger fiber lumps become very hard after drying. Probably this was the reason for slow hydrolysis rate compared to shredded pulp. The initial decrease in Crill values probably fast consumption of small fiber lumps in the reaction. In both cases, we can also observe that the hydrolysis reaction was faster at the beginning and then becomes slower after 2 hours. This is probably due to the hydrolysis of amorphous part of the cellulose pulp. However, after 2.5 hrs of hydrolysis reaction the final Crill value for bleached pulp reached over 250. In case of rejected fibers, it reached below 250. This can also signify that the CNCs produced from bleached pulp is consist of smaller particles size compared to rejected fibers.

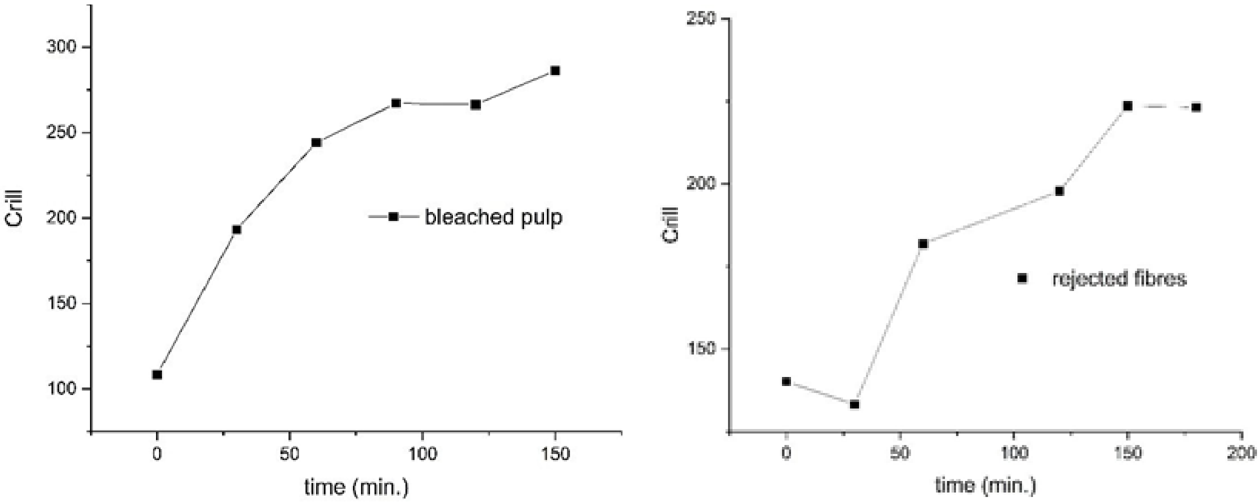

Figure 44. Plot of Crill value of (6a) bleached pulp and (6b) rejected fibers vs hydrolysis reaction time

Conclusions

These experiments proves that it is possible to monitor the acid hydrolysis reaction of pulp for producing CNCs by offline Crill analysis. The sharp increase in Crill values with respect to reaction time clearly indicates the surface area of the cellulose is increasing which significantly resembles to decrease in size distribution. Initial faster rate of reaction corresponds to hydrolysis of amorphous part of the cellulose pulp. However, all these measurements were done via offline Crill measurement. To prove this technique for commercial application, more online experimental data will be required. Furthermore, Crill measurement can be useful also when preparing CNCs with targeted size distribution.

Acknowledgements

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Low Emission Biorefineries and Side-Stream Valorization

LigniOx Process Concept to Produce Lignin Dispersants at a Kraft Pulp Mill and an Organosolv Biorefinery

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Abstract

The LigniOx oxidation process uses O_2 under alkaline conditions to solubilise water-insoluble lignins. The oxidized lignins with increased anionic charge have been demonstrated to work as a concrete plasticiser and versatile dispersants.

Recently, a concept of LigniOx process for producing lignin dispersants at a kraft pulp mill has been developed. In the concept, unwashed kraft lignin (primary cake from CO_2 precipitation stage) is O_2 oxidised partly using oxidised white liquor, available in the mill, as a source of alkali. Thereafter, the oxidised lignin solution is post-treated by membrane filtration to recycle the chemicals (Na, S) and to produce high-performance dispersants. Based on a simulation study, recovering 20% of the lignin in black liquor, and oxidising this unwashed lignin does not increase the need to purge fly ash in a kraft pulp mill, unlike the conventional lignin recovery process alone.

Most lignin precursors carry methoxy groups, which are released as methanol in the course of lignin oxidation. Therefore, in addition to the lignin dispersants produced by the integrated LigniOx process, high quantities of methanol (MeOH) is formed as a by-product. This MeOH is transferred to the evaporation plant at the kraft pulp mill within the permeate fraction from the membrane filtration. The crude MeOH from the evaporation can be purified using an already existing technology. The high quality bioMeOH is a valuable raw material for the chemical industry. Production of bioMeOH would increase the economic viability of the LigniOx process concept for the sustainable lignin dispersants.

Besides kraft pulp mills, the LigniOx process has been demonstrated to apply to organosolv biorefineries. Integration benefits of this technology also exist for the production of organosolv lignin based dispersants with MeOH as a by-product.

Introduction

Ever increasing interest in recovering multiple value-added products from kraft pulp mills has introduced technologies for lignin recovery and upgrading. In the recovery process, lignin is typically precipitated from the black liquor using carbon dioxide (CO_2) followed by further precipitation and washing with sulphuric acid (H_2SO_4) providing a lignin with low ash content. A typical softwood kraft mill has an oversupply of sulphur coming into the process from tall oil separation. When sulphuric acid is used in the lignin precipitation stage, there is increased pressure to remove sulphur from the cycle as a form of fly ash (mainly composed of Na_2SO_4 and Na_2CO_3) and consequently increased need to add make-up NaOH. Besides the challenge of maintaining the mill Na/S balance, NaOH is a major cost item for lignin recovery. Here, LigniOx concept for converting kraft lignin to a dispersant product and methanol (CH_3OH), MeOH (a by-product) without interfering with the chemical balance in the mill is presented. LigniOx technology is also applicable to organosolv biorefinery, proving lignin dispersants and MeOH.

Results and discussion

The LigniOx process uses O_2 gas under alkaline conditions to increase the anionic charge of lignin. The final oxidised lignin product can serve as a concrete plasticiser or versatile dispersant. Besides kraft lignin (KL), the oxidation has been applied to other lignin by-streams, such as organosolv lignin (OSL), to provide water-soluble anionic lignin dispersants (Figure 45). Lately, novel application areas for LigniOx lignins have been presented (Vyörykkä et al., 2022).

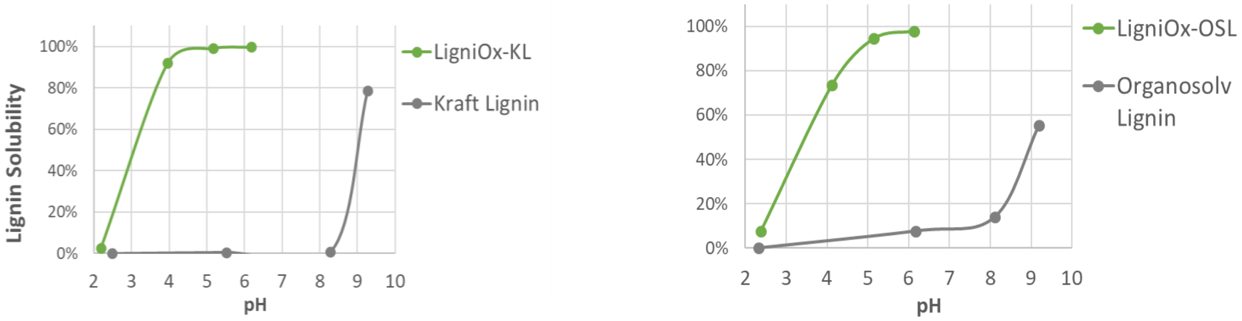

Figure 45. Solubility vs pH: Kraft and organosolv lignin before and after LigniOx oxidation.

PhOHs in lignin are starting point for O_2 oxidation under alkaline conditions. The anionic charge can be attributed to carboxylic acids and hydroxyl-p-quinones introduced in lignin during oxidation (Kalliola, 2015). LigniOx oxidation retains the polymeric structure of lignin. Most lignin precursors carry methoxy groups, which are released as methanol in the course of lignin oxidation. Thus, in addition to the lignin dispersants produced by the oxidation, MeOH is formed as a by-product (Figure 46).

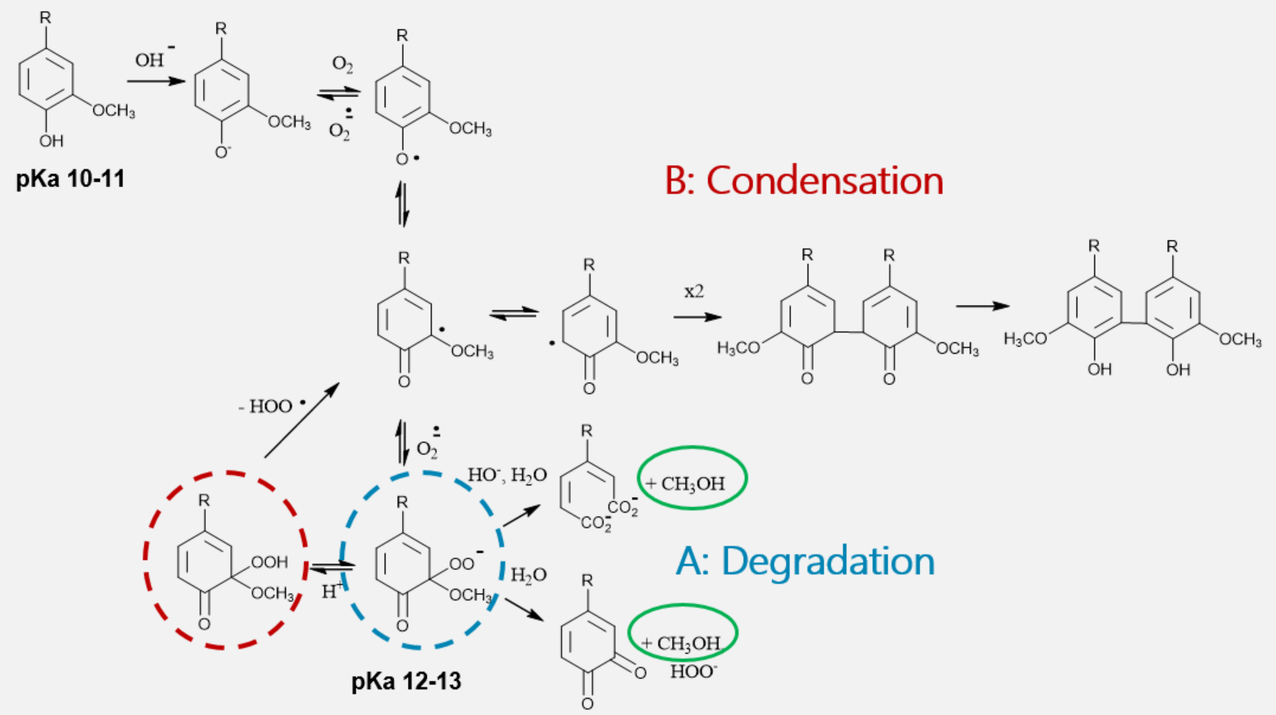

Figure 46. Simplification of reactions during alkali-O_2 oxidation of lignin (Kalliola et al., 2015). Degradation of aromatic ring (A); Coupling of phenoxyl radicals (B). MeOH (CH_3OH) formed as a by-product.

LigniOx concept for kraft pulp mill

A schematic presentation of the process concept for producing LigniOx dispersants in a kraft pulp mill is presented (Figure 47) The integrated process provides several benefits for lignin recovery, the following lignin oxidation, and recycling of chemicals. Firstly, CO_2 precipitated kraft lignin can be used without a sulphuric acid washing step. This simplifies the lignin recovery and no excess sulphur is introduced into mill cycle. As the unwashed lignin is alkaline in nature, the need for fresh alkali in the lignin oxidation is reduced. Moreover, oxidised white liquor, readily available in the mill, can be applied as a partial source of alkali. Finally, membrane filtration of the oxidised lignin solution enables the recirculation of sodium and sulphur back to the chemical cycle and provides a concentrated lignin product. Based on process simulation (Kalliola et al., 2022), recovering 20% of the lignin in black liquor, and oxidising this unwashed lignin does not increase fly ash purging in a softwood kraft pulp mill when compared to conventional lignin recovery or oxidation of acid washed lignin (Figure 4). Thereby, the integrated LigniOx production does not interfere with the main process, and provides cost and environmental benefits over the conventional recovery of kraft lignin (Kalliola et al., 2022).

Along with the production of LigniOx dispersants MeOH is formed. This MeOH is transferred to the evaporation plant within the permeate fraction from the membrane filtration (Figure 47). The crude MeOH from the evaporation can be purified using an already existing technology[3]. If assuming kraft pulp production of 640 kt (adt)/a, and about 20% lignin recovery from black liquor (leading to LigniOx production of 55 500 t/a), the quantity of formed unpurified MeOH will be more than 4 M litres/a.

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[3] https://www.andritz.com/newsroom-en/pulp-paper/2020-03-23-soedra-monsteras-group

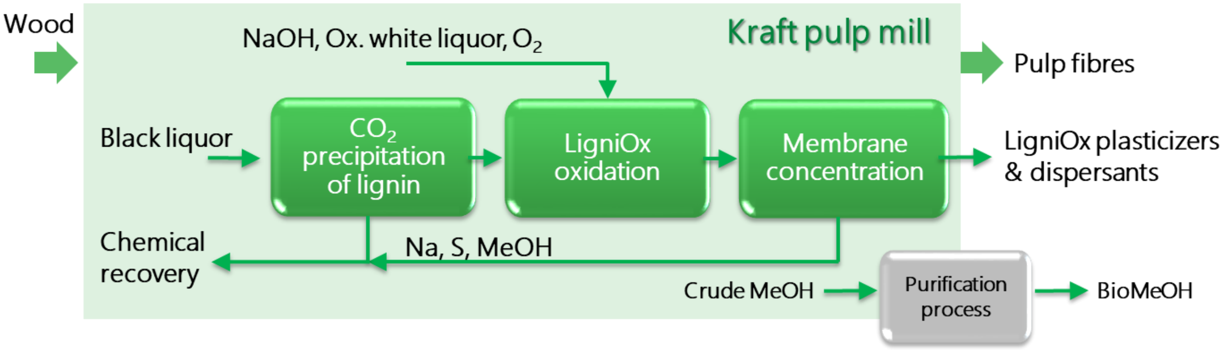

Figure 47. A concept for combined lignin recovery, alkali-O₂ oxidation (LigniOx) and membrane filtration of oxidised lignin for the production of dispersants in a kraft pulp mill. Crude MeOH can be purified to BioMeOH by a separate process.

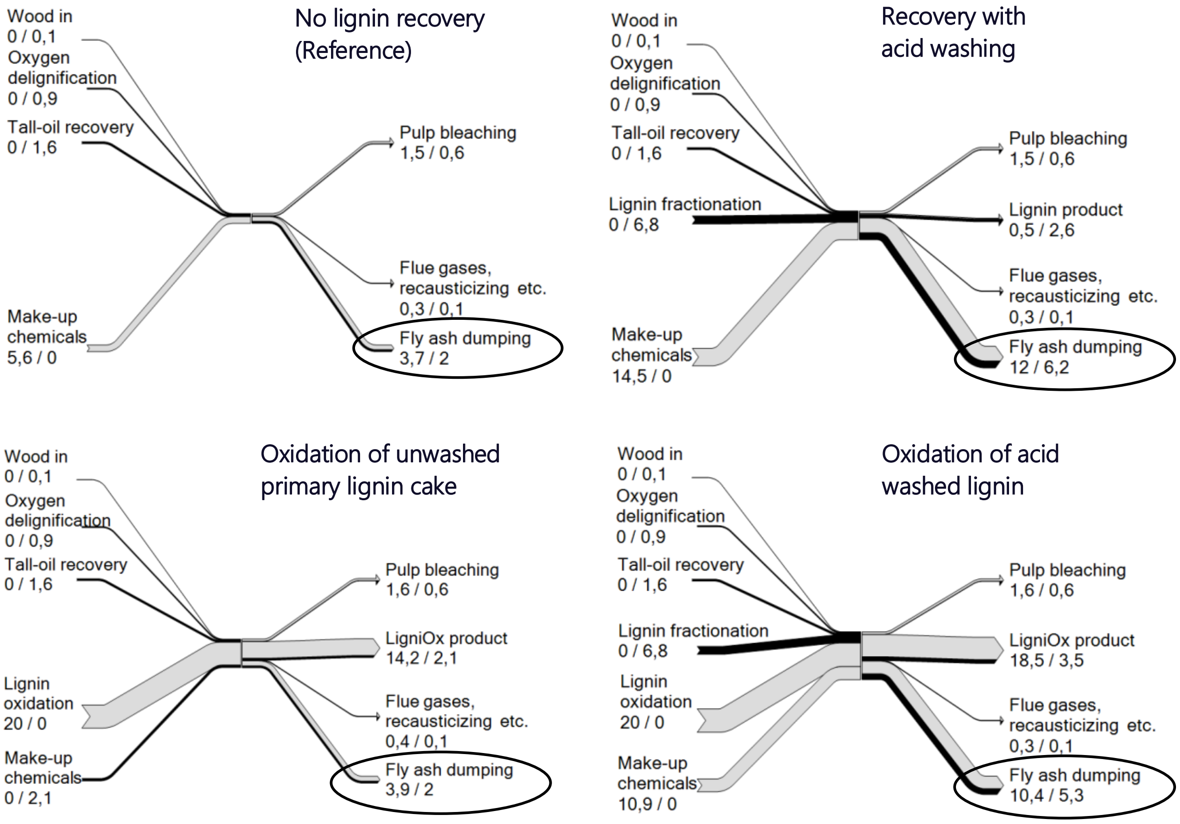

Figure 48. Sodium (Na) and sulphur (S) balances of reference kraft pulp mill and different oxidation options. Grey refers to Na balance and black refers to S balance, unit of Na/S being kg/adt pulp.

Lately, Neethi et al., (2022) completed a life cycle assessment (LCA) of LigniOx kraft lignin (produced at a kraft pulp mill) in comparison with a concrete superplasticizer product and PAA (polyacrylic acid, a dispersant product). The results demonstrated that oxidized lignin performs clearly better than the commercially available oil-based products in most of the impact categories of the LCA assessment. The majority of environmental impacts of LigniOx lignin were from the main kraft pulping process. The study indicated that the production of LigniOx lignin is more attractive than the production of conventionally recovered kraft lignin. Furthermore, the biodegradability of LigniOx lignins was evaluated in a recent study by Vikman et al., (2022). The oxidized lignins exhibited higher biodegradation in soil and in aquatic environments in comparison to a commercial kraft lignin and a commercial lignosulfonate.

LigniOx process at Organosolv biorefinery

Besides kraft pulp mills, the LigniOx process has been demonstrated to apply to organosolv biorefineries[4]. The characteristics of kraft versus organosolv pulping regarding the integrated LigniOx production are presented in *Table 20*. Even though the kraft and organosolv pulping technologies, lignin separation, and chemical recovery differ crucially, there are aspects that favor organosolv lignin conversion to LigniOx dispersant. For example, the lignin purity in organosolv lignin material allows working with less viscous solutions if comparing to the use of unwashed kraft lignin. While there is no need to recover Na in organosolv process, the membrane post-treatment could be excluded, if acceptable for the end-use. However, further investigations on the process integration of the production of organosolv lignin based dispersants are needed.

Table 20. Characteristics of kraft vs organosolv pulping regarding the LigniOx integration.

	Kraft pulping / Metsä Fibre	Organosolv pulping / Fortum
Raw material	Softwood, hardwood	Straw
Pulping chemistry	Alkaline, NaOH, Na_2S	Acidic: formico®
Lignin separation	~20 % of the lignin in BL Precipitation by CO_2, H_2SO_4 washing excluded	>95 % Precipitation with H_2O & washing
Lignin quality	pH 10, rich in inorganics (Na, S)	pH 3, pure lignin
Recovery of pulping chemicals	Recovery boiler (Na, S)	Evaporation: acids No Na in the process
LigniOx production	55 kt LigniOx (pulp 640 k adt/a)	50-60 kt LigniOx (Triticum)
LigniOx by-product	Un-purified MeOH ~5 % of lignin	Un-purified MeOH ~5 % of lignin
Post-treatment	Membrane stage is crucial to ensure chemical recovery	Membrane stage +/-, more studies on applications of crude LigniOx needed
LigniOx Concept	"Ready"	Needs further investigation

Conclusions

The LigniOx process concept makes the production of novel lignin dispersants feasible at kraft pulp mill without interfering with the main process, and provides clear cost and environmental benefits. In addition to the lignin dispersants produced by the LigniOx process, high quantities of crude methanol is formed as a by-product and available for purification using an existing technology. Besides kraft pulp mills, the LigniOx process has been demonstrated to apply to organosolv biorefineries. However, further investigations on the process integration of the production of organosolv lignin based dispersants with MeOH as a by-product are needed.

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[4] https://ligniox.eu/

Acknowledgements

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Scalable Industrial Process for the Production of Nanofibrillated Cellulose Oxalate

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Abstract

Nanocellulose materials have garnered steadily increased attention over the last few decades, since they open up a broad range of new high-end applications with wood as raw material. Most methods to prepare nanocellulose require large amount of water and has relatively low yields. FineCell uses a bulk pre-treatment, which combines both acid hydrolysis and derivatization, to prepare cellulose oxalate which can be further processed into nanocellulose. Together with industrial partners we have demonstrated that our nanocellulose can be used to enhance a diverse range of materials, from cosmetics to composites. We are currently establishing an industrially relevant process allowing for scaling and industrial production. Doing so, we demonstrate that our wood based, high-end nanocellulose material, with commercially desirable properties, can be produced in a cost and energy efficient manner, while being of high interest in many applications.

Introduction

Different types of nanocellulose have for long been regarded as future materials from the forest industry, which will have the potential to improve many products, e.g. surface coatings (Aulin et al., 2010), composites (Moon et al., 2011) and cosmetics (Mihranyan et al., 2012), and to replace fossil based materials in for example packaging (Aulin et al., 2010) and textiles (Lundahl et al., 2017). Cellulose nanofibrils (CNF), high aspect ratio and flexible cellulose particles consisting of both amorphous and crystalline regions, was initially prepared using pure mechanical fibrillation (Turbak et al., 1983) (Herrick et al., 1983) but has later been prepared using for example enzymatic (Henriksson et al., 2007) (Pääkkö et al., 2007) or chemical pretreatments (Saito et al., 2006) (Wågberg et al., 2008) to reduce the energy required for fibrillation. Nanocellulose originating from chemical pretreated wood pulp often results in nanocellulose with a higher degree of fibrillation, higher viscosity and surface functionality compared to using other production methods. These properties make the material better suited for many high value applications, e.g. printed electronics and light-weight aerogels.

Up until now the industry has mainly been working to scale production methods of CNF which has not been chemically pretreated. This is largely due to the difficulties to recycle the used chemicals, which in turns increases the production costs.

Earlier publications have demonstrated an efficient fibrillation of cellulose through the pretreatment of cellulose oxalate (Li et al., 2017) (Henschen et al., 2019). The chemical pretreatment to prepare cellulose oxalate is easily done in a bulk reaction of molten oxalic acid dihydrate. Oxalic acid dihydrate melts around 102 °C, and by mixing this with cellulose, it is possible to obtain a simultaneous acid hydrolysis and esterification (Figure 49) with DS up to 0.35 (Li, Henschen, & Ek, 2017). The combined hydrolysis of the cellulose with the introduction of charge oxalate groups in the material makes it a good candidate to fibrillate to a CNF hydrogel using for example a microfluidizer. The process does not involve any large quantities of water, and the product is washed using an alcohol or acetone, this makes it easy to efficiently recycle the used chemicals and thereby improve the scalability. The current conference contribution describes how the lab process of preparing cellulose oxalate was scaled to 20 kg/day capacity, equivalent to 1,000 kg 2 wt.-% CNF/day.

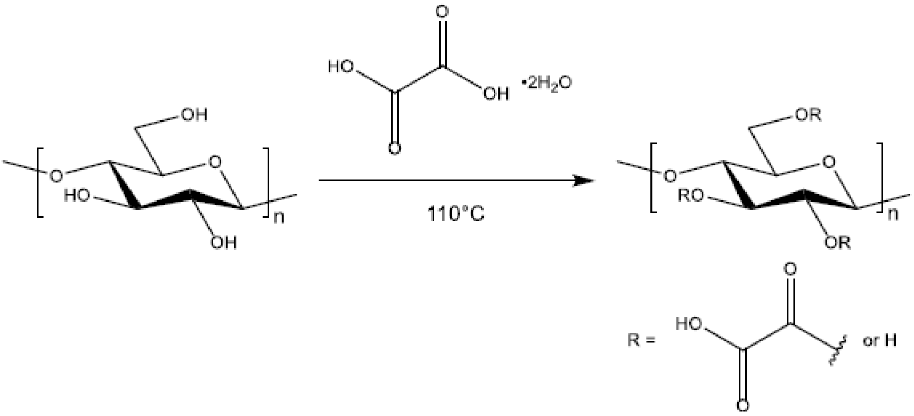

Figure 49. Esterification of cellulose to form cellulose oxalate.

Experimental

The preparation of cellulose oxalate consists of the reaction between cellulose and oxalic acid dihydrate followed by isolation of the product from excess reagent and biproducts. The reaction was performed in a 150 liter mantled stainless-steel reactor with bottom mounted agitator at 110 °C for up to 30 minutes. Bleached softwood kraft pulp sheets were shredded to obtain approximately 2x0,5 cm large pieces before added to the reactor with a ratio 1:4 to the acid, with no other solvent added. The reaction was stopped by cooling the mixture and thereby crystallizing the oxalic acid.

Any biproducts and excess reagent was leached out from the product by mixing it with ethanol. The dissolved impurities were removed by filtration in a woven nylon bag filter. The material was further redispersed and filtered until the conductivity of the washing solution was <10 µS/cm. The obtained cellulose oxalate was collected and dried at ambient conditions, forming a fine powder.

Nanocellulose was prepared from the cellulose oxalate by dispersing it in deionized water at a concentration of approximately 2 wt.-%. To fully dissociate the carboxylic acids and aid the fibrillation, the pH of the dispersions was adjusted to pH 9–10 using sodium hydroxide before they were mechanically disintegrated using a microfluidizer (M-110EH, Microfluidics Corp, United States) similarly as described by Khan et al., (2014). Initially, all samples were passed through two large chambers of 400 µm and 200 µm connected in series. Following this, they were passed through a 200 µm and a 100 µm interaction chamber connected in series. The pressure was set to 925 bar when passing the samples through the large chambers and 1,600 bar when passing through the large chambers

Results and discussion

The bulk reaction between cellulose and oxalic acid dihydrate is performed without adding any solvent other than that which is present as crystal water or that being absorbed in the pulp. This creates a balance point between having a low excess of the acid and adding sufficient acid to allow for a homogenous distribution of the acid in the pulp. It is also important to achieve high heat transfer and material transport in the reactor. The setup with a bottom mounted agitator combined with an oil filled heating mantle proved to provide sufficient mixing of the pulp and the acid to produce a homogenous product while maintaining the ratio 1:4 (pulp:acid) which had earlier been used in labscale experiments.

Following the crystallization of the oxalic acid, a brownish mixture, containing i.e. the product, hemicellulose degradation products as well as the excess acid, is formed. Both the degradation products and oxalic acid is soluble in an alcohol or acetone and can rather easily be removed through a conventional leaching process followed by dead-end filtration. In order to obtain pure enough products, it may be necessary to repeat the dispersion and filtration a couple of times. Despite the relatively low surface area of the filter bags and a positive pressure of only 1 bar the product was rather easy to filter. The use of an organic solvent to wash the products has multiple benefits compared to using water, one of them being that water swells the product more and makes it more difficult to filter the mixture. It has also been shown to be rather easy to recycle both the solvent and oxalic acid which is critical to obtain good production cost.

The collected powder was essentially composed of fiber fragments with size down to about 10 µm. The material had a surface charge of about 400 µeq/g, and disperses well in water. It was also shown to be possible to fibrillate the cellulose oxalate to nanocellulose using microfluidization. The resulting hydrogel has high viscosity and is translucent (85 % transmittance), indicating a high degree of fibrillation with a nanofiber yield of 98 %.

Conclusions

The described work describes scaling the production of cellulose oxalate, a nanocellulose precursor, up to 20 kg/day, equivalent to 1,000 kg 2wt.-% CNF/day. During the work it was concluded that the reaction and washing procedure used in lab scale are rather well suited also for this scale. In order to further validate the feasibility of the process, work is being performed to validate the recyclability of the reagent and solvent. In parallel to this, the authors are also looking to develop application areas where the benefits of cellulose oxalate compared to other nanocelluloses can be taken advantage of.

Acknowledgements

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Delignification of Kraft Pulp with Oxygen, Air and Nitrogen - Effect on Selectivity and Pulp Brightness

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Abstract

The pulp industry has a long history of developing and introducing new technologies with the aim to increase energy efficiency and resource economy and to improve environmental impact. One such technology, an additional delignification after the kraft pulping step using oxygen is widely used in order to remove residual lignin before chemical bleaching during the production of semi- and fully-bleached pulps. In this work, the purpose is to gain a better fundamental understanding of the behaviour of oxygen delignifying systems. In the oxygen delignification process the pH decreases which is an issue since it affects the selectivity of the delignification reactions as well as the succeeding bleaching sequence. In this study the selectivity and pH decrease during an oxygen delignification reaction were determined when the system was overcharged with oxygen, charged with air or with nitrogen. Industrial softwood kraft pulps were subjected to oxygen delignification for the periods between 20 and 120 minutes, the pulp was then tested for kappa number, viscosity, brightness and the filtrate pH was noted. The kappa number reduction rate decreased over time while the brightness increase rate was steadier, a possible explanation being the hydrogen peroxide formed during this stage. After 60 minutes of reaction the pH reached below 10.5, a point where selectivity decreased significantly.

Introduction

Since its introduction in the 1970´s oxygen delignification has become a highly utilized and standard process in the production of semi- and fully bleached kraft pulps. The unit operation is carried out in a single or two step manner after brown stock washing and before the bleaching sequence. By additional removal of residual lignin, the cost-effective oxygen delignification can replace part of the traditional bleaching and has made a major impact on the environmental and economic aspects of the pulp mill and production. Towards the end of the cook the delignification of pulp is less selective and a trend in recent years have been to terminate at a higher kappa number and extend the oxygen delignification. (Hart, 2014; Hsu & Hsieh, 1988) During oxygen delignification it is believed that the phenolic units in lignin are oxidized, forming the more soluble muconic acid (Figure 50) (Asgari & Argyropoulos, 1998). Moreover, depolymerization of lignin take place by breaking 4-O-5 bonds which are stable during the kraft cook.

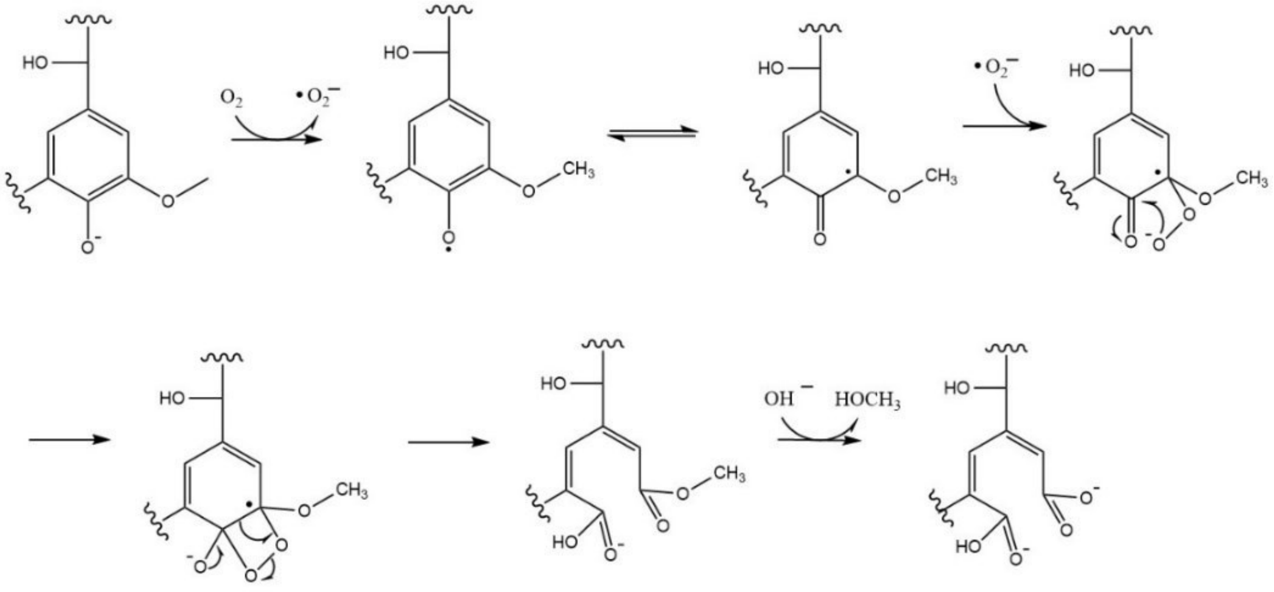

Figure 50. Lignin solubilizing reaction in oxygen delignification

For efficient delignification reactions oxygen must be added in access under high pressure, however during the process conditions oxygen form other reactive species, Figure 51. When transition metals such as Mn^{2+}, Cu^{2+} and Fe^{2+}, are present hydrogen peroxide can generate hydroxyl radicals. (Violette, 2003) (Johansson & Ljunggren, 1994) Hydroxyl radicals attack cellulose resulting in chain cleavage, reducing the degree of polymerization and thereby generating loss of strength of the fibers. (Johansson, 1993)

$$2\,O_2^- \cdot + 2H^+ \rightarrow H_2O_2 + O_2$$

$$O_2^- \cdot + Me^{n+} \rightarrow O_2 + Me^{(n-1)+}$$

$$Me^{(n-1)+} + H_2O_2 \rightarrow OH \cdot + OH^- + Me^{n+1}$$

Figure 51. Oxygen species present during oxygen delignification

Besides attack from oxygen radicals another challenge for oxygen delignification is chain degradation from alkaline hydrolysis. For optimal delignification conditions the pH and alkali charge must be maintained at a high level, which leads to reduction of the degree of polymerization.

Oxygen delignification is a complex three phase system, with gaseous oxygen, liquid liquor and solid fibers. The exact importance of oxygen accessibility is not fully established but believed to be high. Oxygen accessibility can be increased by increasing oxygen charge, minimizing bubble size (Liukkonen et al., 2015) and reducing amount of other particles (both other gases and lignin/cellulose fragments) (Hsu & Hsieh, 1988).

In this work, we investigated oxygen delignification selectivity in the aspects of pH, kappa number, viscosity and brightness in the presence or absence of oxygen. Mechanistic background to the effects is discussed.

Experimental

Oxygen delignification experiments of industrial softwood kraft pulp with a kappa-number of 35 was carried out in steel autoclaves. Alkali and $MgSO_4$ were added to 50 g oven-dried pulp to a charge on pulp of 1.8 % and 0.2 %, respectively. Deionized water was then added to a consistency of 10 % on pulp. Three different experiments were done with the addition of oxygen, air or nitrogen. The autoclaves were placed on rotation in a glycerol heat bath and heated to 90 °C. The oxygen delignification time was 20, 40, 60, 80, 100, 120 minutes before the reaction was terminated and pulp was collected, washed in a mesh funnel, centrifuged, disintegrated and dried in 40 °C for analysis and storage. The filtrate was collected for analysis.

The pulp samples were subjected to kappa number analysis according to ISO 302:2015, intrinsic viscosity analysis according to ISO 5351:2010 and brightness measurements according to ISO 2470-1:2016 with sheets made according to SCAN-CM 11:95. pH of the filtrate was noted.

Results and discussion

The kappa number of industrial softwood pulp with initial kappa number of 35 were subjected to three delignification experiments, Figure 52a, in the presence of oxygen, air and nitrogen respectively. As expected the reduction in kappa number was significantly higher for the reaction with applied oxygen. However, there was some level of reduction of kappa number in the reactions with lower level or no amount of oxygen. This could be explained by leaching of residual lignin.

The loss of viscosity is present in all samples, with the most significant decrease in the sample with added oxygen. This result support the claim that oxygen-derived radicals attack the cellulose chains, but also that alkaline hydrolysis play an important role.

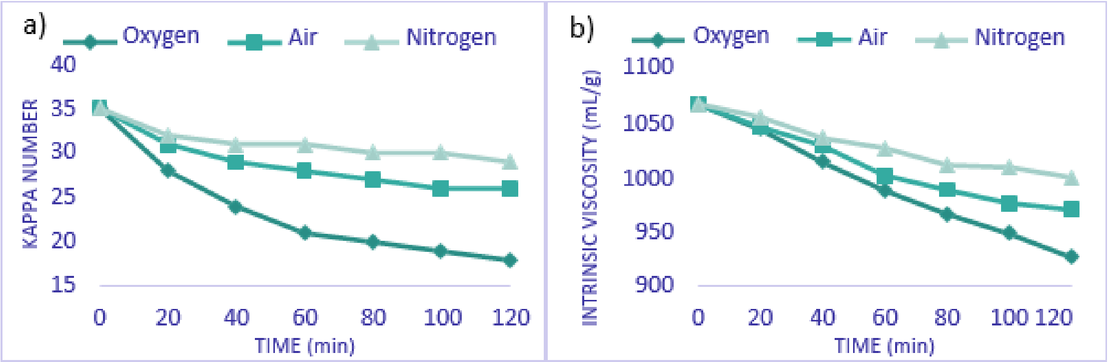

Figure 52. Kappa number (a) and intrinsic viscosity (b) of reaction filtrate from kraft pulp delignified in the presence of oxygen, air or nitrogen.

The pH in all the three experiments decreased during the treatments the oxygen delignification reaction (Figure 53a) with a more significant decrease in the beginning of the reaction, and a stronger effect when oxygen was used. When lignin is depolymerized during the oxygen delignification step the formation of soluble muconic acid (Zou, 2002) could be the reason for the pH reduction. It is important to obtain information about the pH levels during this process to maintain a high delignification rate.

The connection between muconic acid formation and pH reduction is further supported by the almost linear relationship between kappa number reduction especially for oxygen and air treatments and pH reduction showed in Figure 53b.

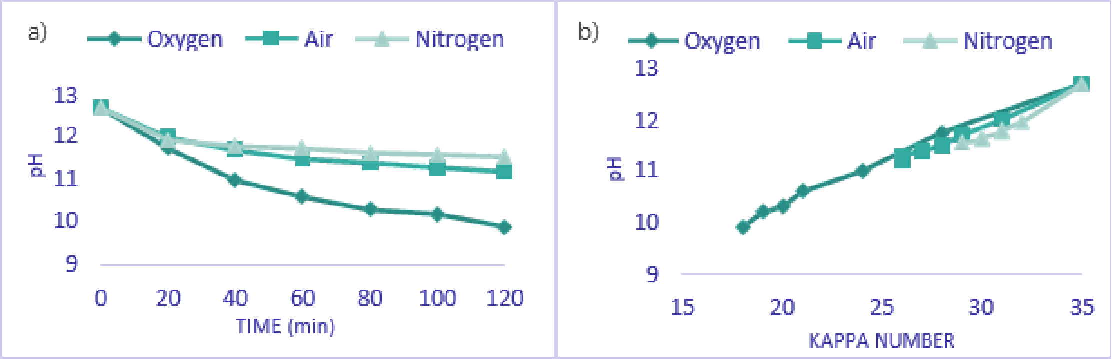

Figure 53. pH of reaction filtrate (a) and relationship between pH and kappa number (b) from kraft pulp delignified in the presence of oxygen, air or nitrogen.

The rate of the delignification decreases after ca 60 min for all three reactions (mainly oxygen and air) but the brightness of the pulp is maintaining its rate, Figure 54, especially when oxygen was used. This could be explained by the other oxygen species that are reactive with the pulp, such as hydrogen peroxide formed *in situ*. Hydrogen peroxide is commonly used in the bleaching sequence in pulp mills. The potential significant increase of pulp brightness by hydrogen peroxide is supporting the claim that oxygen charge and oxygen access in the filtrate play a major part on the efficiency of the oxygen delignification step.

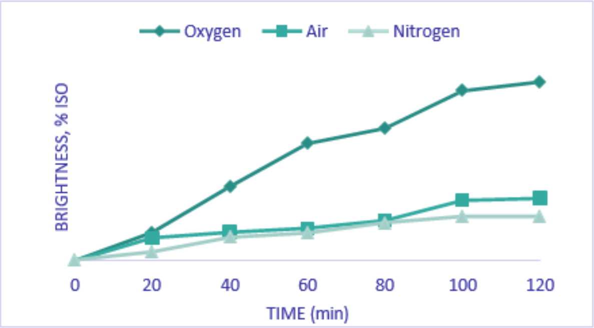

Figure 54. Brightness of reaction filtrate from kraft pulp delignified in the presence of oxygen, air or nitrogen.

Conclusions

During the three experimental set-ups that were investigated the amount of oxygen is revealed to play a major role in the delignification and simultaneous bleaching reactions.

- Most of the delignification is due to oxidation (solubilization and depolymerization) of lignin, however, some of the lignin is removed by leaching.
- Loss in viscosity is explained both by oxygen species (probably radical chemistry) in addition to alkaline hydrolysis
- The degree of delignification is higher when high levels of oxygen is present in the system due to the presence of various oxidative species, including hydrogen peroxide.

- The importance of accessibility of oxygen species for an effective delignification process suggests the need for accurate mathematical models that take mass transfer into account when designing oxygen delignification procedures in the future.
- Degree of delignification is dependent on the pH of the system. The pH levels will be controlled during further experiments to not reach below 10.5.
- Brightness continue to increase even after kappa number reduction rate have declined, which may be due to formation of hydrogen peroxide.

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High Performing Wood-Based Products for Industrial Scale

Techno-Economic Analysis for Novel Biorefinery Concept Producing Biobased Acetic Anhydride

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Abstract

The quality and compatibility of products obtained from forest biomass such as lignin or hemicellulose products can be significantly improved by acetylation, yielding acetylated products. However, acetic anhydride is yet produced only in limited amounts from biomass-based feedstock. Today mainly natural gas or coal is used as raw material. The Eastman company produces acetic anhydride at commercial scale via methyl acetate carbonylation using carbon monoxide. Eastman also produces methyl acetate from methanol and acetic acid using reactive distillation.

Lately, processes for the separation of methanol from Kraft pulp mill condensates have been demonstrated by ANDRITZ and Södra in Mönstrås in Sweden. A new biomethanol plant investment is planned to Metsä Fibre's Äänekoski bioproduct mill by Veolia utilizing this technology.

Acetic acid is needed in the production of acetic anhydride but acetylation of biomaterial using acetic anhydride produces enough acetic acid as by-product so that separate acetic acid production is not needed.

The carbon monoxide needed in the processes can be produced by gasification of bark and separating carbon monoxide from the cleaned gasifier product gas using a membrane. Bark is already gasified using an air gasifier at several pulp mills. However, a part of the bark usually remains and could be used to produce carbon monoxide and methanol, substituting fossil raw material in acetic anhydride production.

In this study, we evaluate the cost and efficiency of bio-based acetic anhydride production using methanol derived from pulp mill side streams, employing literature data and flowsheet simulation models. Furthermore, we evaluate the potential to produce acetylated biobased products. The results indicate that more than 200 000 ton of cellulose acetate products per 1 million air dried ton of pulp could be produced.

Introduction

Anhydride treatment has been researched for improving the properties of lignin, timber or other bio-products. Two wood modification technologies, acetylation and furfurylation, have been commercialized as industrial processes (Mantanis. 2017). Acetylated wood is a sustainable treated-wood alternative with significantly improved properties compared to untreated wood in terms of moisture resistance, shrinking behavior and dimensional stability. It can even replace resistant pressure-impregnated wood containing toxic metal preservatives such as copper and provides a long-term product for carbon storage.

Another area where anhydrides have been used is the modification of cellulose. For example, cellulose acetate, used as a polymer for films, textiles and other applications, is produced when cellulose is esterified with acetic anhydride. Lately, cellulose acetate was identified as precursor for production of 5-acetoxymethylfurfural, which is a similar platform chemical to 5- hydromethylfurfural (Gavilà & Esposito. 2017). Improved lignin properties, for example melt properties or solubility in organic solvents, have been found with anhydride treatment using succinic anhydrides, for example (Yao et al., 2014).

While acetylated lignin can be considered a sustainable product, the acetic anhydride produced today is based on fossil raw materials and the production results in greenhouse gas emissions. Acetic acid anhydride is presently produced by methyl acetate carbonylation at industrial scale by Eastman Chemical Company (Zoeller. 2020). The raw materials for production, methanol and carbon monoxide, could also be produced from forest residues facilitating more sustainable production of high performance products. Furthermore, the products could store biogenic carbon in the product and potentially enable carbon negative biorefineries with net (direct and indirect) CO_2 emissions lower than the uptake of CO_2 during growth of the biomass feedstock.

Information available in open literature about the production of biobased acetic anhydride and the corresponding techno-economic performance is currently very limited. Therefore, in this study the techno-economics of biobased acetic acid anhydride production is compared to fossil production using a similar route. Both the bio- and fossil routes consist of the Eastman process for methyl acetate production followed by acetic anhydride acid synthesis, but with different raw material for methanol and carbon monoxide production. The objective of this work is to calculate a 1st estimate which can be used to understand under which conditions biobased acetic anhydride production could be feasible and also to understand how much biobased acetic anhydride acetylated biobased products could be produced using this concept, based on the biomass input.

The fossil comparison case (Figure 55 in red) considers coal as the feedstock. Following the reference Eastman coal-to-chemical plant but replacing cryogenic CO separation with a membrane consistent with the other case coal is first gasified and the product gas cleaned. The needed part of CO for acetic anhydride carbonylation is separated and the rest of the gas is fed to methanol synthesis. Methyl acetate is produced via reactive distillation utilizing recycled acetic acid obtained when acetic anhydride is used at the same site for production of acetylated products. Subsequently acetic anhydride is produced via carbonylation of methyl acetate with CO. In the last step the produced acetic anhydride is used on-site to produce acetylated product for example cellulose acetate which also produces acetic acid as by-product.

The renewable bio-based acetic anhydride production (Figure 55 in yellow) is based on gasification of the fraction of bark output at a pulp mill that is currently not used for production of fuel gas for the lime kiln. The bark is gasified in an added gasifier using oxygen and steam, the product gas is cleaned, and CO is separated using a membrane and routed to acetic anhydride synthesis. The rest of the gas (containing mainly hydrogen, carbon dioxide and some residual CO) is supplemented with extra hydrogen produced by water electrolysis and used for methanol production. Another methanol fraction is recovered from the pulp mill condensates. Methanol is formed during the cooking process by demethylation of xylan and lignin with the first substrate accounting for the majority of formed methanol (Joyce, 1979).

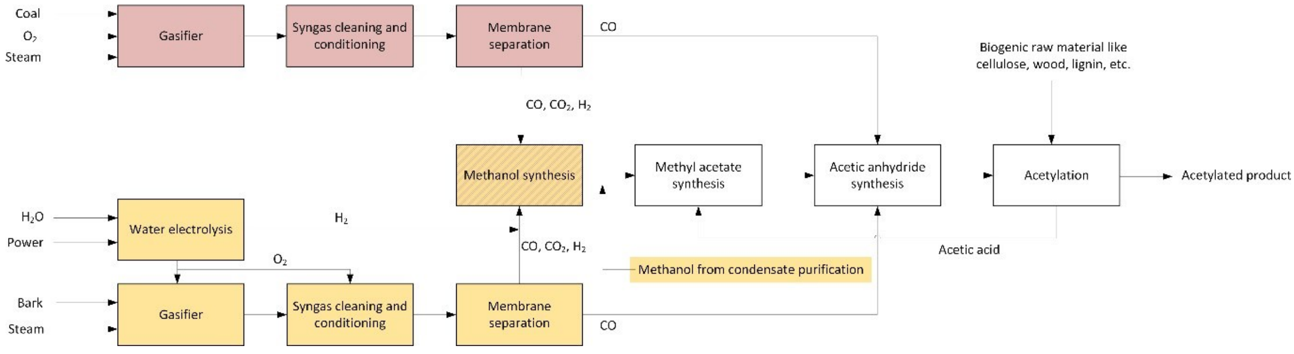

Figure 55. Acetic anhydride production process (The red colored boxes belong to the coal based upstream process and the yellow colored boxes belong to the biobased process. The colorless boxes are not simulated in detail)

First the mass and energy balances of the fossil and bio-based acetic anhydride production routes were evaluated using Aspen Plus (V11) flowsheet simulation program. For the fossil route, coal gasification, CO separation, and methanol synthesis were modelled to estimate the resulting yields of carbon monoxide and methanol.

For the bio-based process, our results from earlier work (Melin et al., 2022) were utilized to estimate the yields of methanol and carbon monoxide. The amount of carbon dioxide in the residual gas from the membrane separation was adjusted to get a molar ratio of 1:1 between methanol and CO.

Process simulation was scaled to a pulp mill producing 1 MT of air-dried pulp (ADP) per year. The amount of methanol obtained in the pulp mill condensate was assumed at 15 kg Methanol per t of ADP input (Valmet. 2018), equaling 15 kt/year. The composition of the raw methanol stream is based on literature data and the following simplified composition is used in the Aspen Plus model to represent it: 50 wt.-% methanol, 47.25 wt.-% water, 1.3 wt.-% dimethylsulfide, 0.8 wt.-% dimethyldisulfide, ammonia 0.8 wt.-%, 0.05 wt.-% alpha pinene, 0.05 wt.-% guaiacol, 0.5 wt.-% hydrogen sulfide.

The methanol recovery part the model consists of two distillation columns. The first column removes light components and gases like H2S and dimethylsulfide. The head product is condensed and split into gas and liquid phases. The liquid phase contains mostly methanol and is recycled. The gas phase is combusted in the odorous gas treatment system of the pulp mill. In the second column, methanol is separated from water and other high boilers like terpentine and dimethyldisulfide. The methanol purity is set to 99.7 wt.-%. The methanol plant design by A.H. Lundberg Systems is the basis for the simulation (Jensen et al., 2012).

In the cost calculation, the annual costs for both the fossil and biobased process are calculated, including cost of raw material (feedstocks, oxygen, electricity) as well as annual payback of the investment cost and maintenance cost). Next the differences in the annual costs of the biobased case and fossil case are calculated varying the bark price between 0 and 200 €/t and the coal price between 100 and 600 €/t. The heating value of bark and coal were assumed at 19.3 MJ/kg and 32.7 MJ/kg, respectively, on dry basis. The electricity price was assumed at 60 €/MWh. The plant was assumed to run 8000 h/a, and the investment capital annual charge factor was 10 % and maintenance cost was assumed to be 5 % of investment cost annually.

In this preliminary cost evalution, the overall costs of the bark and coal gasification processes were assumed equal for the same capacity. Due to the identical downstream steps within the two routes, only the process costs until CO separation and methanol synthesis were included in the cost estimation. The cost of gasification, gas cleaning, CO separation and methanol synthesis steps were scaled to the capacity of this study for each case using a cost exponent of 0.67 for the capital costs. The cost of methanol purification was estimated at 30 €/t and total cost including lost energy was assumed at 200 €/t.

Results and discussion:

Process inputs and outputs are summarized in *Table 21*. The cost difference in annual cost between the bio-based and fossil processes is illustrated in Figure 56 and plotted for different prices of coal and bark.

Table 21. Inputs and outputs of the fossil and biobased process (t/a)

Item	Unit	Fossil Process	Biobased Process
Bark input	dry matter t/a	0	102 591
Methanol from condensate	t/a	0	15 000
Coal input	dry matter t/a	72 630	0
Steam to gasification	t/a	34 281	51 295
Oxygen to gasification	t/a	58 100	15 683
H_2 from water electrolysis to process	t/a	0	333.9
Total methanol production	t/a	72 000	72 000
acetic acid from acetylation	t/a	134 828	134 828
Methyl acetate production	t/a	166 506	166 506
CO to acetic anhydride production	t/a	61 554	61 554
Acetic anhydride production	t/a	224 153	224 153
Acetylated cellulose (triacetate)	t/a	218 900	218 900

In this study the cost of a new gasifier is included gasifying residual bark. However, a more economic option would be to retrofit an existing bark gasifier that uses air as gasification medium to steam/oxygen operation, which usually also increases capacity of the gasifier.

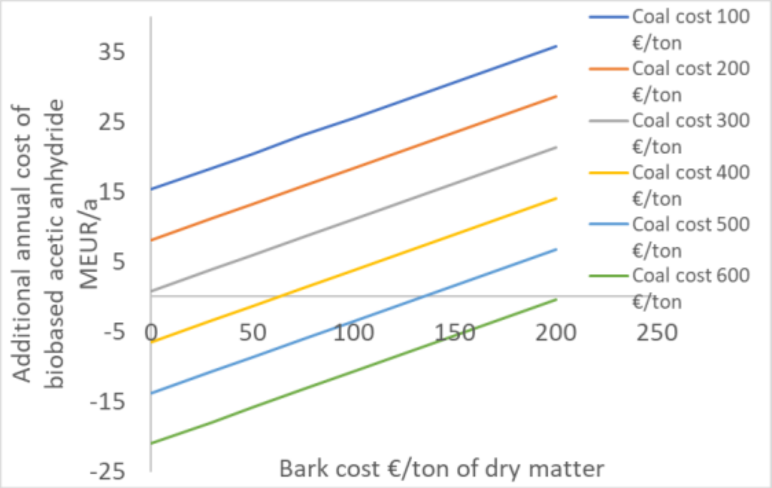

Figure 56. Additional annual difference in Million €/a of biobased and fossil case

Conclusions

A high amount of biobased acetic anhydride more than 200,000 ton per 1 Mio. ADT of pulp can be produced from the excess bark and recovered methanol at a pulp mill with equal cost at 75 €/ton bark price and 400 €/ton coal price. Biobased acetic anhydride would enable production of totally biobased acetylated products for example cellulose acetate for textile applications or acetylated timber, lignin or hemicellulose products.

Acknowledgements

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Catalysis solvolysis of Novel Organosolv Lignin into Phenolic Monomers

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Abstract

Catalytic depolymerisation of organosolv lignin using molybdenum-based catalysts is presented. Using ethanol as solvent, solvolysis and hydrogenolysis of lignin is studied with the aim to produce monophenols.

Introduction

Utilizing lignocellulosic biomass to produce chemicals and fuels is considered to be a second generation (2G) biomass refining technology. Nowadays, 2G biorefineries have been successfully built by converting only cellulosic fraction of agricultural and forestry residues for bioethanol as gasoline blend, but it leaves lignin as large volume unvalorised. In EU project FRACTION, a novel integrated biorefinery approach is proposed to convert lignin and hemicellulose side-streams in 2G biorefineries, while keeping high purity cellulose as main targeted product. This will be achieved through a novel organosolv fractionation using aqueous γ-valerolactone solvent. The targeted products from the novel fractionated hemicellulose and lignin will be furfural/succinic acid/1,5-propanediol and phenols/polyurethanes respectively. Lignin has a great potential to replace fossil-based aromatic-based chemicals, however its valorisation towards aromatic monomers is challenging.

Catalytic solvolysis of lignin route is proposed to be advantageous when aiming for phenolic monomers. Regarding the findings of lignin solvolysis so far, it can be concluded that catalyst as well as process development is still needed. Such development targets are catalysts (low cost and active at moderate temperature) and solvents (suitable to provide H2 and suppress repolymerization) and better understanding of solvolysis reaction mechanism. Herein, unsupported Mo-based catalysts having high surface area are used to convert organosolv lignin with alcohol for production of phenolic monomers at moderate reaction solvolysis conditions.

Experimental

Unsupported MoCx catalysts were prepared using ammonium molybdate and nitrogen containing precursors dicyanamide or a mixture of melamine and cyanuric acid according to Ma et al., (2015) and Tang et al., (2019).

Characterisation of the lignin was done by SEC in alkaline solution to analyse the molecular weight. Monolignol ratio (H/G/S ratio) was analysed by pyrolysis-GC/MS and methoxy group content by GC. The amount of interunit linkages in lignin was determined by 2D NMR using the H/G/S ratio and methoxy content to calibrate the peak intensities.

Lignin depolymerization experiments were carried out in a 200 ml batch reactor (Büchi Novoclave) using ethanol as solvent. Eucalyptus organosolv lignin (supplier by Fraunhofer) was used as a model organosolv lignin in the experiments. For some of the experiments, hydrogen gas was fed to the reactor prior to heating. After the reaction, the reaction mixture was filtered to separate the ethanol-soluble and insoluble fractions. The EtOH-insoluble fraction was further dissolved into THF to separate higher molecular weight fraction from the catalyst and char residue.

Monophenol content of the EtOH-soluble fraction was determined by GC/MS after silylation. Molecular weight distribution of both EtOH-soluble and THF-soluble fractions were determined to evaluate the extent of the depolymerisation.

Results and discussion

The nature of lignin feedstocks and their interunit linkages greatly affect the reactivity and monomer yield; SEC and NMR analyses were used to determine molecular weights and β-O-4 bonds of the starting material. The depolymerisation experiments were carried out in the both with and without a catalyst and in solvolytic (no added hydrogen) and hydrogenolytic (added hydrogen gas) conditions. The reaction conditions exceeded the critical point of ethanol; under these conditions also ethanol can function as hydrogen donor. The main monomeric products of the depolymerisation of lignin studied so far are syringol and methylsyringol. Up to 90 % of the depolymerised lignin is soluble in ethanol and the molecular weight is significantly reduced (from 2500 Da to 1000 Da). The effect of catalyst, hydrogen gas and reaction temperature on the depolymerisation and monophenol yields are discussed.

Conclusions

Molybdenum-based catalysts are shown to catalyse the depolymerisation of organosolv lignin using ethanol solvent.

Acknowledgements

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Spinning of Regenerated Fibres from Paper Grade Pulp

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Abstract

The raw material base for the production of man-made cellulose fibres from wood is limited, as only highly processed dissolving pulps are used industrially. Technologies that enable the use of paper grade pulps as raw material for man-made textile fibres would broaden the raw material base and would enhance the use of wood biomass.

In this work, softwood and hardwood (eucalyptus) kraft pulps with high molecular weights and substantial amount of hemicelluloses were studied. Chemical and enzymatic pre-treatments were carried out to reduce the molecular weight of the pulps to pre-agreed level known to be suitable for good quality spinning dopes, and to produce pulps with different amounts of hemicellulose. The pre-treated kraft pulps were dissolved in an experimental super-base ionic liquid, [mTBNH][AcO] and fibres were spun with a small-scale laboratory spinning unit with dry- jet wet spinning method.

Fibres were successfully spun from both hemicellulose containing kraft pulps after different pre-treatments. The strongest regenerated fibres with >10 % elongation were spun from acid treated softwood kraft pulp. Hemicellulose content was not found to affect fibre strength, but fibre elongation was negatively correlated with hemicellulose content. The hemicellulose composition analysed form the regenerated fibres proved that hemicelluloses were, at least partially, regenerated to the textile fibres.

GRETE project will tackle the challenges caused by increased global demand for sustainable textile fibres by offering new breakthroughs in the wood-to-textile value chain. GRETE will improve the existing textile value chain through technological innovation by using a new raw material based on European paper grade pulps, implementing novel solvent systems based on ionic liquids, and feasible and sustainable modification procedures for cellulose dissolution and regeneration. This project has received funding from the Bio-based Industries Joint Undertaking (JU) under the European Union's Horizon 2020 research and innovation programme.

Introduction

Viscose and lyocell fibres are currently the most prevalent commercial man-made cellulosic fibres. The processes require raw material with high alpha-cellulose content and lower molecular weight cellulose. Currently, these requirements rule out the use of paper grade pulp as a raw material for production of commercial man-made cellulosic fibres. If paper grade pulp could be used in textile fibre production, the economy of fibre production could be substantially improved since dissolving pulp is clearly more expensive than paper grade pulp. Furthermore, environmental advantages could be obtained, because less processed pulps could be used.

Several ionic liquids are found to dissolve cellulose. Already in 2010, almost a hundred ILs capable of dissolving cellulose had been identified (Mäki-Arvela et al., 2010). Certain organic superbase ILs have shown good performance in cellulose dissolution and some structures perform well in fibre regeneration (King et al., 2011). For an economic viable process, recyclability of these ILs, due to demonstrated hydrolytic instability of superbases under the harsh recycling conditions, has to be improved. The development of [mTBNH][OAc], hydrolytically more stable IL, has opened an avenue to study the regeneration of fibres from hemicellulose containing kraft pulps to tackle not only the widening the raw material base but also the economic viability of the spinning process.

Experimental

The solvent used in the trials was a superbase ionic liquid [mTBNH][OAc] (5-methyl-1,5,7- triaza-bicyclo-[4.3.0]non-6-enium acetate). The IL was synthesized by Ilkka Kilpeläinen’s group at University of Helsinki.

The starting pulps were softwood kraft (intrinsic viscosity of 860 ml/g) and eucalyptus kraft (940 ml/g). The pulp pre-treatments were carried out to adjust the average molecular weight of the pulps to the set target level (intrinsic viscosity 430-450 ml/g). The specific effects of each pre- treatment on the pulp polymers are listed in *Table 22* (Spönla, 2020).

The pre-treated pulps were dissolved in [mTBNH][OAc] with 5wt.-% pulp concentration at temperature 85-95 °C and vacuum of 300-500 kPa to remove air bubbles. Dopes of 60 g were packed in 200 ml steel syringe and extruded through spinneret with eight 50 µm holes. The air gap length was adjusted to 1 cm. Fibers were guided through a coagulating bath with water (22.1 L) before collection with a custom-made laboratory-scale spinning equipment. Take-up velocity was set between 0.63-4.31 m/s, depending on spinnability of fibers. (Hannula, 2021)

The mechanical properties of the regenerated fibres were measured at 65 ± 5 r.h. % and 20 ± 2 °C with FAVIMAT+ fiber tester (Textechno, Germany) by using a gauge length of 20 mm and speed of 20 mm/min as an average of ten measurements.

The molecular weight distribution and carboxyl groups were determined with MALLS/RI in DMAc/LiCl and fluorescence labelling according to Potthast et al., (2003) and Bohrn et al., (2006). Hemicelluloses are a major source of carboxyl groups in pulps.

From the regenerated fibres the hemicelluloses were determined with methanolysis according to Sundberg et al., (1996). In methanolysis, polysaccharides are hydrolyzed by means of acidic methanol at 100 °C to form the corresponding methylglycosides, which can subsequently be quantified by GC-FID/MS after silylation.

Table 22. Pre-treatments of kraft pulps and characteristics after pre-treatment

Origin Pre-treatment	Effect on pulp	Intrinsic viscosity (ml/g)	Mw (kDa)	Yield (%)
Softwood kraft Endoglucanase (SW-EG)	Specific depolymerization of cellulose	450	250.5	98
Softwood kraft Acid hydrolysis (SW-acid)	Unspecific depolymerization of cellulose and hemicelluloses	440	149	99
Softwood kraft Endoglucanase+ Cold caustic extraction (SW-EG-CCE)	Specific depolymerisation of cellulose, removal of hemicellulose	450	265.1	96
Eucalyptus kraft Endoglucanase (EUCA-EG)	Specific depolymerization of cellulose	430	224.7	98.6
Eucalyptus kraft Cold caustic extraction + endoglucanase (EUCA-CCE-EG)	Specific depolymerization of cellulose and removal of hemicelluloses	460	225	83.8
Eucalyptus kraft Steam explosion (EUCA-ST-EX)	Unspecific depolymerization of cellulose and hemicellulose	450	233.4	91.8

Results and discussion

Fibres were successfully spun from all the hemicellulose containing kraft pulps listed in *Table 22*. The strongest single fibre from acid hydrolysed softwood pulp had tenacity of 3 cN/dtex, elongation 7.7 % and linear density of 3 dtex. The stress-strain values of the regenerated fibres with similar linear densities (2 dtex), for easier comparison, are presented in Figure 57 with the total amount of hemicellulose left in the regenerated fibres. The linear densities of the regenerated fibres from softwood and eucalyptus pulps after endoglucanase treatments were clearly higher compared to the others and for both samples 2 dtex fibres were not obtained. The amount of hemicellulose left in the regenerated fibre did not correlate with the tenacity of the fibres, the correlation coefficient was -0.3. However, negative correlation, with correlation coefficient -0.9, was found between elongation and the amount of hemicellulose in fibres. The less there was hemicellulose in the regenerated fibre, the more it elongated (Figure 57).

The effect of pre-treatment and fibre spinning on the Mw distribution was studied with two pre-treated pulps: softwood kraft pulp treated with endoglucanase and cold caustic extraction (EG-CCE) and eucalyptus kraft pulp treated with steam explosion (Figure 57). Good spinnability was obtained when cold caustic extraction (CCE) and endoglucanase treatments had been employed as pre-treatment. The CCE treatment was found to partially remove hemicelluloses indicated by the loss of the “hemi-shoulder” from the Mw distribution after CCE treatment Figure 57).

The molecular weight curves of softwood pulp before and after the pre-treatment (EG-CCE) and the regenerated fibres are collected in Figure 57a). The molecular weight of the regenerated fibres was slightly decreased compared to the corresponding pre-treated pulp, but the shape of the curve was rather similar than for the pre-treated pulps. The carboxyl groups in the regenerated fibres from softwood after endoglucanase and CCE were concentrated in the low molecular weight fraction, (Figure 57b indicating the presence of hemicellulose in the low Mw end of the distribution.

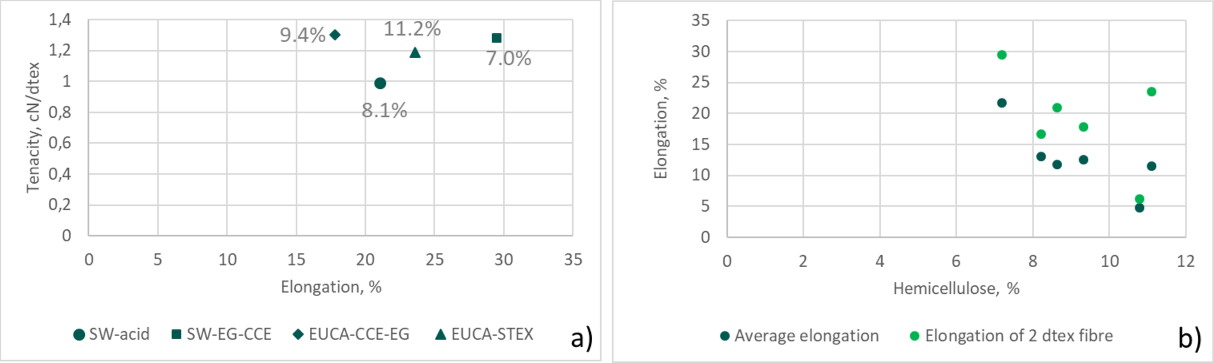

Figure 57. a) Stress-strain values of regenerated fibres from differently pre-treated pulps, amount of total hemicelluloses left in fibres indicated; and b) effect of hemicellulose left in regenerated fibres on elongation.

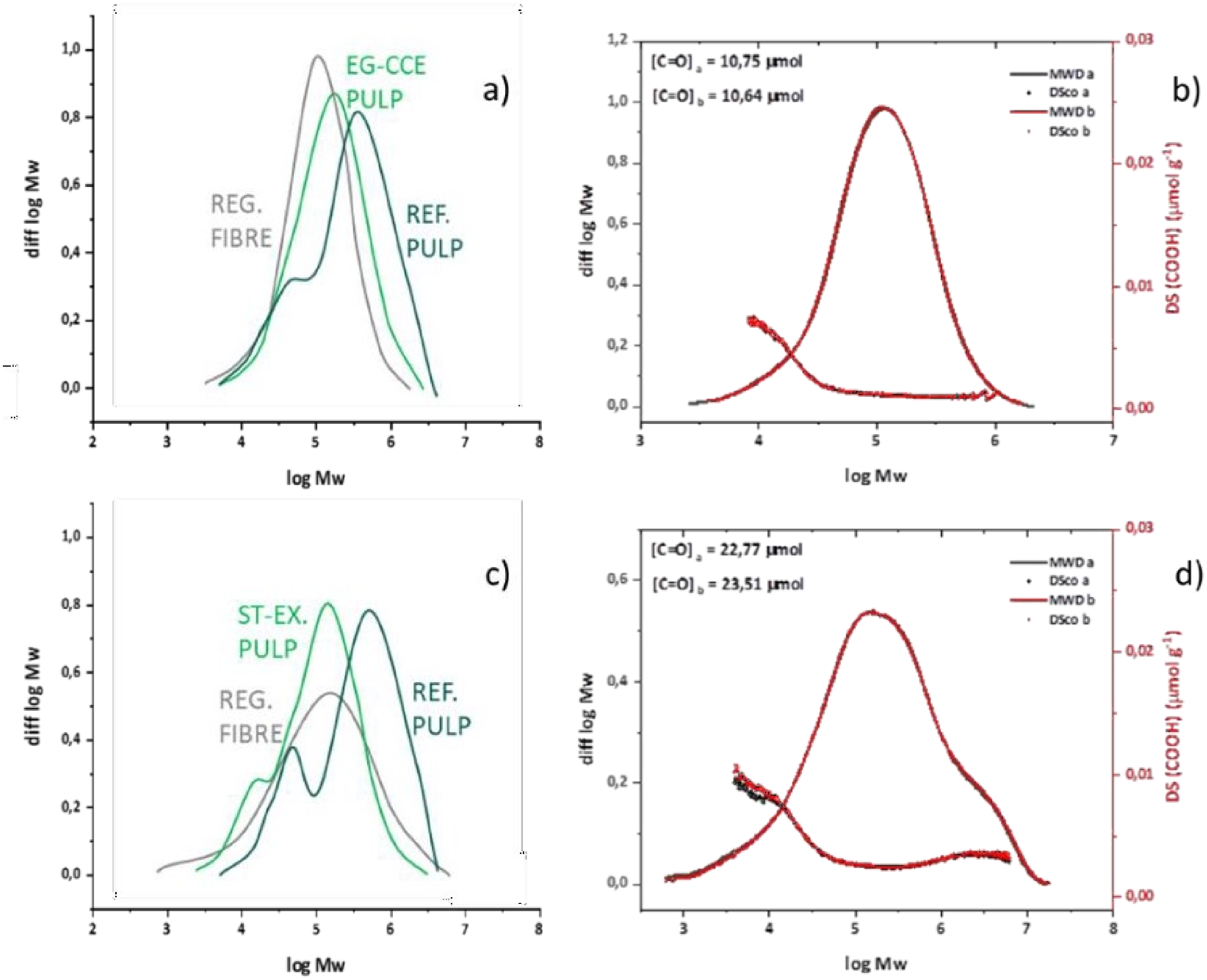

Figure 58. Molecular weight curves a) softwood pulp before (REF) and after enzymatic and cold caustic extraction (EG-CCE) and corresponding regenerated fibres, b) carboxyl profile relative to Mw curve of the regenerated fibre (from EG-CCE pulp); c) eucalyptus pulp before (REF) and after steam explosion (ST-EX) and corresponding regenerated fibre; d) carboxyl profile relative to Mw curve of regenerated fibre (from ST-EX pulp).

The steam explosion effectively decreased the molecular weight of cellulose and hemicelluloses Figure 58c). Depolymerisation of the remaining hemicelluloses in pulp was evident from the Mw distribution curve where a long tail was seen in the low Mw end of the distribution. From the molecular weight curve of the regenerated fibres, the hemicellulose shoulder was smoothened, but clearly the carboxyl groups were present and concentrated in the low molecular weight fraction (Figure 58d.

Conclusions

The pre-treated kraft pulp samples had different amounts of total hemicelluloses and the pulps had slight variation in the shape of their molecular weight distributions. As fibres could be successfully spun from hemicellulose containing kraft pulps the first obtained results were found promising. The tenacity of the produced fibres was rather low and titer of fibres high. We suggest that this was due to the small scale of the spinning equipment and the early stage in experimentations of this process. For further studies, the improvement of the tenacity of the fibres is important. Additionally, the location of hemicelluloses in the regenerated fibres, a topic for further studies, may give us valuable further understanding on their effects on fibre properties.

Acknowledgements

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Spinning and Additive Manufacture for Multiscale Cellulose Structures on Textiles and 3D Printed Materials

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Abstract

We use dry-jet wet spinning in a coaxial configuration by extruding an aqueous colloidal suspension of oxidized nanocellulose (hydrogel shell) TOCNF combined with airflow in the core. The coagulation of the hydrogel in a water bath result in hollow filaments (HF) that are drawn continuously at relatively high rates. Additionally, Blueberries pruning waste or BPw was dissolved in an ionic liquid, 1-ethyl-3-methylimidazolium acetate ([emim][OAc]) and regenerated into ligno- cellulose filaments with highly aligned nanofibrils (wide-angle X-ray scattering) that simultaneously displayed extensibility (wet strain as high as 39 %). Finally in alkaline conditions we investigate the interplay between cellulose crystallization and aggregation with interfibrillar interactions, shear forces, and the local changes in the medium's acidity. The latter is affected by the CO_2 chemisorbed from the surrounding atmosphere, which, combined with shear forces, explain cellulose gelation. Different instrumental techniques are combined to unveil the fundamental factors that limit cellulose gelation and maximize its dissolution in NaOH(aq).

The obtained solutions are then proposed for developing green and environmentally friendly cellulose-based materials at different dimensions, such as filaments (1D), films(2D) and printed meshes (3D).

Introduction

The use of renewable resources in advanced bioproducts is the subject of current interest (Liu et al., 2021), given the promise of positive environmental impacts (Pacala & Socolow, 2018). For instance, innovative applications are being developed in the area of biomedical devices, tissue engineering, cell scaffolds, and smart textiles (Eichhorn, 2011; Foster et al., 2018; Rebouillat & Pla, 2013). The markets associated with the latter industry segment benefit from traditional cellulose- based materials and their potential "decarbonization" benefits (Foster et al., 2018; Rissman et al., 2020). Hence, related efforts consider bio-based polymeric structures and cellulose nanofibers (CNF) as platforms for synthesizing strong, functional materials (Iwamoto et al., 2009; Lahiji et al., 2010). For example, spinning has been suggested as a technology to achieve the maximum theoretical mechanical performance shown by the individual cellulose building blocks (CNF) but in the form of textile filaments. Such strength optimization is best achieved in highly oriented cellulose fibrils under shear or flow-focusing effects (Lundahl et al., 2017; Marais et al., 2020; Mittal et al., 2018; Reyes et al., 2020).

Cellulose is a very stable molecule with low reactivity; its dissolution is not a straightforward process and requires strong solvents able to disrupt the multiple inter and intramolecular hydrogen bonds (Budtova & Navard, 2016). Industrially, there are two processes widely used for cellulose dissolution and regeneration; these are the viscose process and the lyocell process (Liebert et al., 2010). These technologies possess numerous environmental drawbacks; for instance, a significant fraction of the carbon disulfide is released into the atmosphere in the viscous process. In the lyocell process, about 10 % of the solvent is not recovered (Liebert et al., 2010; Vehviläinen, 2015). Currently there is an additional group of solvents gaining importance commercially for dissolving cellulose; these are the so- called Ionic Liquids (I.L.s); these types of solvents are difficult to recover and expensive; nonetheless, new types of I.L.s are being developed and patented under the name Ioncell™ (Sixta, 2015; Sixta et al., 2013). A third type of solvents are the alkali or aqueous systems. Aqueous-based dissolving systems started with the discovery in 1897 of the cuprammonium hydroxide process, which is still used in low quantities due to the high cost of the raw materials (Liebert et al., 2010; Vehviläinen, 2015). On the other hand, alkali or NaOH aqueous solutions already used in the viscose and mercerization processes started to gain importance in 1934 when it was found that cellulose is soluble in NaOH–water solutions in a specific limited range at low NaOH concentrations and low temperatures (Davidson, 1934, 1936, 1937). NaOH aqueous-based solutions for dissolving cellulose are an attractive pathway for cellulose regeneration due to the low environmental impact, and low cost (Vehviläinen, 2015; Vehviläinen et al., 2015). However, several factors such as the sub-zero temperatures required for dissolution, low solution stability, provoking and earlier gelation, and limited cellulose concentration, have inhibited the complete industrialization of the alkali dissolution system (Budtova & Navard, 2016; Vehviläinen et al., 2015).

The present work demonstrates that rheological and mechanical properties of cellulose dopes are drastically affected by CO_2 absorption; even more, the control of temperature and shear forces extend the gel stability and dissolution capacity to the maximum. The obtained dope is then considered to produce multidimensional materials 1D-3D. In the present work, a novel approach considering the control of the chemical environment during the dissolution step, together with a freeze/thawing step under centrifugal force, has proved to dissolve up to 12 % w/w microcrystalline cellulose successfully in alkali conditions. Additionally, the shear and viscous forces play an important role in the spinning and regeneration of lignocellulose material regenerated from an Ionic Liquid and nanocellulose TOCNF regenerated from aqueous gels.

Experimental

Dissolution. Microcrystalline cellulose (MCC, Avicel PH-101, 50 µm particle size, DP 300) was purchased from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany) and used with no additional modification. NaOH (99.6 % purity) from VWR Chemicals (Radnor, PA, USA) and ZnO (pro analysis) from Sigma Aldrich were used to prepare the cellulose solvent. All dissolutions were prepared in Milli-Q water (Millipore Corporation, Merck KGaA, resistivity 16 µS/cm). Fines-free Kraft bleached birch fibers were supplied by UPM Finland (lignin % 0.18, DP 4700) and used to prepare hydrogels of TEMPO-oxidized cellulose nanofibrils (TOCNF) (2 % w/w content). Blueberries pruning waste (BPw), sourced as residues from agroforestry operations in Chile, were used to produce added- value products, including platform chemicals and materials (1D filaments) (Reyes, Pacheco, et al., 2022).

Rheology. The shear rheology of the dissolved cellulose was monitored under steady and oscillatory modes using an Anton Paar Physica MCR 302 rheometer (Anton Paar GmbH, Graz, Austria). The rheometer was equipped with a Peltier hood H-PTD 200 for controlled temperature and humidity. A light source with a cross-polarized light and a camera were used to monitor the birefringence during the tests, which were carried out with a parallel plate geometry (25 mm diameter and 1 mm gap).

NMR. All NMR spectra were recorded on a Bruker Neo 600 MHz with a triple resonance probe-head. 2.5 wt.-% MCC samples were prepared as above, except for using 50 % v/v D_2O in purified H_2O. The probe temperature was 25 ºC for all experiments. The diffusion-edited 1H experiment (ledbpgp2s1d) used a diffusion delay of 0.2 s, a gradient pulse length of 2 ms at 90 % intensity, a relaxation delay of 3s, an acquisition time of 0.5 s, and 32 transients. The HSQC (hsqcedetgpsisp2.3) and HSQC-TOCSY (hsqcdietgpsisp.2) experiments used 256 f1 increments (real and imaginary), 4 transients, an acquisition time of 0.064 s, a relaxation delay of 1.5 s and the HSQC-TOCSY has a TOCSY mixing time of 15 ms. The WET-NOESY water suppression experiment (noesywtpr1d) used 4 transients with an acquisition time of 4 s and a relaxation delay of 10 s. All data were initially processed in Topspin 4, and final images were prepared in Mestrenova 14.

SAXS/WAXS. Small and wide X-ray scattering were measured using a bench beamline SAXS/WAXS device (Xeuss® 3.0 C, Xenocs SAS, Grenoble, France). The generator worked at 45 kV and 200 mA, with Cu Kα radiation. Samples at 2.5 wt.-% cellulose were measured in capillary tubes with a diameter of 1.5 mm.

Results and discussion

Previous studies (Gunnarsson, 2019; Gunnarsson et al., 2017, 2018, 2021) showed that CO_2 (g) absorption capacity drastically impact the gelation of cellulose in alkali conditions. However, the mechanism of this gelation and the effect of CO_2 (g) absorption as a function of cellulose concentration and viscosity are subjects that remain for elucidation. Cellulose dissolution in a CO_2(g)-depleted atmosphere followed by freezing and thawing under centrifugal forces was carried out. The dissolution and enhanced flow behavior are then confirmed by optical microscopy and rheometry. The elastic moduli (G') of the samples (7, 9, and 12 wt.-% concentration). The maximum elastic moduli measured at high frequency of cellulose solutions (12 % and 9 % concentration) plateau at G'=1x104 Pa, indicating a gelated system. Moreover, with the increased concentration, the system reached terminal values of elastic modulus, complex and dynamic viscosities. The optical images confirm a dissolved gel state at 12 wt.-% cellulose concentration, indicating a dissolution limit. A sample saturated with CO_2(g) formed a solid-like structured gel becoming a rigid solid, which prevented any attempt to assess the flow properties. Samples produced in the air-tight container formed a metastable gel, with a reversible structure and a liquid-like behavior at high frequency ideal for filament spinning (see Figure 59). By contrast, the elastic modulus revealed that the samples prepared in open-air and with added CO_2(g) formed a stable gel ideal for printing materials (see Figure 59).

Similar to this latter cellulose gels are the stable gel-type behavior for TOCNF observed with an elastic modulus one order of magnitude above the loss modulus. Besides the solid-like behavior (G'>>G"), we observe shear-thinning at high shear rates and CNF alignment above the shear rate of 10 s-1; above this point, the dope exhibited birefringence characteristic of well-aligned TOCNF underflow (Lundahl et al., 2018). ideal for spinning stable hollow filaments (Reyes, Ajdary, et al., 2022).

The processability of dissolved cellulose was found to depend on the delayed gelation, which is affected by CO_2(g) absorption (atmospheric conditions) and temperature for alkali dissolved cellulose; analogously the lignin content play an important role in the mechanical performance of dry and wet lignocellulose filaments regenerated from the ionic liquid 1-ethyl-3-methyl imidazolium acetate (Reyes, Pacheco, et al., 2022).

In sum, the viscosity and flow behavior determine the dopes' suitability for 1D or 3D materials production.

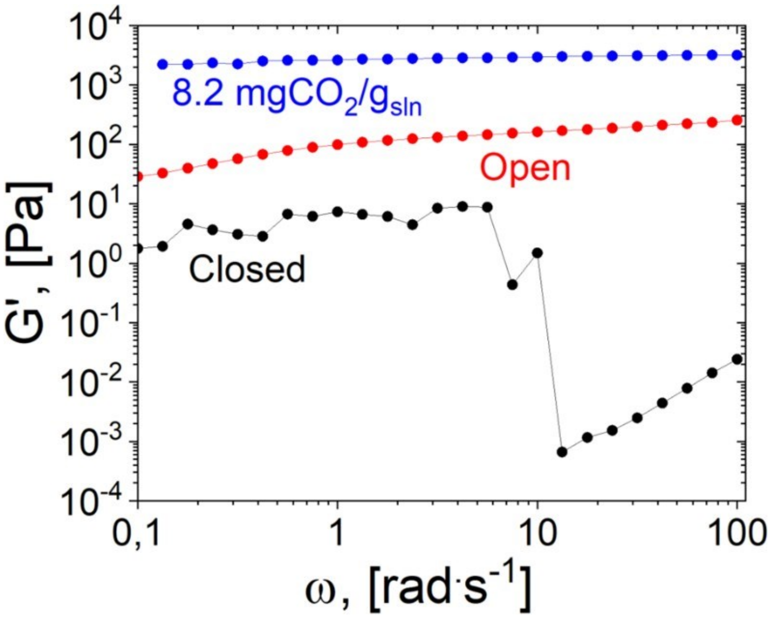

Figure 59. Elastic moduli and effect of atmosphere condition (air-tight and in contact with open air at room

Conclusions

TOCNF was successfully spun into hollow filaments (HF). The Young modulus of the HF reached values as high as 9 GPa, 170 % higher compared to hollow filaments produced from flat membranes (Carter, 2021). The HFs did not exhibit delamination or instability and were shown to effectively hold phase change materials of hydrophilic or hydrophobic nature (Reyes, Ajdary, et al., 2022).

Adjusting time-dependent variables (CO_2 (g) chemisorption, ionic environment, temperature, and hydrophobic interactions) and processing shear forces allows an elegant control over the gelation phenomena, giving access to the production of cellulose solutions with a wide range of rheological properties, suitable for the preparation of different regenerated cellulose materials.

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Sustainable Chemistries for Cellulosic Textiles

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Abstract

The development of textile industry is currently driven by sustainability. In sustainable cellulosic fibre production, not only the carbon footprint and environmental burden, but also the chemical safety and chemical risk mitigation have a central role. Besides of local laws and regulations, also voluntary initiatives pave the road to more safe and sustainable chemistries along the entire textile value chain. This requires transparency and communication between all parties acting in textiles industry. Several biobased and sustainable chemistries exist to tailor the cellulosic fibre properties. In this paper, we discuss the chemical safety in textile value chain and present chemical solutions to improve the whiteness or hydrophobicity of cellulosic textile fibres.

Introduction

Textiles are commodities utilized by all people in their everyday life and textile fabrics are applied in garments, furniture and other interior design materials, geotextiles, medical and industrial applications. However, the sustainability issues of the textile sector has expanded drastically during the recent decades due to the population growth, higher average income of consumers, and fast fashion trend. Today, according to European Commission (2022) the sector has the fourth highest impact on the environment and climate change, after food, housing and mobility. In addition, it is the third sector for the water and land use and fifth for the use of primary raw materials and greenhouse gas emissions. Furthermore, there are issues with the end-of-life management of textiles, since each European throws away in average 11 kg of textile waste annually, most of which is currently landfilled or incinerated.

During the last decade, several novel technologies have been developed to manufacture textile fibres from renewable or recycled raw materials in environmentally sustainable manner. Especially cellulose from certified forest resources, recycled raw materials or agricultural side streams are the most promising raw materials for future renewable textile fibres since they are available in high quantities. The development of novel textile fibre production processes requires improved sustainability measures, when compared to the existing technologies. This means reduction of the use of harmful chemicals, minimizing the environmental burden of the processes and transition to biobased or recycled raw materials throughout the entire value chain.

Sustainability and chemical safety in the textiles value chain

Product and process safety are essential throughout the textile value chain and in textile circulation. This creates a need for high transparency and efficient communication between the companies and other stakeholders throughout the value chain. There are numerous chemistries that are restricted in textile products, either by law and regulations, or via voluntary initiatives.

In Europe, the main regulation that sets limits to textile chemical industry is REACH, which sets the base level on which companies need to operate. REACH is adopted to minimize the chemical risks for humans and environment, and it is applied to all substances and articles utilized across the EU. According to REACH, the burden of proof is placed to companies, and therefore all companies must identify and manage the risks that are linked to the substances that they manufacture and market in the EU. Companies must demonstrate for the European Chemical Agency that the substances they use can be used in a safe manner, and communicate any chemical risks to the users. In other regions, there are different regional legislations that set boundaries for the textiles industry, and therefore understanding the local regulations is essential in global operations.

Proactive management of potential risks and safety of all chemicals utilized in textiles industry is a key factor in enabling safer and more sustainable textiles for the future. Several big brand owners are proactively monitoring the residual components in the fabrics that they are utilizing in their products. The companies expect that their business partners are in full compliance with the local laws and regulations regarding the environmental and product safety. In addition, they expect that the suppliers avoid the intentional use of several substances of very high concern. The residues of such components are monitored in the supplied materials to verify the compliance with the standards.

Voluntary initiatives and standards, such as Oeko-tex or EU Ecolabel, define the detailed criteria on safety of textile products along the entire textile value chain. Obtaining the compliance with these initiatives or standards require detailed chemical management, environmental performance, environmental management, social responsibility, quality management and occupational health and safety.

Sustainable chemistries for cellulosic textile fibres

Cellulosic textile fibres can be modified using several different strategies, some of which depend on the fibre production technologies, while some others are more generic regardless of the production technologies. Tailoring of fibre properties can take place as a fibre pretreatment prior to cellulose dissolution and spinning, during the spinning process or as a post-treatment of fibres after spinning. Several chemical solutions exist to modify cellulosic fibre properties, such as optical properties, purity or hydrophilicity.

Bleaching of natural or man-made cellulosic fibres (MMCF) is an important step to improve the fibre quality in terms of whiteness and purity. Utilization of dissolving pulp as a raw material mitigates color from lignin and other wood-based chromophores, however, during dissolution and spinning certain process additives and some conjugated structures origin from carbohydrates may be the source of color in the spun fibers. Hydrogen peroxide (P) and distilled peracetic acid (dPAA) are both oxidizing bleaching chemicals utilized for natural and MMCF bleaching, and the reaction products from these oxidative treatments are non-toxic. Of these oxidative chemicals, distilled peracetic acid commonly outperforms hydrogen peroxide in several processes. Peracetic acid increases staple fibre whiteness of the certain MMCF more efficiently compared to peroxide with equal chemical dosage under similar conditions (Figure 60). Peracetic acid is highly selective in removing the chromophores that cause the yellowish or brownish color to the fibres. When performed under optimized conditions, peracetic acid does not attack the cellulose chains which could cause their depolymerization or oxidation. Therefore when peracetic acid bleaching is performed under optimal conditions, the fibre strength is not much affected. In addition to improving the brightness of MMCF or natural cellulose fibres, peracetic acid increases also the purity of the fibres. This may be have significant importance in selected end uses of textile fibres, such as in medical or hygiene textiles or nonwovens.

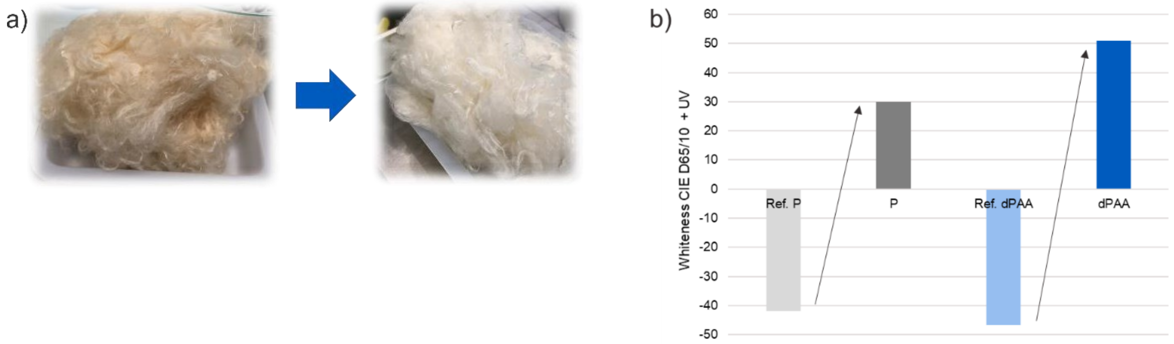

Figure 60. Man-made cellulosic fibers a) after spinning and bleaching with distilled peracetic acid,

In several textile applications, for example in outdoor and sport garments, effective moisture management properties of the fibres is required to exhibit low water and dirt sorption as well as fast drying. Synthetic fibers are explicitly used for this purpose although moisture absorption and swelling properties of cellulose based fibers can be modified. One of the existing and proposed strategies to control hydrophilicity/hydrophobicity of cellulose based fibers is to post-treat the cellulose material with hydrophobation agent.

Maleated sunflower oil high-oleic (MSOHO, Figure 61) is one example of a renewable hydrophobation agent for cellulosic materials that can be produced in industrial scale (Lackinger et al., 2009, 2011). When applied on cellulosic fibres, the MSOHO is bound by physisorption on the surface, and a small fraction is linked via covalent ester linkages uniformly on cellulose (Lackinger et al., 2016). The hydrophobation effect obtained with MSOHO is comparable to the result obtained by alternative fossil-based hydrophobation agents.

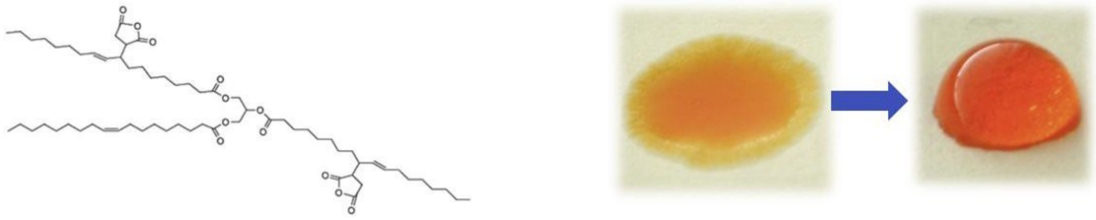

Figure 61. Chemical structure of maleated sunflower oil high oleic (MSOHO) and impact of hydrophobation treatment on cellulosic fibres.

Cellulosic textile industry is growing rapidly and this sets a need for sustainable chemistries to enhance the cellulosic fibre properties. Each MMCF type and different end product application have specific requirements for fibre properties and chemical solutions, and therefore variety of chemistries are needed to fulfill the needs for sustainable production of cellulosic textiles. Developing sustainable solutions to produce tailor-made fibres for textile industry require collaboration, transparency and communication along the entire textile value chain.

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Unlocking the Potential of Lignin in Material Applications via its Simultaneous Isolation and Multi-Functionalization

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Abstract

During biomass fractionation lignin undergoes uncontrolled side reactions and loss of chemical functionalities that result in the isolation of a highly condensed aromatic polymer. Thus, it is generally necessary to perform additional functionalization reactions on the remaining active sites of isolated lignin to enhance its reactivity towards other materials. Even when additional functionalization reactions are performed, high-performance lignin-based materials are still difficult to obtain. Here we show that by using a multifunctional aldehyde assisted fractionation process (AAF) we can isolate bi-functional lignins with controlled chemical structures and added functionalities, in one step from biomass. We used these lignins to produce new lignin-gelatin- based hydrogels with possible applications in soft-tissue engineering. These hydrogels have improved and controllable mechanical, temperature-resistant, adhesive and self-healing properties based on the functionalities imparted on the lignin during extraction. We hence demonstrate the importance and potential of controlling multiple functionalities on lignin during extraction, paving the way for new and high-performance applications of this polymer.

Introduction

Lignin is an aromatic heteropolymer that is exploited for materials application given its natural abundancy and unique structure. However, its use is challenged by obstacles arising from the traditional biomass fractionation methods. Traditional fractionation methods, such as the Sulfite or Kraft pulping, lead to lignin condensation (Amiri et al., 2019). Numerous β-O-4 linkages are lost and an array of C-C bonds forms within the lignin polymer, leading to the loss of native functional groups, such as hydroxyl groups (Figure 62, top) (Gellerstedt, 2015). This loss of functionalities makes lignin isolation with other materials quite challenging. A common strategy to overcome these problems and increase the reactivity and compatibility of lignin is to perform additional functionalization reactions on lignin's remaining hydroxyl or aromatic groups (Bertella & Luterbacher, 2020). However, the several additional synthetic and purification steps undermine the overall sustainability of these functionalized lignins, and are often not enough to make the lignin suitable for high-end materials applications (Sternberg et al., 2021). Recently, we demonstrated that when aldehydes are used during biomass fractionation (Aldehyde-

Assisted fractionation, AAF), condensation is avoided as β-O-4 ether linkages are preserved via the formation of stable acetals. (Figure 62, bottom) (Shuai et al., 2016). Moreover, by using multifunctional aldehydes during AAF we demonstrated the simultaneous extraction and functionalization of lignin at high yields (Benítez-Mateos et al., 2021; Bertella et al., 2022; Bertella & Luterbacher, 2021).

For several high-end material applications, e.g. engineering of soft tissues, the material developed must be biocompatible and present precise mechanical, adhesive and tensile properties as well as resistance to the biological environment. Engineered gelatin-based hydrogels are a case where these multiple properties are very important, as gelatin possesses excellent biocompatibility, bioactivity and is often used in the development of novel soft materials (Li et al., 2012). Gelatin-based hydrogels are however held together by physical non-covalent interactions, therefore often exhibit poor mechanical properties and melt at body temperature, unless they are chemically modified or cross-linked with other molecules (Yang et al., 2021). Lignin would be an interesting additive to strengthen gelatin-based hydrogels. However, the lack of water solubility and appropriate functionalities to perform cross-linking reactions with gelatin hydrogels prevents its incorporation into these biomaterials. Imparting water solubility and reactivity lignin in a controlled way has not been achieved before. In this work we demonstrate that lignin can be extracted and functionalized with two non-native functional groups (carboxylic acids and aldehydes), in one step from biomass, by employing the AAF process in presence of glyoxylic acid (GA) and terephthalic aldehyde (TALD) (Figure 62, bottom). The two new functionalities impart, respectively, water solubility and reactivity towards gelatin, without the need to perform additional functionalization reactions. The lignin-gelatin hydrogels that we produced showed enhanced and controlled mechanical, temperature resistant and self-healing properties. None of the abovementioned qualities could be improved when mono-functional lignins (bearing only carboxylic acids or aldehydes) were employed, demonstrating the unique potential of being able to develop high-performance material with lignin engineered and precisely functionalized during the extraction process.

Experimental

Lignin Extraction and Characterization

Eight lignin samples were extracted and simultaneously functionalized by performing the AAF procedure using terephthalic aldehyde (TALD) and glyoxylic acid (GA) in different ratios (Figure 62, bottom). We performed two additional extractions in presence of only GA or TALD to obtain monofunctional lignins, that we used as controls. We confirmed the structure of the obtained TALD/GA-lignins by Heteronuclear Single Quantum Coherence (HSQC) NMR experiments where we could observe the signals of the native lignin structure as well as those relative to the acetal formation between lignin, TALD and GA. We could also precisely quantify the amount of each functionalization obtained in each sample by using 1H NMR and 31P NMR for aldehydes and carboxylic acids respectively. We noticed that the initial ratio of TALD/GA introduced in the reactor for the extraction had a linear correlation with the TALD/GA ratio measured on the lignin after extraction.

Hydrogel preparation

Before preparing the lignin-gelatin hydrogels we tested the TALD/GA-lignin solubility in water, and we found out that, as expected, the solubility increased with decreasing TALD/GA ratio. The water solubility limit was reached for the lignin extracted with equimolar amounts of TALD and GA. We prepared different lignin-gelatin hydrogels (TALDGA-Gel) that had a constant total solid content of 8 wt.-%, of which 1-5 wt.-% was lignin. We also prepared, as controls, the same hydrogels with monofunctional lignins and a hydrogel composed of only gelatin.

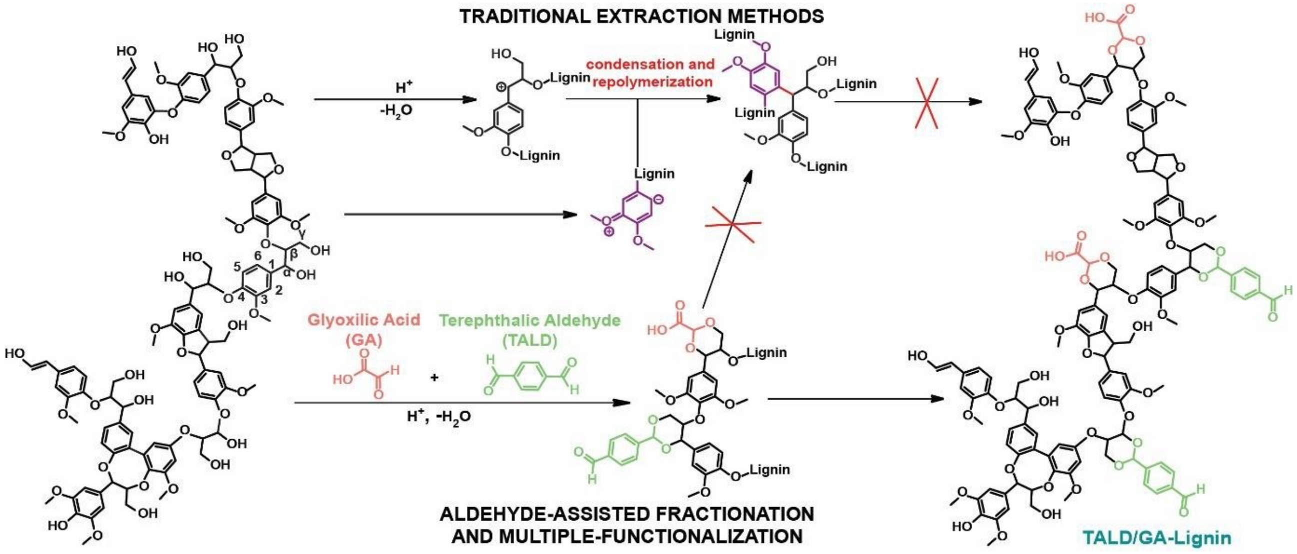

Figure 62. Overview of traditional extraction method side reactions (top) and the extraction and simultaneous functionalization of lignin with TALD and GA via AAF (bottom).

Results and discussion

Rheology

The viscoelastic behavior of the hydrogels was confirmed by measuring the storage oscillatory shear moduli (G') which was consistently higher than loss shear moduli (G''). The G' and G'' values between the different TALDGA-Gel, GA-Gel and TALD-Gel hydrogels presented a constant difference in storage and loss moduli. The storage moduli of TALDGA-Gel were up to three times higher than those of the control hydrogels prepared with monofunctionalized lignins while the loss moduli of TALDGA-Gel were up to seven times higher than the controls.

Compressive, tensile and self-healing properties

The compression curves of the various hydrogels showed that TALDGA-Gel had both higher compressive strength and strain-to-failure than all controls. While controls reached a strain-to- failure up to 80 %, TALDGA-Gel exceeded it, did not break upon compression and fully recovered its shape upon release of pressure. The elastic/tensile modulus (E) of the TALDGA-Gel hydrogel also increased up to 159 % compared to the controls. We finally tested the hydrogel's self-healing properties by preparing two set of each hydrogel and staining one of each set with Crystal Violet. We cut each set in two and recombined together two halves of each set, placing them afterwards in an incubator set at 37°C for 30 minutes. We noticed that only TALDGA-Gel preserved its shape and didn't melt at such temperatures (indicating a strong array of chemical cross linking), but in addition to this we observed that the two halves of the stained and unstained TALDGA-Gel hydrogel sets did not separate upon stretching of the material, indicating complete self-healing. The possibility to reverse chemical cross-linking in the hydrogel structure, combined with resistant to physiological temperatures (and biocompatibility), could facilitate the use of TALDGA-Gel in novel soft-tissue engineering applications.

Conclusions

In this work we used AAF to simultaneously extract and precisely functionalize lignin with carboxylic acids and aldehydes. The lignin/gelatin-based hydrogels produced showed that only the lignin with a dual functionalization was able to enhance the mechanical, self-healing and temperature resistant properties, while when monofunctional lignins were used, no benefits were observed. Because of this, these newly developed hydrogels are promising candidates in applications concerning soft tissues engineering. The versatile approach of lignin extraction and functionalization here presented could be extended to the obtainment of lignin with potentially any type of added functionalities, opening the way for the use of lignin in many high-value applications.

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Lignin Based Polyacids to Substitute Fossil-Based Materials in Coatings Formulations

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Abstract

Coatings provide protection against moisture, can improve fire resistance properties and simultaneously act as decoration. The aim of this work is to develop sustainable bio-based polyacids to substitute fossil-based materials in polyester and alkyd resin coatings. A sustainable process aims for reduced energy use, efficient resource use, minimal waste production and utilization of renewable and non-toxic products. However, very few commercial options and technologies for biobased materials are currently available.

Lignin, a renewable side stream from pulp mills and biorefineries, is currently underutilized. However, it has a high potential to provide not only higher economic returns, but also environmental benefits by substituting fossil-based coating formulations. The LigniOx technology, where lignin is oxidized by O_2 under alkaline conditions, produces water-soluble polymeric lignin by increasing its anionic charge. These oxidized lignins have successfully been applied as concrete plasticizers and versatile dispersants. Currently, the LigniOx process conditions were adjusted to produce lignin based polyacids at high yield. The target is to obtain low molecular fractions of lignin polyacids for alkyd coatings. The high molar mass fraction is utilized as dispersants for coating formulations.

The development of sustainable alternative for synthetic polyacids for coatings using the LigniOx process also supports the feasibility and commercialization of other end-use applications developed and tested for the LigniOx lignins as well as aids in reaching the European target of carbon neutrality.

Introduction

Coating- formulations consist of several components: resin (binder), liquid (solvent or water), pigments, and additives. Today, majority of resins, paints and varnishes are produced from fossil- based raw materials. The key feature that distinguishes alkyds from other polyesters is the presence of monoacids (commonly fatty acid) as a major part of the composition (Jovičić et al., 2020). Alkyds are mainly solvent-born formulations, which leads to high fossil-based VOC content in the final product.

Water-based solutions reduce VOC content, however, derive a major proportion of their resin components from fossil-based sources.

Synthetic polycarboxylic compounds utilized in alkyd coatings could be replaced by bio-based alternatives. The use of bio-based carboxylic acids in coating systems usually is limited to plant oil-delivered fatty acids utilized in the formulations of alkyd resins (Derksen et al., 1995). Nowadays, the development of bio-based polyacids for above mentioned applications is strongly supported by the industry. Bio-based carboxylic acids can be produced from carbohydrates in lignocellulosic materials (basically cellulose) e.g. lactic acid, formic acid, levulinic acid, glycolic acid (Yang 2015). Additionally, lignin can be treated in different ways to recover the carboxylic acids. Lignin carboxylation e.g. by carboxymethylation (Konduri et al., 2015) or using anhydrides (Kazzaz et al., 2019) are well known methods. Recently, also more sustainable enzymatic carboxylation (Tommasi 2019) has been reported. In carboxymethylation, toxic chemicals are used, and the enzymatic means are still far from industrial applicability. Furthermore, lignin remains in polymeric form without reduced molecular weight, which would ease the application in resin formulation similarly to the current monomeric aromatic di- tri- or polyacids. Oxidative degradation of lignin is an approach to produce monomeric/dimeric aromatic acids. However, lignin is rather recalcitrant for depolymeration; the monomer yields are typically rather low (< 15 %), and complex mixtures of aromatic aldehydes and acids, quinones, and aliphatic (di)carboxylic acids are formed (Costa and Rodrigues 2021; Zhou et al., 2022). These are also prone to secondary repolymerisation reactions. Objective of the current work is to develop a new conversion route to produce intermediate chemicals based on lignin, specifically to produce oligomeric lignin-derived polyacid fractions (for alkyd coatings) at high yield by alkali-O_2 oxidation.

Approach

Technical lignins have been explored as polyols in polyester coating applications (Haridevan et al., 2021). However, to perform as polyacids, lignin has to be modified and new carboxylic acid functionalities should be introduced to its structure. In the current work, industrial lignin raw materials: softwood kraft lignin (KL) and wheat straw organosolv lignin (OSL) (provided by Stora Enso and CIMV, respectively) are oxidized to perform as polyacids in alkyd and polyester coating formulations. The scheme of lignin polyacids production is illustrated in Figure 63. Industrial lignins are oxidized under different process conditions (e.g. pH profile, catalyst, O_2, pressure, time, temperature and concentration). Further, oxidised lignins are fractionated according to the molecular weight by cross-flow membrane filtration, to produce fractions with low enough molecular weight for the alkyd and polyester applications. The remaining larger molecular weight fractions are tested as dispersants in coating formulations. The fractionation and purification of oxidized lignin solutions has special emphasis on removal of sodium to produce material with less than 0.5-1 % of Na. The optimization of oxidation and post-treatment parameters for the variable lignin raw materials is performed according to the feedback of project partners on the performance of lignin-based polyacids in applications.

Batch reactor is used for screening of the oxidation conditions, after which the oxidation will be scaled up using a pilot reactor (215 L) constructed by ANDRITZ. Membrane filtration protocols are elaborated and optimised for the recovery, fractionation, and purification of all variable oxidized lignin types. Bench-top crossflow test rigs (1-20L) are used for screening trials, proof-of-concept testing and process optimization of membrane filtration, whereas the actual samples for application testing and product demonstrations are produced on pilot test units (20-200L).

Final lignin fractions are analysed for the molecular weight, acid value, anionic charge, inorganic compounds, Gardner index, TGA as well as ^{31P}NMR for lignin functionalities and GC/MS for composition of small molecular weight compounds. Acid value and Gardner index parameters specifically important for coating formulations preparation.

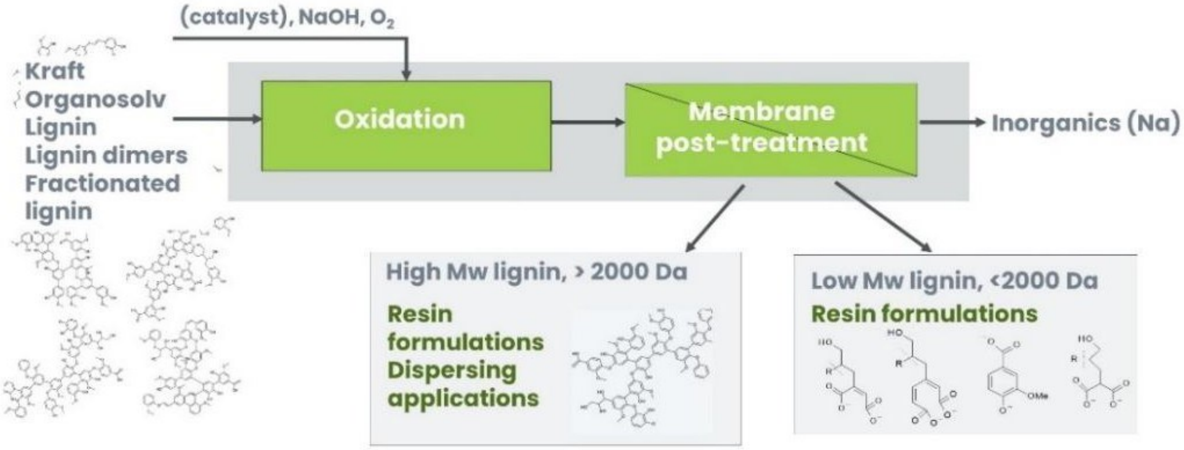

Figure 63. Concept for production of lignin polyacids.

The major challenge for converting lignin into small lignin-based polyacids is the selective bond cleavage during the oxidation process. The reaction mechanism, product yield, and product distribution of lignin oxidation strongly depend on processing conditions, especially pH and selection of an oxidant. Oxidative conversion of lignin through LigniOx technology for concrete plasticizers and versatile dispersants aims to retain the polymeric structure of lignin (Kalliola et al., 2022). Varying the LigniOx oxidation conditions towards more degrading process, gives a complex mixture of lignin structures as well as a high share of secondary oxidation products such as aliphatic acids. Yield of lignin polyacids should be high enough to allow a feasible conversion process. However, it is well known that lignin is difficult to degrade with high yield at any conditions, e.g. vanillin could be recovered with the highest yield ~14 % (Wang et al., 2018). The yield of lignin has direct correlation with a final molecular weight as presented in Figure 64. Preferably, having a lignin raw material with rather low molecular weight at the start would easy the production of lignin polyacids with acceptable yield.

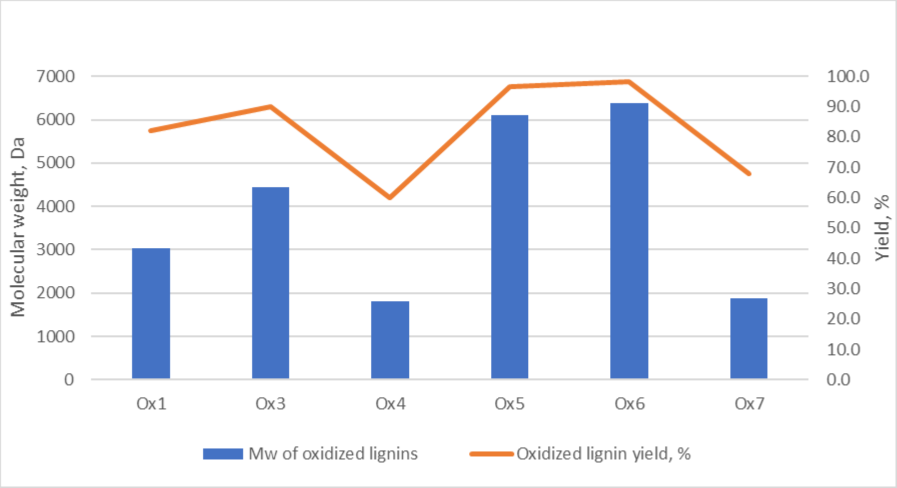

Figure 64. Molecular weight and yield of oxidized ligninswith varying oxidation parameters. Should you include the initial Mw of KL in the fig? Yield axis without a decimal.

Carboxylic acid functionalities could be introduced to lignin structure in relatively fast and mild oxidation conditions (Kalliola et al., 2022). However, to decrease lignin molecular weight - harsh oxidation conditions should be applied to break bonds. It leads to secondary degradation of lignin structures to aliphatic acids with low yield of lignin (Kuitunen et al., 2011). Therefore, refining lignin using organic solvents, e.g. EtOH/water, is a promising strategy to obtain homogenous fractions with controlled quality in terms of structure and properties. The EtOH/water soluble lignin fraction poses low molar mass, higher phenolic (PhOH) and carboxylic groups (-COOH) content than insoluble fraction (Jääskeläinen et al., 2017). The soluble fraction, having molar mass below 2000 Da, is preferable used for coating applications after being alkali-O_2 oxidized to increase the - COOH content in the lignin fragments. The insoluble fraction having molar mass of > 5000 Da, is preferable carbonized to produce lignin based hard carbon. End-uses of lignin based hard carbons include energy storage and harvesting. The insoluble fraction can also be valorised to a versatile dispersant by applying the alkali-O_2 oxidation (LigniOx). The lignin starting material can be fully used after the EtOH/water fractionation and by applying the given modification strategy to produce modified lignins for high-performance applications as presented in the Figure 65.

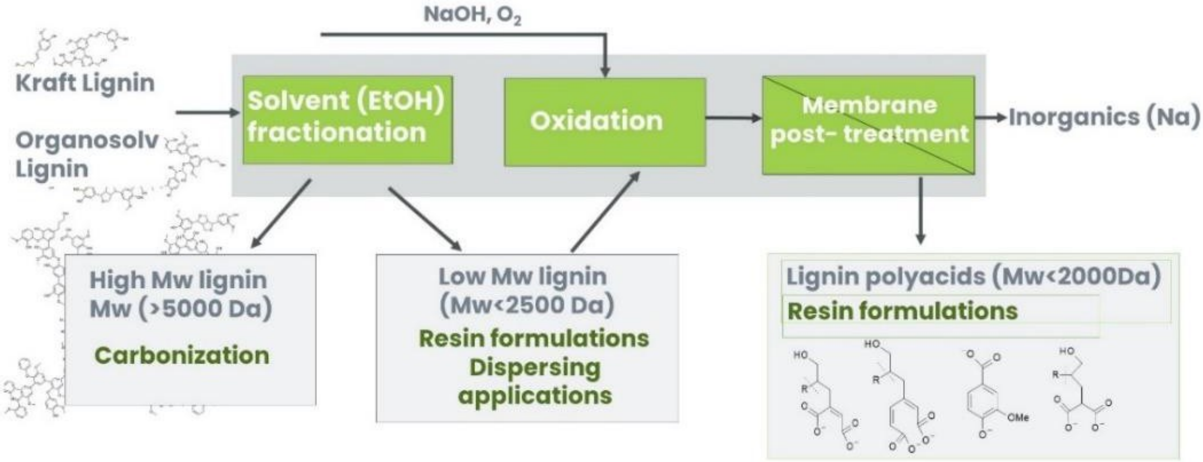

Figure 65. Lignin polyacids production concept with fractionation step

Utilizing already fractionated lignin for the oxidation gives freedom in oxidation parameters which could be tuned to modify structure of lignins (functionalities) and not focusing on breaking lignin bonds. Sodium content in the final fraction could be also decreased by fractionation step, due to lower alkali (NaOH) dosing in oxidation and more efficient membrane post treatment.

Conclusions

Alkali-O_2 oxidation technology with tuned process parameters converts various industrial lignin raw materials to low molecular weight lignin-based polyacids. However, it is critical to have application(s) for high molecular weight fractions to have a feasible process. The final decision, between oxidation at harsh conditions or solvent fractionation and mild oxidation will be done based on the performance in application test and techno-economic analysis.

Acknowledgements

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Engineered Lignin Products

Sustainable Lignin Polymer in Thermoformed Fiber Products

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Abstract

The main purpose of this study was to investigate the feasibility of both organosolv fibers and organosolv lignin in thermoformed fiber products. For this purposed, organosolv fibers and organosolv lignin from softwood (Norway Spruce) were produced in-house. The organosolv process was tuned to produce lignin-coated cellulose fibers with desired amount of lignin on the fiber surfaces, which yielded fibers with increased hydrophobicity. The obtained results were compared with those of Northern bleached softwood Kraft (NBSK) fibers. The surface morphology of both kraft and organosolv fibers was investigated by scanning electron microscopy (SEM). The mechanical properties, water resistance, and contact angle of all thermoformed pulp products were studied. A decrease in density, strength, and stiffness were observed for thermoformed fiber products where lignin was added to the fibers compared to the reference, i.e., thermoformed fiber products without the addition of lignin. However, the addition of organosolv lignin decreased the wettability and swelling of the thermoformed product. These results are due to the distribution of organosolv lignin on the surface, filling in the pores and cavities, and rendering the thermoformed materials less hydrophilic. In conclusion, the results from our study encourage the use of organosolv lignin as sizing additive to thermoformed products, which can improve water resistance to be used in sustainable packaging applications.

Introduction

In recent years, the environmental demands, and a shift towards a sustainable and economically biorefinery have focused on valorization of entire biomass, both pulp-products and value-added products to reduce their environmental footprint. The concept of using fiber materials and polymers from the biomass to thermoformed fiber products is interesting, since the product would be completely based on renewable resources. Lignocellulosic fibers, both chemical and chemi-thermomechanical pulp fibers (CTMP) have been extensively used for thermoformed fiber products. The thermoforming technology enables manufacturing products that can replace plastic, such as single-use food packaging products. Traditionally, paperboard packaging materials are coated with synthetic polymers that enhance their resistance to water, moisture, grease, oxygen, and odour (Talja et al., 2011). It has been shown that the introduction of biopolymers as alternatives to petroleum-based plastics potentially reduce carbon dioxide emissions by 30 to 70 %, induce hydrophobicity, and may promote inter-fiber adhesion and mechanical properties (Lackner 2015; Joelsson et al., 2020).

As such, application of lignin in thermoformed fiber products is a promising alternative to replace plastics in packaging materials, while additionally creating high-value applications for lignin and a fully biobased material. The properties of organosolv lignin, such as the absence of sulfur, high reactivity, and high purity, render organosolv fractionation an excellent method to produce lignin and lignin-coated cellulose fibers with high compatibility for subsequent manufacturing of lignin-cellulose fibers and biocomposites. Moreover, lignin and its blends have been reported to provide both gas and UV light barrier properties, as well as they can work as an antimicrobial coating (Hult et al., 2013; Yu et al., 2016; Rai et al., 2017). The mechanical strength of molded fiber products is believed to result from hydrogen bonding between the fibers, condensation reactions of lignin, and partial degradation of hemicellulose (Liu et al., 2021). Literature data showed that 6-17 % residual lignin in the fibers may distinctly contribute to the strength, stiffness, and water resistance of molded pulp products (Oliaei et al., 2021).

To produce a 100 % renewable thermoformed pulp product, the interactions between lignocellulosic fibers and the lignin biopolymer arecrucial. In our study we therefore tested in- house produced lignin-coated cellulose fibers and organosolv lignin to prepare thermoformed pulp products. The mechanical properties and hydrophobicity of these materials were analyzed and discussed in this work.

Experimental

Organosolv pulping was conducted in a displacement reactor according to previously published procedure (Joseph et al., 2021). The organosolv lignin was precipitated from the cooking liquor by addition of 3 volumes of water per volume of liquor. The precipitated lignin was filtered, and the filter cake washed with 500 ml water. The lignin was subsequently air dried and crushed to a particle size of < 300 μm.

Both the organosolv and the Kraft fibers were first dispersed in hot water (> 85 °C) according to ISO 5263:1995(E) and subsequently diluted. All material specimens were made from pulp suspensions with 3 g/l consistency. Handsheets with grammage of 300g/m^2 were formed in a custom-made sheet former, which uses gravity- and vacuum-filtration to obtain test sheets with a dimension of 8 cm by 15 cm. In one additional experiment, 2.4 gDM Organosolv lignin were added to the fiber suspension, which yielded 40 wt.-% added lignin per dry fiber mass. After blending the lignin and the pulp suspensions, 200 ppm cationic flocculant (PCB 20, Solenis Norway) per dry fiber weight were added to facilitate binding of the particles to the fibers and hence ensure a homogeneous distribution in the final product. After sheet formation, the laboratory handsheets were pressed between absorption paper at 20 bars (24 kN) for 5 minutes at room temperature. Then the sheets were dried in the climate chamber overnight (23 °C, 50 % rel. humidity). After air-drying, the sheets were thermoformed at 175 °C and 500 bar (600kN) between stainless steel plates for 10 min.

Tensile testing was conducted on a Zwick material tester using a 2.5 kN KAF-W force transducer and 100 mm/min test speed. Each sample sheet was cut into long stripes with a width of 15 mm, testing 6 – 8 stripes per sample. The morphology of both kraft and organosolv fibers were analyzed by scanning electron microscopy (SEM).

Results and discussion

SEM analysis

Figure 66 shows the surface morphology of both kraft and organosolv fibers. Spherical and irregular lignin particles were clearly visible on the surface of organosolv fibers. Lignin can serve as an adhesive agent between the cellulose fibers. Our results are in accordance with the literature results of Wang et al., (2020). The kraft fibers had a smoother surface, when compared to organosolv fibers. Its appears that the kraft process did not yield lignin deposition, as was the case with the organosolv fibers.

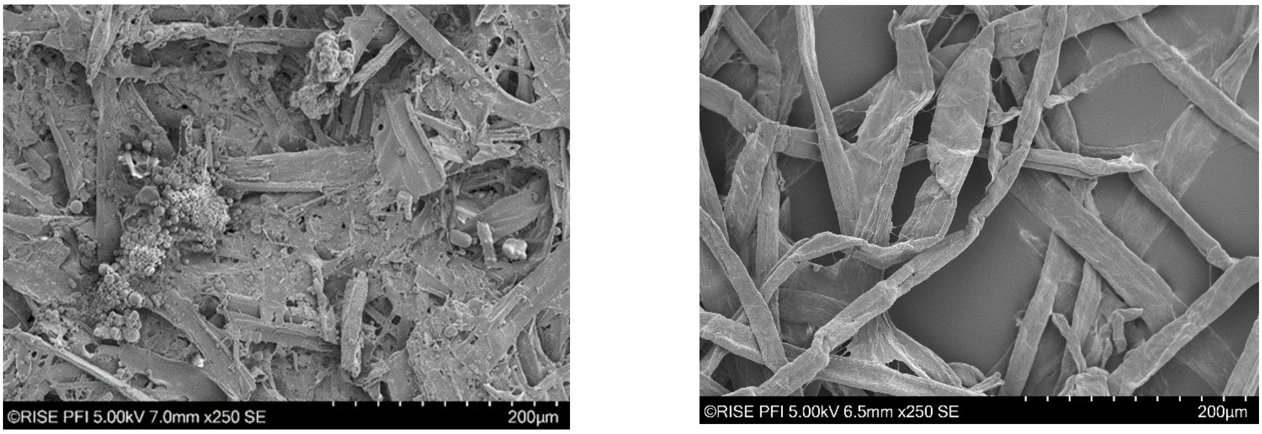

Figure 66. SEM images of lignin coated-cellulose fibers (left) and kraft fibers (right)

Dimensional characteristics and mechanical testing

All handsheets were measured and weighed to determine the density and basis weight. As can be seen in Figure 67 (left), the sheets without added lignin were closely within the target basis weight of 300 g/m^2. Addition of organosolv lignin increased the basis weight to above 400 g/m^2, as the fiber-weight was kept constant. Small deviations are evident, which can be attributed to mass-loss during filtration and the experimental error. A density of approximately 1000 kg/m^3 was obtained for all sheets without added lignin. This density is higher than for conventional paper and hence confirms the thermoforming induced compaction. After adding organosolv lignin, the density decreased, which disagrees with our previous findings (Ruwoldt & Tansase-Opedal, 2022). Adding lignin would be expected to increase the density, as the lignin can fill in pores and act as a binder. The previously studied materials exhibited a thickness of 1 – 2 mm (Ruwoldt & Tansase- Opedal, 2022), which is considerably larger than the materials in this study (250 – 500 µm). An increased surface roughness was observed in this work, which is partly due to the handsheets sticking to the stainless-steel plates after thermoforming. This roughness in combination with the smaller sheet thickness are likely contributors, which can explain the observed density.

The mechanical strength of handsheets was studied by tensile tests, see Figure 67 (right). The highest yield strength was obtained for organosolv fibers as well as the blend of organosolv and Kraft fibers (50/50 by weight). Kraft fibers alone showed a 20 % lower tensile strength, which is likely due to the lack of fines. The elongation at break of the Kraft fibers was higher than for the organosolv fibers. Moreover, the tensile modulus was greatest in case of organosolv fibers. It therefore seems that organosolv fibers produced a stiffer material, whereas the extensibility was greater for the Kraft fibers. Blending organosolv and Kraft fibers appeared to combine the beneficial attributes of both types, yielding a material that had the highest ultimate strength, while also preserving extensibility. Addition of organosolv lignin reduce both stiffness and tensile strength. It appears that the material became more brittle, which would suggest a less beneficial effect on mechanical characteristics. This would also agree with the observed decrease in density (see Figure 67), as the tensile strength is related to the cross-section of the specimen.

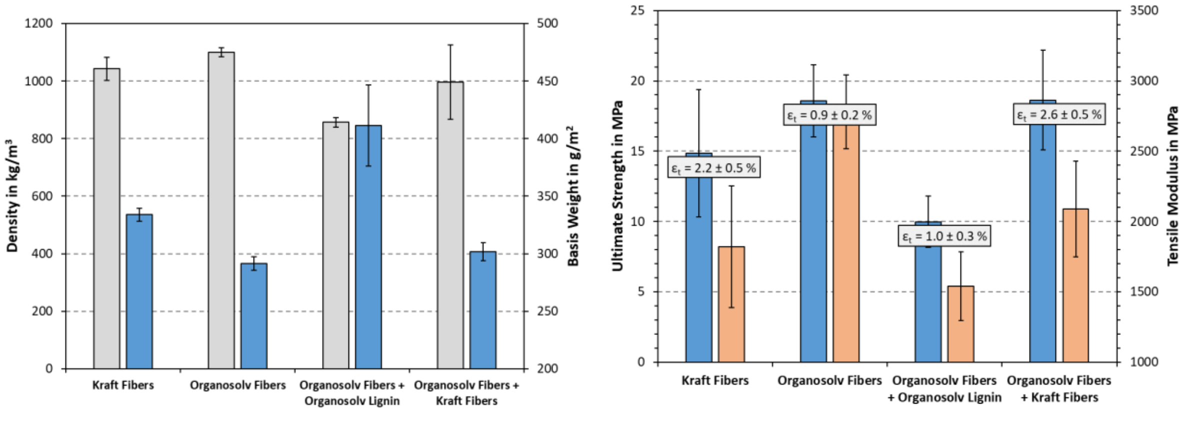

Figure 67. Density and basis weight (left) and mechanical testing results (right) of handsheets

Water-uptake and contact angle of thermoformed pulp products

The water-uptake and the time dependent contact angle results are plotted in Figure 68 The water-uptake was lowest for the material with added lignin, followed by the organosolv fibers. Materials containing Kraft fibers exhibited the highest water-uptake, which shows that the Kraft fibers absorbed water to a much greater extent. The contact angle is a measure of the hydrophobicity of the material. A surface is considered hydrophobic when the contact angle is greater than 90 ºC. As one can see, the thermoformed specimens made from kraft fibers exhibited the lowest and second lowest contact angles, which agrees with the results from the water-uptake. In case of Kraft fibers only, the measurement ceased after less than a second, implying that the water was quickly absorbed by the fiber material. The contact angle of organosolv fibers was above 90°, hence attesting a hydrophobicity to the material. Compared to this, addition of organosolv lignin slightly decreased the contact angle, which is likely related to a different surface morphology. All in all, the results attest a promising potential to both organosolv fibers and organosolv lignin, which can be utilized to reduce the wetting and water-uptake of thermoformed materials.

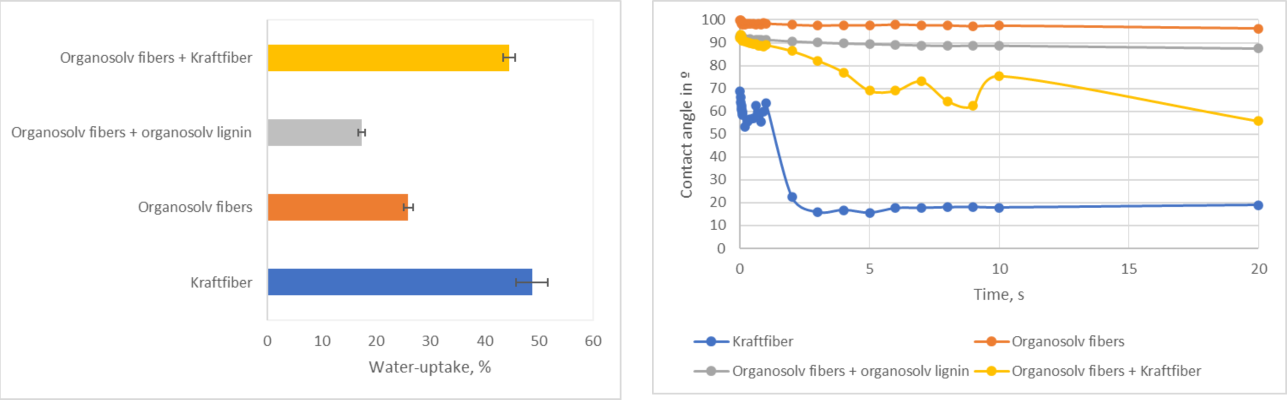

Figure 68. Water-uptake (left) and contact angle (right)

Conclusions

Overall, the results from our study show the possibility of using organosolv lignin and organosolv fibers to thermoformed pulp products with improved the water resistance, reduced fiber swelling, and increased contact angle. As such, these thermoformed products provide an alternative solution to replace the current petrochemical non-biobased products used for a wide range of packaging applications, which may in addition have a favorable impact on the economy of sustainable biorefineries.

Acknowledgements

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Engineered Lignin Products

Product Development and Scale-Up of The Lignin Platform in an Aldehyde-Assisted Fractionation (AAF) Biorefinery

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Abstract

The establishment of novel biomass processing schemes is key for achieving carbon neutrality and a fully circular economy. Biomass provides a versatile feedstock for sustainable monomers and macromolecules with great potential to replace petro-based materials in a wide range of applications, and several technologies are currently being developed with the aim to valorise it integrally. Among those, the promising aldehyde-assisted fractionation (AAF) process allows the isolation of the three main biomass components (cellulose, hemicellulose and lignin) while preventing lignin degradation, thus opening a unique pathway for the production of highly performant and cost-competitive lignin-based products. Bloom Biorenewables, a science-driven spin-off from EPFL, is scaling the AAF biorefinery and extensively working on the development of an AAF product platform that includes novel engineered lignin products suitable for a multitude of industries. Here, the major advancements in the industrialisation of the AAF technology will be presented, with a focus on its innovative lignin platform and targeted applications (such as flavour & fragrances, cosmetics & homecare, fuels and materials). Furthermore, the main challenges faced in the biorefinery space will be highlighted, as well as how cross-sectoral multidisciplinary partnerships can help accelerating the industrialisation of novel technologies.

Engineered Lignin Products

LignoCity – Flexible Production of Tailor-Made Lignin

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Abstract

The market for kraft lignin is growing. Existing markets for lignin-based products are growing and several new applications are close to commercialization. To enable this growth and facilitate the new lignin-based products under development, it is important to understand the requirements in different applications and which lignin properties can be changed. It is thus important to use the type of lignin suitable for the targeted end application.

Lignin´s properties are dependent on raw material and process for separation. Several parameters like purity, oxygen content, and content of volatiles can be tuned. Different end- products have very different demands on the feedstock for the process. One lignin quality is therefore not sufficient to unlock the vast potential that lignin has in the transition to a more sustainable society with more biobased materials.

LignoCity offers knowledge, experience, and a flexible process for the production of tailormade lignin qualities. With the knowledge of the demand on the feedstock for different applications, we can support different stakeholders in the development of various lignin value chains.

Introduction

Lignin is the second most abundant natural polymer in the world. Due to its availability and aromatic structure, lignin is an attractive renewable resource with great potential to replace fossil- based resources in materials, chemicals, and fuels. A wide range of application areas is being developed such as resins, thermoplastics, asphalt, barriers, and carbon fiber for composite and energy storage (Bajwa et al., 2019). However, these different application areas require different properties of the lignin feedstock.

The kraft lignin separation and purification process affects many of the lignin properties in different ways, depending on the process design. Some of the parameters that can be affected are purity (the content of ash, carbohydrates, and extractives), reactivity (more or less covalently bound oxygen and sulfur), the content of volatiles, and particle size and morphology. Depending on the intended end-product, the demands on the raw material differ. However, since many lignin- based products are still under development and not yet on the market a complete overview and understanding of this area are still missing. Therefore, it is important to understand which parameters can be controlled and how to access different qualities for testing.

LignoCity is an open test facility, a testbed, for the development of various lignin value chains. LignoCity has the capability to serve different companies and other actors with tailor-made lignin qualities by tuning the separation and purification process. By combining this possibility with the experience of our experts we can help our customers to find the optimal quality for their products. LignoCity does also cover the whole range from gram scale via kg to ton scale production.

Application areas

There is a wide range of potential end products for lignin in different application areas. All of them have slightly different demands on the different properties of the lignin feedstock. All these areas cannot be reviewed here, but some are discussed below.

Plastics

The plastic market is screaming for alternatives to fossil plastics that are biodegradable, renewable, etc. Lignin has the potential to play an important role as a feedstock in some applications. However, the plastic industry has some special demands on the lignin feedstock. The most important one is that the smell of kraft lignin is not accepted. The release of odorous compounds from the lignin during both processing of it and in the final product is both a work environmental issue and an issue for the perception of the product. Odor-free lignin is needed (Arkell, 2022). Several technologies are available for the deodorization of lignin (Wallmo, 2016; Guggenberger et al., 2022; Uhlin et al., 2018; Kouisni et al., 2016), but not all of them target all the compounds in the lignin that are responsible for the odor. Therefore, the deodorization of lignin must meet the requirements of the downstream process and product.

If the lignin is reacted with an oil (esterified or etherified) there is also a demand for a certain reactivity of the lignin. This put some requirements on the separation process to preserve the reactivity of the kraft lignin and not continue the condensation processes that have taken place in the digester.

One property that is of less importance in this area is the ash content. Normally, plastics contain inorganic fillers to reduce the content of the polymer and thereby reduce the cost. This product has therefore no requirements for extensive washing of the lignin material.

Carbonized materials

Lignin has great potential as a raw material for different carbonized materials, including carbon fibers (Bengtsson, 2019), anode material for batteries (Wang et al.), activated carbons (Suhas et al., 2007), graphene (Lawson, 2022), etc. However, the demand for raw materials is very different. For example, the presence of volatile compounds in the raw material for activated carbon is a benefit since they create voids during the carbonization process, generating the active surface area. However, this property is not as welcome in the production of carbon fibers since it makes the fibers weaker. Here a fractionation or separation of low molecular weight material or volatiles might be needed to improve the product quality. A condensation of the lignin to reduce the content of oxygen and sulfur might also be beneficial.

Another property where the demands differ a lot is the content of ash in the raw material. Activated carbon has a limit of about 10-15 % ash content in the final product, while the purity demand is much higher in carbon fibers and anode materials.

Bitumen replacement

Bitumen replacement is an area where huge volumes of renewable binders are needed. Lignin has great potential (Yao et al., 2022) and has been tested by many companies. The demand for purity is not as high in this application as in some others. However, there are other more practical aspects to consider. One is the odor and the work environment. Odor-reduced lignin is preferable in some cases (Arkell & Ölmhult, 2022). Another aspect is dust formation. Lignin with larger particles (granules or pellets) or lignin dissolved in a solvent might be preferable when it comes to handling the product.

Lignin has the potential to replace some parts of the bitumen. Tests between a few percentages and up to 50 % replacement have been made. However, a modification of the lignin is needed if a 100 % replacement is required or blending with other bio-based raw materials.

Hydrocarbons

The petrochemical industry is in great need of renewable hydrocarbons. Lignocellulosic biomass generally contains too much oxygen for being a preferable feedstock. However, lignin with its lower oxygen content requires less hydrogen when being converted to hydrocarbons. Somewhat condensed lignin with an even lower amount of oxygen and sulfur is even more preferable.

Another aspect, which might be the most important one, is the purity of the lignin. The catalysts in the hydrotreaters and crackers in the refineries are normally very sensitive to metals in the feedstock. Therefore, extensive washing of the lignin is needed to ensure that the level of several catalyst poisons is kept below the limits.

Process optimization

Several examples of how different downstream processes and end products puts different demands on the separation and purification process have been presented. However, the lignin separation process has also to be adopted to the black liquor feed and its composition. Two aspects are presented below.

Low residual alkali and low ionic strength

When pulping agricultural waste streams like wheat and rice straw, bagasse, corn stover, etc. the ionic strength of the liquor is usually low with almost zero residual alkali after the pulping process. This makes lignin separation processes based on two-step acidification with carbon dioxide in the first step very difficult to use. Instead, direct precipitation to low pH should be used and, in some cases, combined with membrane filtration for a pre-concentration of the liquor.

Fines and carbohydrates

Fines and high molecular weight carbohydrates, especially xylans, are known to cause performance issues in lignin separation. They can affect particle growth in the precipitation and reduce the filterability of the lignin. Fines can be separated from the black liquor by filtration and/or centrifugation. Carbohydrates can be removed by membrane filtration and/or precipitation. Another way to remove fines and high molecular weight carbohydrates is by degradation in a heat pre-treatment (Hulteberg, 2019). However, this pre-treatment affects the properties of the lignin. For some applications it might be good, but not for all.

What LignoCity can offer

Ligno-City is a unique open testbed for developing different lignin value chains. The testbed has the possibility, in g to ton scale, to adjust the separation method and tailor the right lignin properties for the application e.g., more condensed, or reactive lignin, more or fewer impurities like polysaccharides and metals, odor-free lignin, etc. With this knowledge and the flexibility that the testbed offer, lignin can be tailor-made for many different applications.

LignoCity does also offer a pilot area, workshop areas, laboratories, and office space for start- ups and SMEs. There is an opportunity to place their equipment in the pilot space and benefit from access to industry energy support, steam, compressed air, and of professional support from experienced operators while running a process in pilot scale. With the close collaboration of key persons in a network including as well technical and business development expertise as the closeness to researchers within the lignin field many challenges can be handled at an early stage and even be predicted before they occur. The geographical location in region Värmland is also a success factor since bioeconomy is a focus in the area with cluster organization, several mills, and forest industry with corresponding competencies.

Outlook

There are a lot of movements in the lignin market right now. Several lignin-based products that have been developed during the past years are very close to commercialization and the market for existing products is growing. The demand will increase. To facilitate this market growth, it is important to understand the different lignin properties that can be adjusted and how to adjust them to make a lignin feedstock better suited for the different emerging lignin-based products. LignoCity has the intention to be the facilitator in this area. Therefore, we continuously develop our process equipment and our offer so that we can serve the stakeholders in the emerging lignin market.

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Lignin Nanoparticles-Based Antibacterial Coatings for Development of Antimicrobial Surfaces

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Abstract

Antibiotic resistance development in bacteria is a serious threat to human health all over the world. One of the common ways of transmission of bacteria is contact with contaminated surfaces. Antimicrobial surfaces are promising solution for containment of spread of infection. Use of bio- based and biodegradable materials for antimicrobial coatings of disposable products are of great interest due to their lower environmental impact in comparison with synthetic compounds.

In this study filter paper samples were uniformly coated with different amounts of softwood Kraft lignin nanoparticles using spraying or immersion methods. Presence of the particles on the samples' surfaces were confirmed by Scanning Electron microscopy (SEM). Surface density of the particles on the surface were determined by weighing and by X-ray Photoelectron Spectroscopy (XPS). The Minimum Inhibitory Concentration (MIC) of LNPs dispersions for Staphylococcus aureus was 0.16 wt.-% in 24h contact time. The LNPs' coatings demonstrated antimicrobial properties against methicillin-resistant Staphylococcus aureus (MRSA) which makes LNPs promising bio- based antimicrobial agent for development of antimicrobial surfaces.

Introduction

Controlling the spread of infection is one of the greatest challenges of healthcare organizations around the world. Among bacterial infection antibiotic resistant bacteria such as MRSA pose the greatest treat for people with health disorders. Very often bacteria are transmitted trough contact with contaminated surfaces. Bacteria are found on door handles, tables, curtains, medical gowns etc. Antimicrobial surfaces are promising solution against spread of pathogenic bacteria.

Renewable materials are of interest for design of new functional materials including antimicrobial surfaces due to their low environmental impact. Lignin is the second most abundant biopolymer on the earth which is produced in large quantities as a side product of pulp and paper industry, and biorefinery. Lignin poses antimicrobial, antioxidant, and UV-shielding properties (Norgren & Edlund, 2014). However, despite all the advantage of raw lignin its use for high-value applications is limited by lignin's heterogeneity and low solubility in water. Conversion of raw lignin into spherical lignin nanoparticles with well-defined surface structure allows to get over limitations of raw lignin and at the same time benefit from lignin's useful properties such as antimicrobial activity (Lievonen et al., 2016).

The goal of this study was to explore feasibility of application of spherical LNPs as antimicrobial coating for the fabrication of antimicrobial surfaces. In this study we prepared two sets of Whatman 1 filter paper samples coated with spherical LNPs by spraying and by immersion of the papers into LNPs dispersions of different concentration. Coating density was determined by weighing of the samples and by XPS. Additionally, coated surfaces were imaged using SEM. Minimum inhibitory concentrations against S. aureus and E. coli were determined for the LNPs dispersion. Antimicrobial efficacy of the samples against MRSA were determined as well.

Experimental

The Softwood Kraft lignin BioPiva100 from UPM was used for the preparation of LNPs. Whatman 1 filter paper was used as substrate for coating. Staphylococcus aureus (VTT E-70045), MRSA (VTT E-183582) and E. coli (VTT E-94564) were used for antimicrobial tests.

For the preparation of LNPs lignin was dissolved in aqueous tetrahydrofuran (v/v 3:1). The solution was then filtered through a Whatman® glass microfiber filter, Grade GF/A to remove any undissolved residues. Then the lignin solution was rapidly added to excess amount of water to start the particle formation. Obtained LNPs dispersion was purified and concentrated. Malvern Zetasizer Nano-ZS90 was used for determination of the size and zeta potential of LNPs. Z-average particle size of the lignin nanoparticle was 189.2 ± 2.5 nm and the average zeta potential was - 22.8 ± 0.5 mV.

For the preparation of LNPs-coated filter papers samples pure filter papers were immersed into LNPs dispersions of concentration 0.3 wt.-%, 0.5 wt.-%, 0.7 wt.-% or 2.6 wt.-%, or sprayed with LNPs dispersions with the same set of concentrations. Whereupon the filter paper samples were dried at ambient condition. For the determination of surface density of LNPs on the surface the filter paper were weighed before and after applying of the coating. Stability of dried coatings were tested by soaking of the samples for 5 min. in warm water at 40 °C followed by rinsing, drying at ambient conditions and weighing of the samples.

Zeiss Sigma VP Scanning Electron Microscope was used for the imaging of the samples. Before measurements 4 nm layer of Gold/Palladium were sputtered on each sample using Leica sputter coater to increase their conductivity and avoid surface charge effects. The samples were imaged attached onto carbon tape.

The XPS measurements were performed with a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer using a monochromated AlKα X-ray source (1486.7 eV) run at 100 W. Photoelectrons were collected at a 90° take-off angle under ultra-high vacuum conditions, with a base pressure typically below 1 x 10-9 Torr. The diameter of the beam spot from the X-ray was 1 mm, and the area of analysis for these measurements was 300x700 µm. Spectra were collected from at least three different spots on each sample surface, in order to check for homogeneity and surface charge effects. The relative amounts and lignin and cellulose have been calculated as the root- mean-square deviations from the theoretical values for pure cellulose (Johansson et al., 1999). An amount equal to the contamination on the pure filter paper has been subtracted from the aliphatic carbon content of each of the other samples.

MIC tests were performed according to Clinical Laboratory Standards (CLSI, 2009). MICs against S. aureus and against E. coli were performed by using same amounts of microbe suspensions with concentration level 105 colony forming units (CFU)/ml and dilution of sample from two-fold dilution series and after 2 h and 24 h exposure time culturing on Plate Count Agar (PCA) was performed followed by 2 d incubation in 37 °C. MIC value was defined by mildest concentration of sample liquid which could inhibit the microbe growth.

Antimicrobial efficacy of coated surface samples was studied using modified ISO 22196 method. Volume of 0.4 ml of overnight culture of MRSA was spread on 5 cm x 5 cm sample piece and it was covered with 4 cm x 4 cm plastic. Contaminated sample pieces were kept at ambient temperature 24 h and after exposure time 10 ml of peptone saline was poured on sample which was on Petri dish. After 5 min stirring sample was cultured on PCA and incubated 1 d at 37 °C.

Results and discussion

To model disposable but eco-friendly surfaces Whatman 1 filter paper was chosen as a substrate for coating. It was found that LNPs form stable coatings of Whatman 1 filter paper without addition of binders thus two sets of samples were prepared by spraying of the filter paper and by immersion of filter paper into LNPs dispersion of different concentration. The photograph of LNPs coated filter paper samples tested for antimicrobial activity is presented on the Figure 69. It is seen that in both cases coating is uniform and coloring intensity increases with increase of concentration of used LNPs dispersion.

Figure 69. Photograph of LNPs-coated samples. A) pure Whatman 1 filter paper; (B-E) LNPs-coated samples prepared by immersion of filter paper into LNPs dispersions and (F-I) LNPs-coated samples prepared by spraying of filter paper with LNPs dispersions of 0.3 wt.-%, 0.5 wt.-%, 0.7 wt.-% and 2.6 wt.-% respectively.

Surface density of LNPs of different samples is present in the *Table 23*. The results of weighing showed that theoretically up to 5 g/m2 of LNPs can be attached to the surface of filter paper. The XPS is significantly more sensitive to the surface composition than weighing. Only cellulose and lignin materials were detected on the surface of the samples. XPS data was converted into lignin and cellulose content on the surface (*Table 23*). In our case most of lignin signal belongs to LNPs but it should be noted that aliphatic carbon was also detected on pure filter paper. This is typically caused by the presence of advantageous carbon contamination, which to a first approximation should be present at similar concentrations on all samples. XPS results showed increasing of LNPs amount on the filter paper surface with increase of LNPs dispersion concentration used for making of the coatings.

SEM images demonstrate (Figure 70) presence of LNPs on the surface of filter paper. At the nanoscale LNPs cover the surface unevenly in both cases of spraying of the nanoparticles and immersion of the filter paper into the LNPs dispersions. At some places on the surface of filter paper LNPs form clusters but other places are stay uncovered with the particles.

Determination of MIC was done for LNPs dispersion in water. In dispersion LNPs completely suppress growth of gram-positive S. aureus at concentration 1.3 wt.-% in 2 h contact time and at concentration 0.16 wt.-% in 24h contact time. For gram-negative E.Coli MIC of LNPs dispersion was determined as 0.56 wt.-% in 2h and 24h contact. These results are in agreement with previous studies reported that Kraft lignin active against both gram positive bacteria and gram negative bacteria (Gregorova et al., 2011).

Table 23. LNPs' surface density and antimicrobial properties of LNPs-coated samples

Nro	Samples	LNPs' surface density, g/m^2	Lignin relative content on the surface, XPS, %	Standard inocula, CFU/sample	Antimicrobial efficacy, log10-reduction CFU
Reference	Pure Whatman 1 filter paper	0	16.0	1 050 000	0
1	0.3 % sprayed	1.45	30.0	301 667	0.54
2	0.5 % sprayed	1.92	33.6	187 500	0.75
3	0.7 % sprayed	0.85	42.3	69 167	1.18
4	2.6 % sprayed	4.11	49.0	297 500	0.55
5	0.3 % immersed	1.80	35.6	200 833	0.72
6	0.5 % immersed	2.46	45.1	121 667	0.94
7	0.7 % immersed	1.53	56.9	145 833	0.86
8	2.6 % immersed	5.35	49.3	12 000	1.92

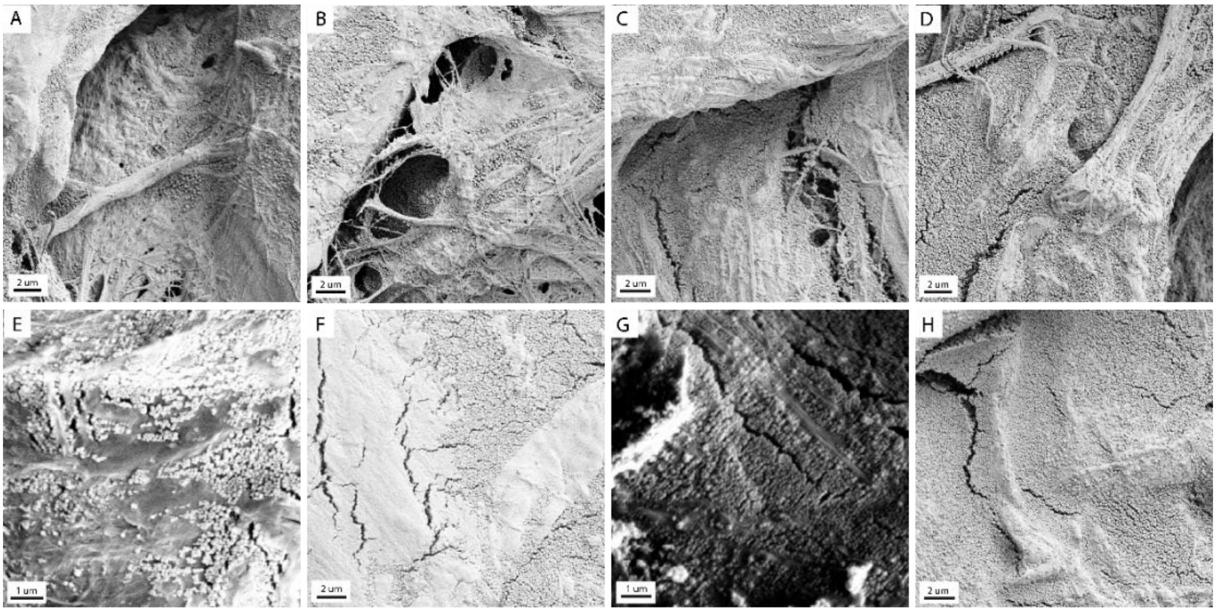

Figure 70. SEM image of LNPs-coated filter papers. (A-D) LNPs-coated samples prepared by spraying of filter paper with LNPs dispersion of 0.3 wt.-%, 0.5 wt.-%, 0.7 wt.-% and 2.6 wt.-% respectively and (E-H) LNPs-coated samples prepared by immersion of filter paper into LNPs dispersions of the same set of concentrations

Antimicrobial efficacy of LNPs-coated samples is presented in *Table 23*. Antimicrobial efficacy of LNPs coated samples against MRSA did not demonstrate pronounced dependance on surface density of LNPs. All samples except 2.6 % immersed sample possess antimicrobial efficacy against MRSA around 1 log10-reduction of CFUs. Moderate antimicrobial efficacy of LNPs-coated surfaces can be related to immobilization of LNPs on the surface of the filter paper. Few possible antimicrobial mechanism of lignin and lignin nanoparticles is described in literature (Yang et al., 2018). Polyphenols can damage of bacterial cell walls causing cell death, while LNPs as strong antioxidant can carry on their surfaces reactive oxygen species which could release by contact with bacterial cell and induce oxidative stress of the bacterial cell, also nanosized LNPs can infiltrate into bacterial cell and bring inside the cell lignin-originated monophenol compounds which can decrease intracellular pH of bacteria. Thus, immobilization of LNPs on the surface hinders the implementation of antimicrobial mechanism of LNPs and, consequently, decrease their antimicrobial activity. Higher antimicrobial efficacy of 2.6 % immersed sample - about 2 log10- reduction of CFUs - can be caused by unexpected release of LNPs from the surface.

Conclusions

In present work two sets of LNPs-coated filter paper samples were prepared by spraying of Whatman 1 filter paper with LNPs dispersion and by immersion of the filter paper to LNPs dispersion. Presence of LNPs on the surface of filter paper samples was confirmed by SEM imaging. MIC of LNPs dispersion against S. aureus was 0.16 wt.-% in 24h contact time. Nevertheless, LNPs-coated filter paper samples demonstrate moderate antimicrobial efficacy against MRSA which can be caused by immobilization of LNPs on the surface of filter paper. Further studies of antimicrobial LNPs-based coating will be focused on revealing of mechanism of antimicrobial activity of LNPs-based coating with the aim to optimize design of the coatings for achieving maximum antimicrobial efficacy.

Acknowledgements

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Upgrading Biorefinery Lignins Through Green and Cost-Efficient Reactive Extraction

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Abstract

AquaSolv Omni (AqSO) process showed a great potential as a parameter-controlled type of biorefinery, which allows for tuning the properties of the produced lignins and functional ligno-carbohydrate hybrids (LCHs). Herein, a reactive extraction (REx) streamline was introduced to AqSO integrated biorefinery. It allowed for a simultaneous lignin functionalization during its extraction in order to obtain lignins with different tunable properties and chemical structure. For this purpose, hydrothermal treated (HTT) wood solids were refluxed with EtOH:H_2O mixtures (70-99 %) in the presence of catalytic amounts of H_2SO_4 (C = 0.15-1.2 M). Wet chemistry methods and comprehensive NMR studies showed that both alkylation (ethoxylation) of aliphatic -OH groups together with esterification occurred during REx. We were able to extract partially ethoxylated lignins in 27-52 % yield (per available lignin) and tune their degree of substitution (DoS) with ethoxy groups in the range 9.3-27.4/100 Ar. An increase in [EtOH], the time, and the catalyst concentration increased the DoS, while preserving some key linkages present in lignin (e.g., lignin carbohydrate complex).

Introduction

Our group recently developed a green and flexible biorefinery concept for the integrated utilization of all major biomass components for high-value applications with the focus on lignin- carbohydrate functional hybrids (LCHs) in general and lignin-carbohydrate complexes (LCCs) specifically (Tarasov et al., 2022). The established process consisted of a modified hydrothermal treatment (HTT) of wood followed by solvent extraction of the resulting solids (under ambient conditions), and it has been therefore named as AquaSolv Omni (AqSO) biorefinery. AqSO allows for tuning products characteristics, and it can be easily coupled with other biorefinery streamlines.

Certain lignin modifications, for instance alkylation and acylation, are able to upgrade lignin towards important applications, such as thermoplastic blends, CFs, surfactants, and sorbents Li & Sarkanen (2005). When lignin modification is concerned, 100 % degree of substitution is usually targeted.

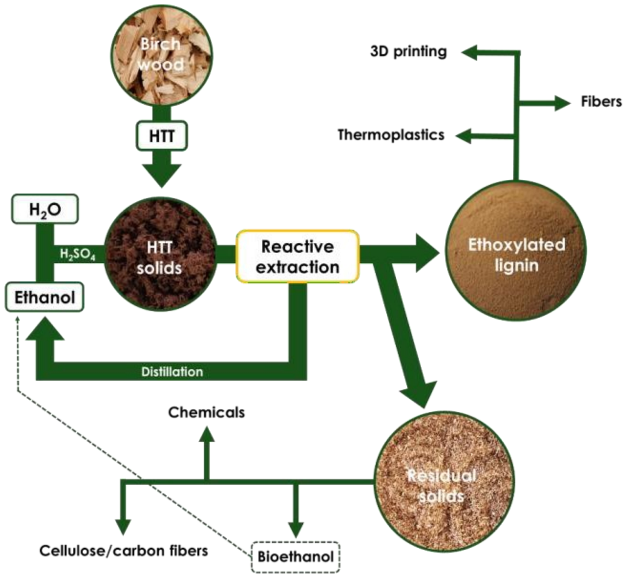

Figure 71. Outlook of reactive extraction (REx) integrated biorefinery.

However, such complete lignin modifications typically require expensive or/and toxic chemicals. In addition, the optimal degree of substitution depends on the application lignin is intended for and might not be 100 % in all the cases Balakshin et al., (2021).

We herein demonstrate the possibility of integrating a reactive extraction (REx) streamline process within an established biorefinery at a proof-of-concept level, similarly to earlier works (Balakshin et al., 2019; 2021). One of the major strengths of REx approach is its simplicity suitable for easy industrial scale-up. Throughout this study, the effect of multiple variables, such as time, solvent and catalyst concentration on the yields, composition and chemical structure of the major products was elucidated. An outline of the possible integrated

We herein demonstrate the possibility of integrating a reactive extraction (REx) streamline process within an established biorefinery at a proof-of-concept level, similarly to earlier works (Balakshin et al., 2019, 2021). One of the major strengths of REx approach is its simplicity suitable for easy industrial scale-up. Throughout this study, the effect of multiple variables, such as time, solvent and catalyst concentration on the yields, composition and chemical structure of the major products was elucidated. An outline of the possible integrated biorefinery is depicted in Figure 71.

Experimental

Reactive extraction (REx). Prior to reactive extraction (REx) a hydrothermal treatment of birch wood was performed (Tarasov et al., 2022). at the liquid to solid ratio (L/S) = 1 and process severity (P-factor) = 500. The hydrothermal treated solids were labelled as S-500. In a typical experiment, a round bottom flask was filled with S-500 (1.5 g dry matter), EtOH:H_2O mixtures (70-99 %; 20 mL), and variable amounts of H_2SO_4 as the catalyst (C = 0.15-1.2 M). Then, the mixture was set to reflux for variable times (0.5-8h). Once the reaction was complete, the residual solids (RS) were filtered and exhaustively extracted with 70% EtOH:H_2O mixture. The reactively extracted lignins (RELs) were precipitated by diluting the 70 % EtOH:H_2O solution with water to 10 % EtOH concentration, and then filtered. The yields of RELs and the residual solids (RS) were evaluated gravimetrically. RELs were analyzed by NMR and wet chemistry methods, while the DoS on RS was evaluated by wet chemistry methods (Sumerskij et al., 2017).

Results and discussion

Reactive extraction (REx)

Our previous study demonstrated that process severity (P-factor) and the liquid to solid (L/S) ratio are key parameters to tune the characteristics of the extracted lignins (Tarasov et al.., 2022). The process severity (P- factor) was set at 500 and L/S = 1 for the preparations of the starting material, so called hydrothermal treated solids-500 (S-500). Reactive extraction (REx) was carried by applying different

EtOH:H_2O mixtures (70-99 %) to S-500 with variable catalytic amount of H_2SO_4 (C = 0.15- 1.2 M) for different time frames (0.5-8 h) at reflux temperature followed by exhaustive extraction with 70 % EtOH:H_2O. The reactive extracted lignins (RELs) were isolated by precipitation followed by filtration.

2D NMR (HSQC) analysis of RELs showed that ethoxylation of aliphatic -OH groups of lignin is occurring together with esterification of -COOH (Figure 72). The number of ethoxy-ethers/-esters depends on the reaction conditions.

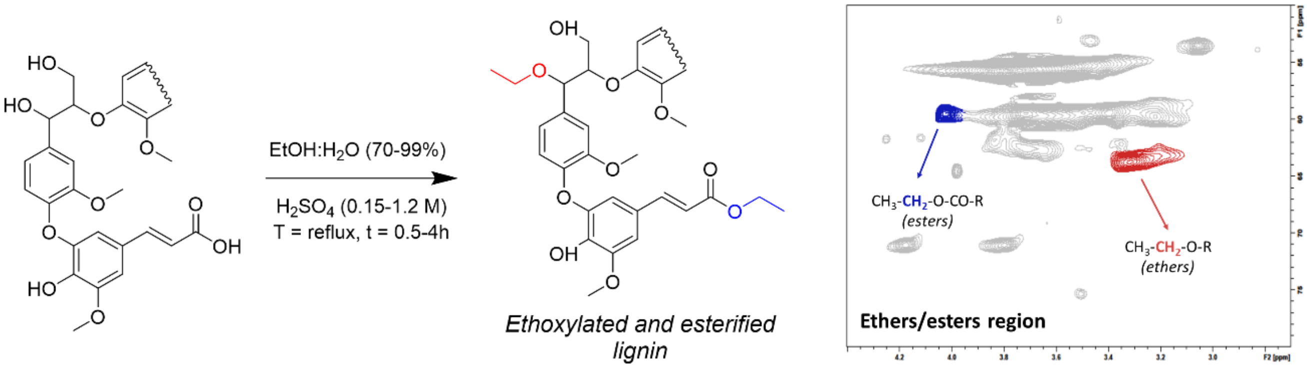

Figure 72. Left: modification of lignin during reactive extraction (ethoxylation and esterification). Right: an HSQC spectrum of REL produced at reaction time (reflux) of 1h, [EtOH] = 70 % and [H_2SO_4] = 0.15 M.

The effect of parameters is then briefly illustrated (Figure 73). With the aim of maximizing the DoS and the lignin yield, S-500 were initially set to react with a 70 % EtOH:H_2O solution in the presence of catalytic amount of H_2SO_4 (C = 0.15 N) for 0.5-8h. It was found that the yields of REL increases until 4h (yield = 48 % per available lignin), and then maintains rather constant (Figure 73b). Consistently, an increase of the reaction time increases the amount of ethoxy groups in REL determined by wet chemistry methods,[5] reaching 18 EtO/100 Ar (simplified mol %) from 4h on (Figure 73a). Noteworthy, ethoxylation occurred in the residual solids as well. This may facilitate the valorization of RS for various application (i.e. carbon fibers). The [EtOH] was found a crucial parameter for increasing the DoS of both REL and RS. The DoS of REL was increased by a factor of 2.4 with increasing the EtOH concentration from 70 to 99 %, where ethoxy groups increased from 12 to 29/100 Ar unit, respectively (Figure 73c). A similar trend was observed in RS, in which the DoS increased from 18 to 33 (% 100 Ar).

To make the procedure more economically attractive, the reaction time was decreased to 0.5h and simultaneously the amount of catalyst was increased ([H_2SO_4] = 0.15-1.2 N). The best outcome in terms of both yield and DoS was achieved with the highest H_2SO_4 amount. Within a short time (0.5 h) we were able to isolate REL in 54 % yield with 23 EtOH/100 Ar (Figure 73, e, f). This value is more than 2 times higher than typical data for organosolv lignins (Balakshin & Capanema, 2015).

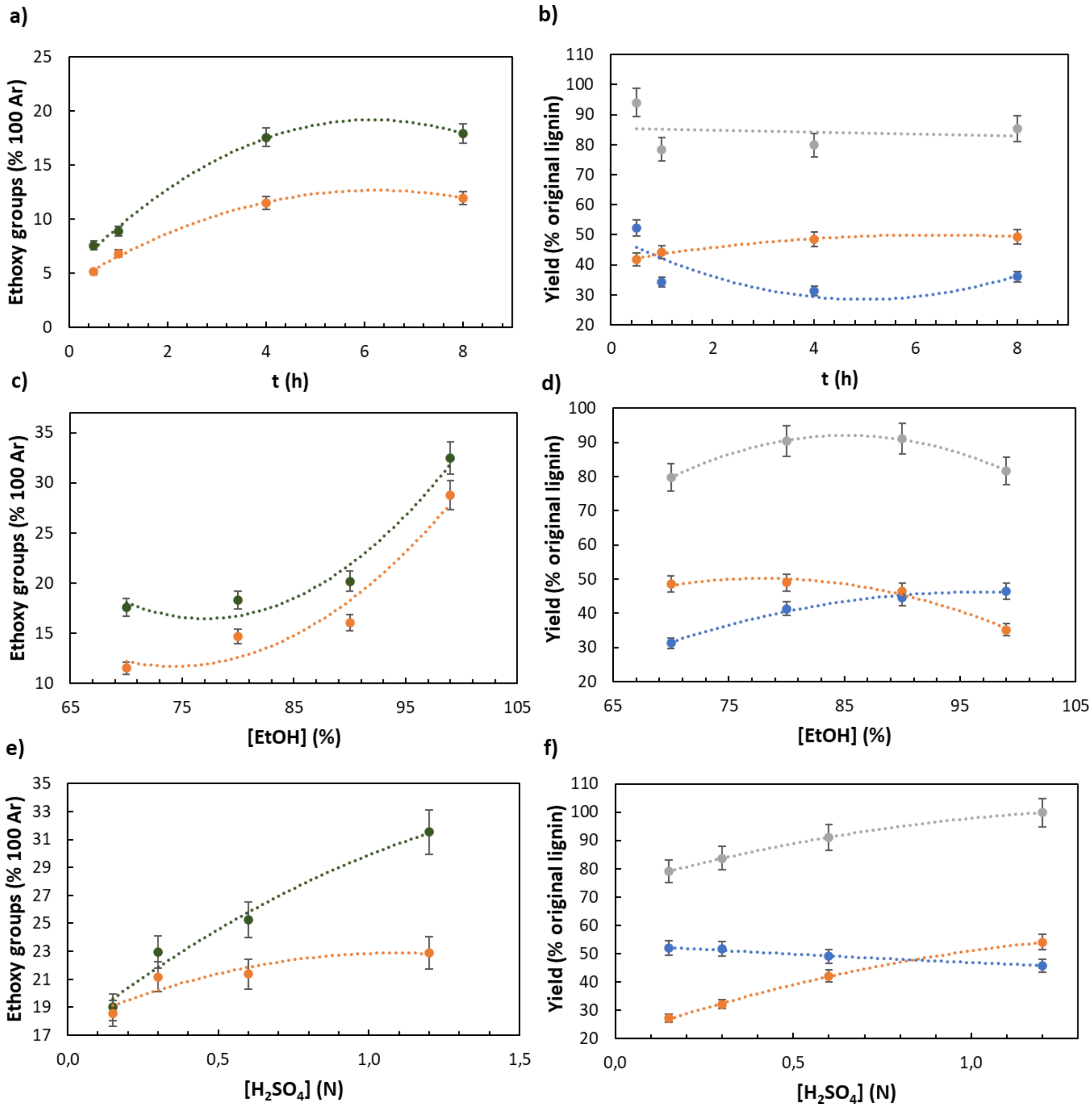

Figure 73. The effect of time (a, b), [EtOH] (c, d), and $[H_2SO_4]$ (e, f) on the outcome of REx. T = reflux in all cases. Other conditions: a, b: [H2SO4] = 0.15 M, [EtOH] = 70 %; c, d: t = 4h, [H2SO4] = 0.15 M; e, f: t = 0.5h, [EtOH] = 99 %. -●- REL = reactive extracted lignin. -●- RS = residual solids. -●- RL = residual lignin. -●- REL+RL.

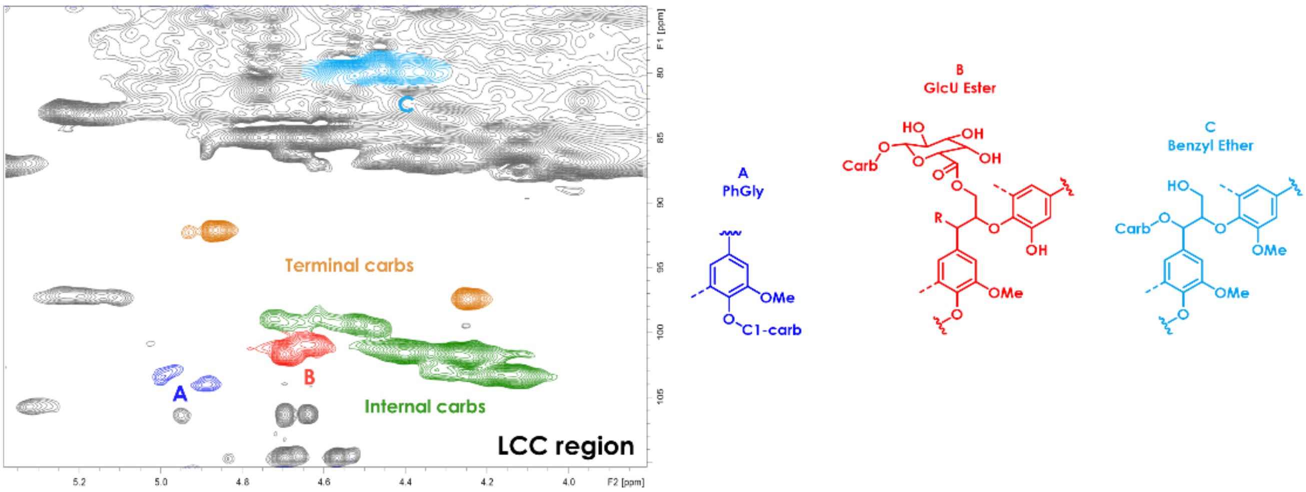

Figure 74. LCC region of HSQC spectrum of RELs. Conditions: T = reflux, t = 1h, [EtOH] = 70 %, [H_2SO_4] = 0.15 M.

Conclusions

We herein demonstrated that a reactive extraction (REx) streamline can be added to an emerging wood biorefinery at a proof-of-concept level. Throughout this study, the effect of multiple variables, such as time, solvent (EtOH) and catalyst (H_2SO_4) concentrations on the yields, degree of substitution (DoS) with ethoxy groups and chemical structure of the major products has been elucidated. Noteworthy, by the tuning of the reaction parameters, within a short time (0.5 h) we were able to isolate REL in 54 % yield (based on lignin original content) with 23 ethoxy groups each 100 Ar, which is almost twice higher when compared to other established organosolv processes (i.e. Alcell). Noteworthy, ethoxylation occurred in the residual solids as well.

Acknowledgements

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POSTER
Presentations

Oxygen Delignification – its Strong Oxidative Power to Increase Mechanical Pulp Properties and Reduce Energy Requirements

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Kraft pulping and oxygen delignification are the two well-known and established processes in the pulp industry. The oxidation by oxygen delignification can substantially increase the carboxylic acid groups in pulp fibres, leading to significant changes in the fiber properties, such as swelling ability, conformability, ions interaction, and fibrillation. Besides the pulp properties, increased fiber charges can decrease the refining energy required to achieve the same strength index up to 55 %. The energy improvement can be even higher if the kraft cooking is reduced and replaced by a more extensive oxygen delignification by using a lower temperature in the delignification process. It is, therefore, important to evaluate the impact of oxygen delignification on the chemical and mechanical properties of the fibers and on the process economy.

Pulps with different cooking times and consequently different lignin contents were oxygen delignified and compared to pulps with similar lignin content delignified only by kraft cooking. The total fiber charge, water retention value, and mechanical properties were determined, and their relation was investigated. It was concluded that water retention values are highly dependent on the fiber charge, even for different lignin contents. The mechanical properties were evaluated through the tensile index. The oxygen delignified pulps with a higher increase in the carboxylic acid content presented a greater increase in the mechanical strength and lower refining requirement than the pulps obtained from kraft cooking only.

Oxygen delignification – its strong oxidative power to increase mechanical pulp properties and reduce

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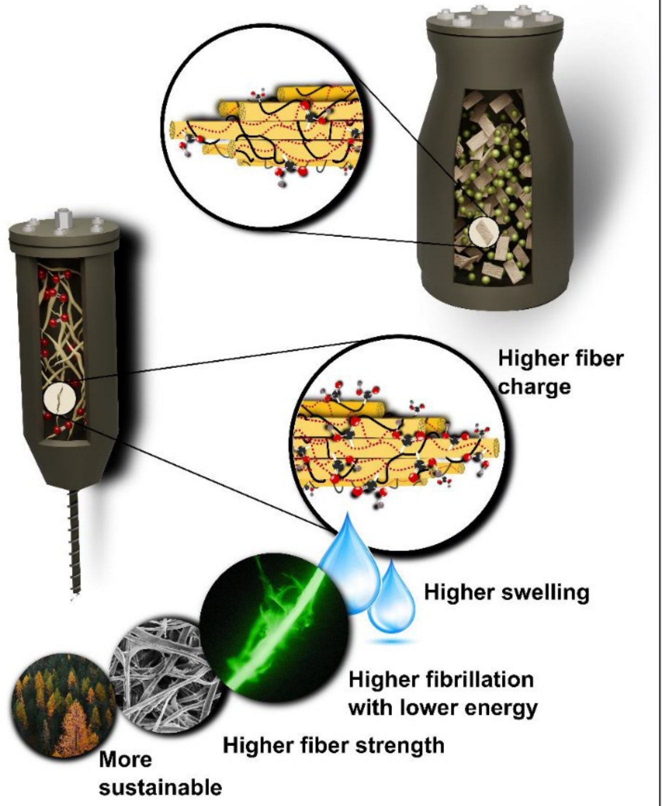
1. Introduction

Kraft cooking and oxygen delignification are important steps in the pulp and paper process, with crucial impacts on the final pulp properties. Oxygen delignification has economic and environmental benefits when compared to the kraft process. Due to the oxidation of lignin and some carbohydrates, it is possible to increase the amount of acid carboxylic groups, present in the fibers. Higher charges lead to an increase in fiber swelling and, consequently, to a better fiber conformability and bonding. The main goal was to investigate whether this increase in charges is useful to improve the mechanical strength of paper or not.



Higher fiber charge

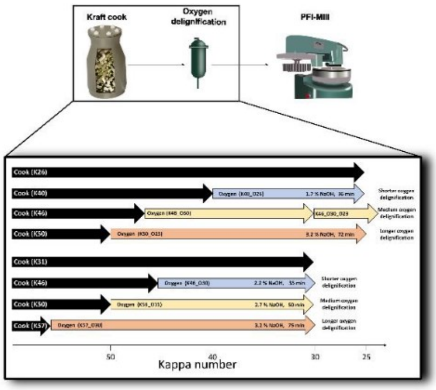
Higher swelling

Higher fibrillation with lower energy

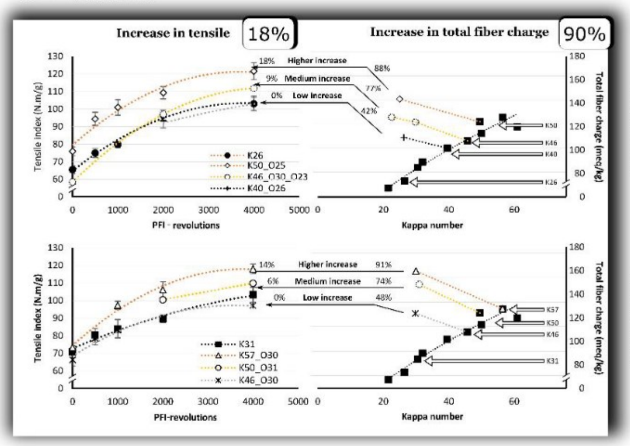
Higher fiber strength

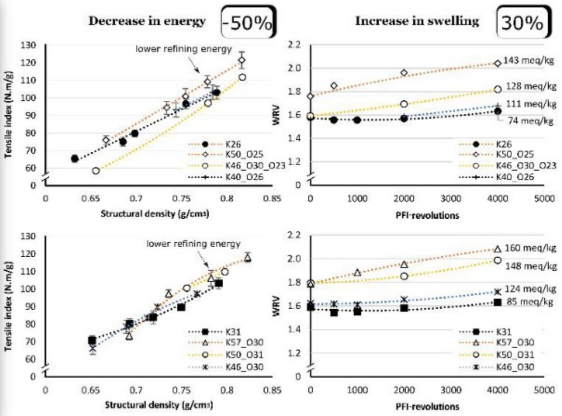
More sustainable

2. Experimental



3. Results





4. Conclusions

Oxygen delignification:

- increases the tensile index up to 18%;
- increases the water retention value up to 30%;
- reduces in 50% the refining energy needed to achieve similar strength;
- increases fiber charges up to 90% when compared to the kraft cooked pulps with similar delignification degree.

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STFI Intressentförening

LigniOx Lignins - Sustainable Depressants for Froth Flotation in Mineral Processing

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Froth flotation is a widely used technology in the mining industry to enrich valuable minerals for further processing. To aid the separation of high value minerals from lower value minerals, depressants and collectors can be added to adjust the enriched components. Sulfidic minerals, such as chalcopyrite ($CuFeS_2$), are one of the main sources of copper, zinc, and lead. However, the most abundant sulfidic mineral pyrite (FeS_2) has low economic value and is closely associated with these minerals. In flotation, depressant are commonly used to separate pyrite. Currently, the depressants used for pyrite separation are inorganic compounds, such as cyanide. These compounds can be toxic and harmful for the environment and new sustainable and environmentally friendly depressants are needed. Recently, an alkali-O_2 oxidation (LigniOx) process for producing lignin dispersants from different lignin by-streams, such as kraft, organosolv, and hydrolysis lignin, has been introduced. These anionic LigniOx lignins have high potential to serve as depressing agents in froth flotation.

To investigate the depressant potential of four LigniOx lignins, pyrite-adsorption tests were conducted under different pH conditions. All the LigniOx lignins adsorbed on the pyrite surface. Organosolv lignin based LigniOx (LigniOx-OSL) had the highest adsorption. In addition, it was observed that increase in pH decreased the adsorption of all lignins. Presumably, it was because the mineral surface become negatively charged at high pH causing repulsion to the anionic lignin. Adsorption experiments of LigniOx-OSL to chalcopyrite with or without a collector were performed. LigniOx-OSL did not adsorb on chalcopyrite to the same degree as on pyrite. Furthermore, the presence of a collector decreased the adsorption of LigniOx-OSL. The results are promising and the work will be carried on with further flotation experiments.

LigniOx lignins - sustainable depressants for froth flotation in mineral processing

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VTT Technical Research Centre Ltd.

Introduction

Froth flotation is a widely used technology in the mining industry to enrich valuable minerals for further processing. To improve the selectivity of the process, a range of flotation reagent are used. One of these is depressants which are used to modify hydrophobic unwanted minerals to hydrophilic. These anionic oxidized LigniOx lignins have high potential to serve as depressing agents in froth flotation

Materials and methods

The experimental setup composed of four stages presented in Figure 1. Milling ensured sufficient particle size of the feed for the adsorption experiments which aimed to reveal the effect of various flotation reagents and pH on the four different LigniOx lignin adsorption on pyrite and chalcopyrite. For the calculation of adsorption, supernatant samples were analysed with UV-Spectrometer.

Milling → Adsorption → Solid-liquid removal → UV-analysis

Figure1. Experimental procedure of the adsorption studies.

LigniOx lignin adsorption

All lignin samples adsorbed on the surface of pyrite (Figure 2). Organosolv lignin having the highest and kraft lignin 1+2 the lowest adsorption. The experiments in different pH values revealed that when pH increase the adsorption of lignin decreased.

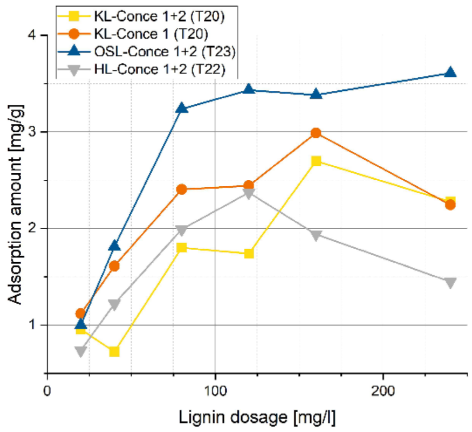

Figure 2. The adsorption amount of four different LigniOx lignins in pH 9.

The effect of collector on lignin adsorption

Experiments with collector (SIBX) present in the slurry showed lower adsorption amounts of organosolv lignin. As more molecules compete for the surface of the mineral lower adsorption of lignin is expected. However, in the flotation process other more attractive minerals such as chalcopyrite is present. Additionally, the chalcopyrite experiments revealed that organosolv lignin do not adsorb with as high degree on the chalcopyrite surface as on the pyrite with an exception in pH value 4. In practice however, chalcopyrite flotation is seldom carried out in acidic conditions.

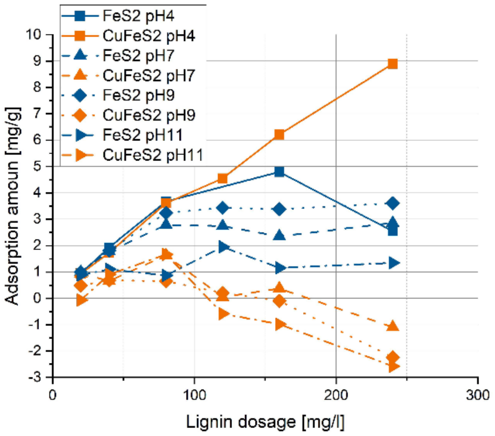

Figure 3. Organosolv lignin adsorption on pyrite and chalcopyrite in various pH.

Conclusion

- **LigniOx lignins demonstrate the potential to be a depressant for pyrite in neutral and high pH**
- **The promising results promote further flotation studies**

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beyond the obvious

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Engineered Lignin Products

Lignin-Based Carbon Materials for Energy Storage Applications

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The expanding electrification of transportation and other industrial sectors increases the demand of different chemistries and materials in energy storage devices. Carbon materials are common electrode constituents in in many energy storage devices, such as supercapacitors and Lithium-ion batteries. However, fossil-based or naturally mined carbon materials face a major sustainability problem due to the scarcity and depletion of their resources.

Sustainable energy storage devices need therefore alternative renewable carbon materials. The increasing volumes of lignins from paper mills and biorefineries offer an unprecedent opportunity for the design of future lignin-based renewable carbon materials. The aromatic nature of lignin and its high carbon yield upon thermal conversion makes it particularly attractive for this application. Turbostratic hard carbons, activated carbons and semi-graphitized carbons can be synthesized from lignins following different thermal conversion strategies and used as electrode materials in energy storage devices. The botanical and process heterogeneity of lignins, however, translates into different thermal reactivities and carbon materials with variable properties and performance. To better understand and control this variability, we devised a systematic approach based on the analysis of the lignin thermal reactivities, the in-depth characterization of their derived carbons, and the use of chemometric tools for performance optimization and structure-properties-performance relationship identification. Although little distinction is often made between lignins when used as precursor for carbon materials, their structural heterogeneity and purity are found to be key factors to consider in the design of lignin-derived carbons.

Lignin structure defines the properties of activated carbons and their performance in supercapacitor application.

Authors Guizani C, Siipola V, Sorsa O, Vilkman M, Pasanen A, Widsten P, Fearon O, Ohra-Aho T, Virtanen T, Kalliola A, Mäkelä M, Torvinen K.

Context

Carbon materials (CMs) remain largely fossil-based and unsustainable. A necessary shift to renewable sources is needed to engineer the future sustainable CMs.

Objectives

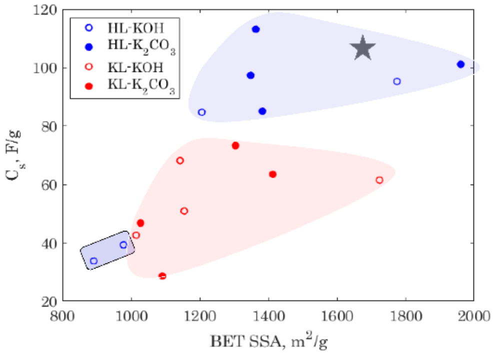
- Engineer activated carbons (ACs) from renewable lignins for supercapacitor application.
- Understand the effect of lignin structure on the AC electrochemical performance.

Methods

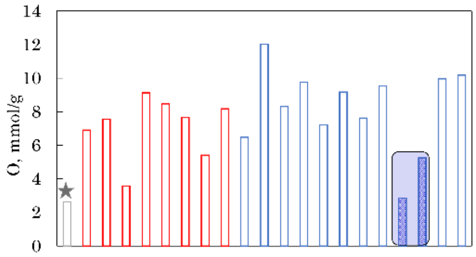
- ACs were produced from Hydrolysis (HL) and Kraft (KL) lignins using chemical activation.
- The lignins and their derived ACs were extensively characterized.
- Specific capacitance was measured using a three-electrode test cell.

Results

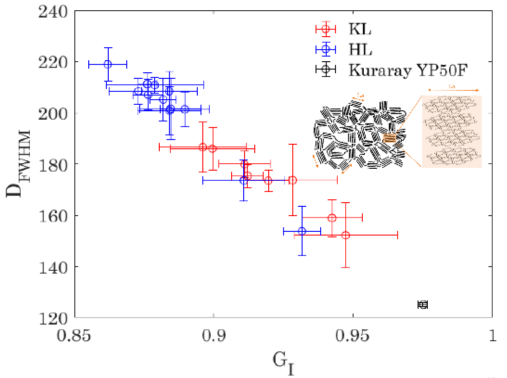
ACs from HL have higher specific capacitance than ACs from KL despite similar BET areas. In certain conditions, ACs from HL outperform the commercial Kuraray AC★.



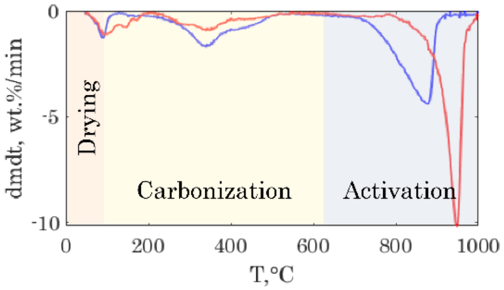
TPD-MS reveals slightly higher concentration of surface oxygen functional groups (O-FG) in HL ACs. The two HL outlier ACs have also the lowest concentration of O-FG.



Raman spectroscopy reveals a clustering of ACs according to the lignin type, which implies different structural and textural organizations at the nanoscale.



Thermal analysis shows that HL and KL have different thermal reactivities during K_2CO_3 activation, most likely resulting into different porosities and surface oxygenation.



Conclusion

Although it is agreed that lignin represents a promising precursor for renewable ACs, the influence of its structure on the properties and performance of the derived ACs is still poorly understood. Using two representative Kraft and Hydrolysis lignins, we showed that structurally different lignins result into ACs having different properties and electrochemical performance in supercapacitor application. A systematic engineering of lignin-based CM should build on this important conclusion.

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beyond the obvious

Potential of a Bio-Based Additive in the Prevention of Lignin-Induced Recalcitrance under Severe Pretreatment Conditions

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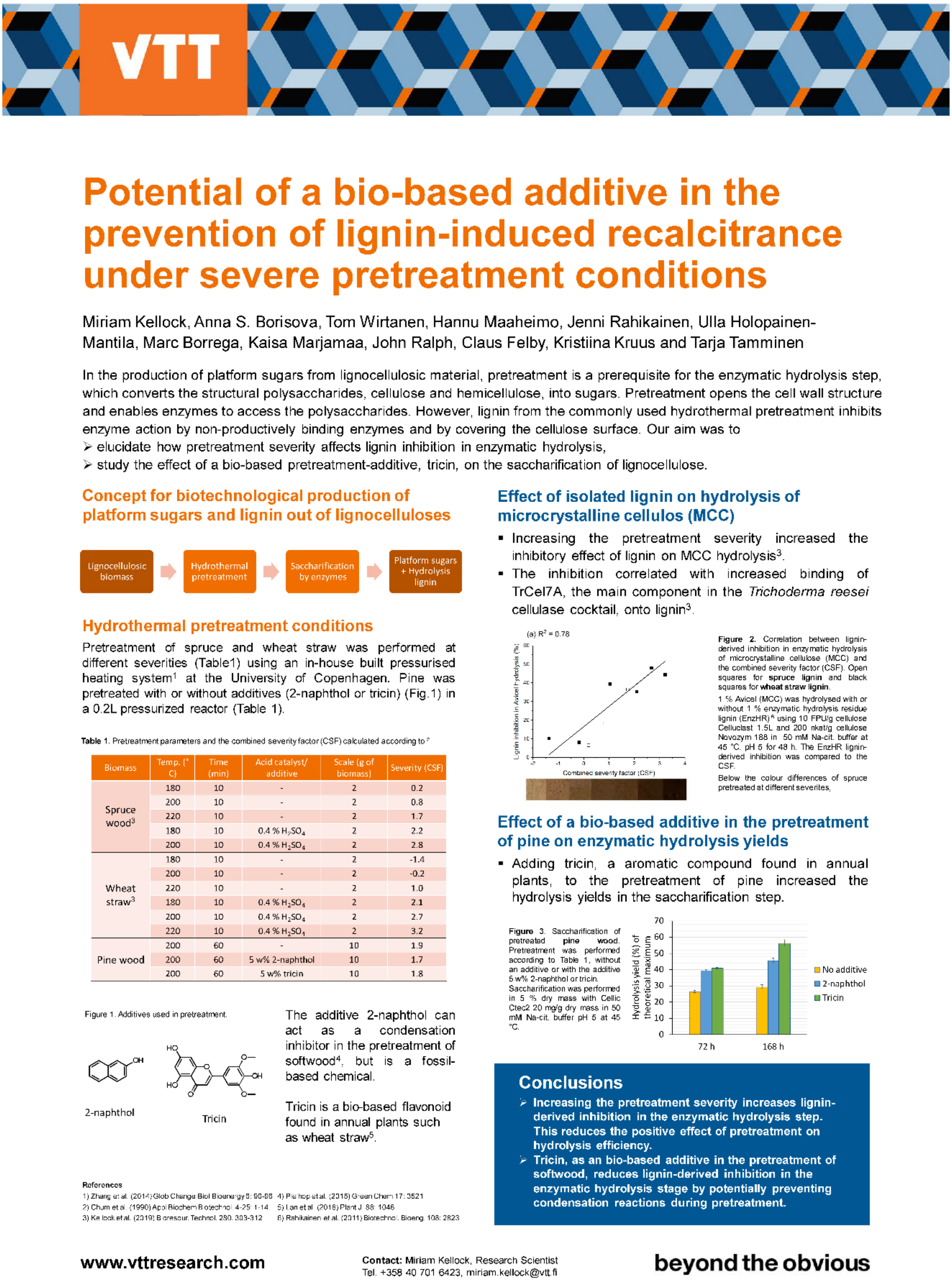
Abstract

Second-generation biorefineries converting lignocellulose to renewable fuels and chemicals require pretreatment to open the cell wall structure and enable enzymes to access polysaccharides. However, lignin from the commonly used hydrothermal pretreatments can restrict enzyme action by covering the cellulose surface and non-productively binding enzymes. The resulting residual lignin typically contains a relatively high amount of carbohydrates, restricting its solubility and utilisation in applications. The aim of this work was to elucidate how pretreatment severity affects lignin inhibition in enzymatic hydrolysis and how lignin from softwood and herbaceous plants changes during pretreatment. Understanding these factors can aid in developing pretreatments with simultaneously improved hydrolysis yields and improved applicability of the hydrolysis lignin.

Spruce wood and wheat straw were hydrothermally pretreated at 180-220 °C with or without an acid catalyst. Increasing the pretreatment severity increased the inhibitory effect of lignin in Avicel hydrolysis. The inhibition arose from increased non-productive binding of enzymes to lignin. For both raw materials, the levels of aryl ether bonds decreased as pretreatment severity increased. Furthermore, for wheat straw lignin, a decrease in the amount of hydroxycinnamates and tricin was observed. Several publications have reported that introducing additives, such as 2-naphthol, to pretreatment can reduce lignin condensation resulting in improved hydrolysis yields. The flavonoid tricin, found in herbaceous plant, has an electron-rich aromatic ring structure similar to 2-naphthol. Softwood pine was hydrothermally pretreated at 200 °C with the additives tricin or 2-naphthol. Pretreatment with tricin resulted in higher sugar yields in the following enzymatic hydrolysis step when compared with the

pretreatment with 2-naphthol. This may be due to modifications made to the lignin structure during pretreatment, which could be promising for both saccharification and lignin valorization pathways.



Potential of a bio-based additive in the prevention of lignin-induced recalcitrance under severe pretreatment conditions

Miriam Kellock, Anna S. Borisova, Tom Wirtanen, Hannu Maaheimo, Jenni Rahikainen, Ulla Holopainen-Mantila, Marc Borrega, Kaisa Marjamaa, John Ralph, Claus Felby, Kristiina Kruus and Tarja Tamminen

In the production of platform sugars from lignocellulosic material, pretreatment is a prerequisite for the enzymatic hydrolysis step, which converts the structural polysaccharides, cellulose and hemicellulose, into sugars. Pretreatment opens the cell wall structure and enables enzymes to access the polysaccharides. However, lignin from the commonly used hydrothermal pretreatment inhibits enzyme action by non-productively binding enzymes and by covering the cellulose surface. Our aim was to

- elucidate how pretreatment severity affects lignin inhibition in enzymatic hydrolysis,
- study the effect of a bio-based pretreatment-additive, tricin, on the saccharification of lignocellulose.

Concept for biotechnological production of platform sugars and lignin out of lignocelluloses

Lignocellulosic biomass → Hydrothermal pretreatment → Saccharification by enzymes → Platform sugars + Hydrolysis lignin

Hydrothermal pretreatment conditions

Pretreatment of spruce and wheat straw was performed at different severities (Table1) using an in-house built pressurised heating system[1] at the University of Copenhagen. Pine was pretreated with or without additives (2-naphthol or tricin) (Fig.1) in a 0.2L pressurized reactor (Table 1).

Table 1. Pretreatment parameters and the combined severity factor (CSF) calculated according to [2]

Biomass	Temp. (° C)	Time (min)	Acid catalyst/ additive	Scale (g of biomass)	Severity (CSF)
Spruce wood[3]	180	10	-	2	0.2
	200	10	-	2	0.8
	220	10	-	2	1.7
	180	10	0.4 % H_2SO_4	2	2.2
	200	10	0.4 % H_2SO_4	2	2.8
Wheat straw[3]	180	10	-	2	-1.4
	200	10	-	2	-0.2
	220	10	-	2	1.0
	180	10	0.4 % H_2SO_4	2	2.1
	200	10	0.4 % H_2SO_4	2	2.7
	220	10	0.4 % H_2SO_4	2	3.2
Pine wood	200	60	-	10	1.9
	200	60	5 w% 2-naphthol	10	1.7
	200	60	5 w% tricin	10	1.8

Figure 1. Additives used in pretreatment.

The additive 2-naphthol can act as a condensation inhibitor in the pretreatment of softwood[4], but is a fossil-based chemical.

Tricin is a bio-based flavonoid found in annual plants such as wheat straw[5].

Effect of isolated lignin on hydrolysis of microcrystalline cellulos (MCC)

- Increasing the pretreatment severity increased the inhibitory effect of lignin on MCC hydrolysis[3].
- The inhibition correlated with increased binding of TrCel7A, the main component in the *Trichoderma reesei* cellulase cocktail, onto lignin[3].

Figure 2. Correlation between lignin-derived inhibition in enzymatic hydrolysis of microcrystalline cellulose (MCC) and the combined severity factor (CSF). Open squares for **spruce lignin** and black squares for **wheat straw lignin**.

1 % Avicel (MCC) was hydrolysed with or without 1 % enzymatic hydrolysis residue lignin (EnzHR)[6] using 10 FPU/g cellulose Celluclast 1.5L and 200 nkat/g cellulose Novozym 188 in 50 mM Na-cit. buffer at 45 °C. pH 5 for 48 h. The EnzHR lignin-derived inhibition was compared to the CSF.

Below the colour differences of spruce pretreated at different severites,

Effect of a bio-based additive in the pretreatment of pine on enzymatic hydrolysis yields

- Adding tricin, a aromatic compound found in annual plants, to the pretreatment of pine increased the hydrolysis yields in the saccharification step.

Figure 3. Saccharification of pretreated **pine wood**. Pretreatment was performed according to Table 1, without an additive or with the additive 5 w% 2-naphthol or tricin. Saccharification was performed in 5 % dry mass with Cellic Ctec2 20 mg/g dry mass in 50 mM Na-cit. buffer pH 5 at 45 °C.

Conclusions

- **Increasing the pretreatment severity increases lignin-derived inhibition in the enzymatic hydrolysis step. This reduces the positive effect of pretreatment on hydrolysis efficiency.**
- **Tricin, as an bio-based additive in the pretreatment of softwood, reduces lignin-derived inhibition in the enzymatic hydrolysis stage by potentially preventing condensation reactions during pretreatment.**

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beyond the obvious

Enzymatic Upgrading of AqSO Biorefinery Cellolignins for High Value Applications

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Abstract

Production of high-value chemicals and materials through plant biorefinery is a green alternative to the current petroleum-based industry. One of promising directions in a new biorefinery approach is the focus on ligno-carbohydrate functional hybrids (LCFH) to take advantage of the synergism between lignin and carbohydrates in specific high-value applications. AquaSolv Omni (AqSO) Biorefinery developed in our group is a green cost-efficient integrated biorefinery allowing for engineering of the reaction products in a wide range of composition, structure and properties. In addition, further engineering of LCFHs is possible combining AqSO Biorefinery with other traditional operations, such as enzymatic hydrolysis. However, in stick contrast to the traditional biorefineries, the goal of the enzymatic hydrolysis is the engineering of the resulted Cellolignins (lignins containing residual cellulose) rather than optimization of sugars/bioethanol yields. Depending on the AqSO process severity and enzyme (cellulase cocktail) load, LCFHs with lignin contents from 10 to 90 %, different lignin structures and properties were obtained. They were tested in replacement of phenol-formaldehyde (PF) wood adhesive using the automatic bond evaluation systems (ABES). It was demonstrated that the Cellolignins containing 20–40 % residual cellulose enhanced PF performance. The promising results of these application tests demonstrated a high potential of creating precursors for value-added products on the base of the AqSO biorefinery approach.

Introduction

One of promising directions in a new biorefinery approach is the focus on ligno-carbohydrate functional hybrids (LCFH) to take advantage of the synergism between lignin and carbohydrates in specific high-value applications (Balakshin et al., 2021). In that regard, our group recently reported a new biorefinery concept, called AquaSolv Omni (AqSO) Biorefinery, which allows for efficient engineering of lignin and lignin carbohydrate functional hybrids (LCFHs) in a wide range of composition, structure and properties (Tarasov et al., 2022).

Enzymatic hydrolysis is a valuable opportunity to covert carbohydrates into fermentable sugars (Jørgensen et al., 2007). However, in contrast to the established biorefineries, the goal of the enzymatic modification in our approach is the engineering of the resulted Cellolignins (lignins containing residual cellulose) rather than optimization of monomeric sugars yields. Thus, the goal of the current research is to engineer Cellolignins of different compositions, structures and properties via process variables and test the resulted products in high-value applications.

We herein report that by utilizing enzymatic hydrolysis to tune the composition of solids we can showcase that the synergism between lignin and carbohydrates can positively affect application such as partial replacement of PF resins in wood adhesives, carbon fiber and carbon foam production.

Experimental

Hydrothermal treatment (HTT)

Birch sawdust was treated according to recently reported AqSO process (Tarasov et al., 2022), where the hydrothermal treatment severity was expressed via P-factor value. Solids obtained after biomass treatments at P-factors of 500, 1000 and 2000 were labeled as S500, S1000 and S2000, respectively.

Enzymatic hydrolysis (EH)

Enzymatic hydrolysis of the HTT solids was performed with CTec2 (60 mg protein g−1 cellulose) cellulase (Novozymes). Enzyme was added to the solids suspension in a buffer solution (pH 5.1) and mixed with proportions of 20, 40 and 100 mg per 1 g per dry biomass material. The reaction mixture was placed into an incubator with constant mixing mode at 50 °C for 48 hours. After 48 hours the samples are centrifuged in Eppendorf centrifuge 5804 R at 10 000 rpm for 40 min to separate the solids and the supernatant. Next, solution is collected and analyzed for monomeric carbohydrates content, whereas solids are washed with 1 % acetic acid (2 times with 50 ml), water and freeze-dried until constant weight.

HTT solids produced at P-factor 500, 1000 and 2000 obtained after enzymatic hydrolysis with enzyme load of 20 mg/g were labeled as ES500-20, ES1000-20 and ES2000-20, respectively. The rest of the solids with enzyme load of 10, 40 and 100 were labelled in the same manner.

Automatic bond evaluation system (ABES)

An industrial liquid phenol formaldehyde (PF) resin (Prefere 14J021, Dynea Chemicals Oy) was used as supplied and changed by replacing 30 % of the solids content with enzymatic solids. For ABES test, 0.5 g of phenol-formaldehyde resin was mixed with 0.110 ml of 8 % NaOH solution (to compensate pH decrease after ES addition). Afterwards 0.105 g ES were added and mixture thoroughly stirred to form a homogeneous glue. For the test, 2B veneers (Silver birch, Betula pendula Roth) were selected and veneer strips (20 × 117 mm^2) were cut. The resins (0.011 - 0.012 g) were applied to a 5 x 20 mm^2 area at one end of the veneer strips. The veneer-resin assembly was placed in the ABES machine (Adhesive Evaluation Systems, Incorporated) after adhesive application and hot pressing began immediately.

Results and discussion

The focus of this work was to evaluate the effect of AqSO conditions and enzyme load on the lignin-carbohydrates ratio of ES and their adhesive performance in partial replacement (30 %) of commercial PF resin.

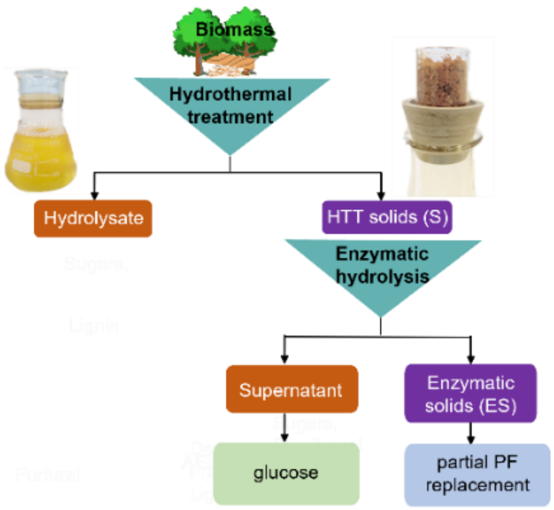

Figure 75. Experimental approach.

Lignin content in enzymatic solids

The results regarding content of lignin in ES are summarized in Figure 76 An increase of enzyme load leads to higher lignin content in the residual solids. For example, there was a significant increase in the lignin content (ES1000) of residual solids (73.5 %) at enzyme load of 40 mg/g, meanwhile the lignin content at enzyme load of 10 mg/g constitutes for almost half of the value (42.9 %). Specifically, the enzyme load of 40 mg/g in different severity factors (P-factor) gives various materials with different lignin to carbohydrates ratio. The lignin content in the sample ES500-40 is around 45 %, whereas the same enzyme load at more severe pretreatment (ES2000-40) produces a sample with almost twice as much lignin in composition, roughly 95 %. Around 70 % to 30% lignin to carbohydrates ratio is obtained in the sample ES1000-40. According to Figure 76, it is possible to reach a tunable lignin content by altering the enzyme load and P-factors. Thus, it is possible to utilize these samples in a broad application area considering the residual cellulose content. Practically, the enzymatic modification is used to produce material with different compositions, structure, and properties via process variables.

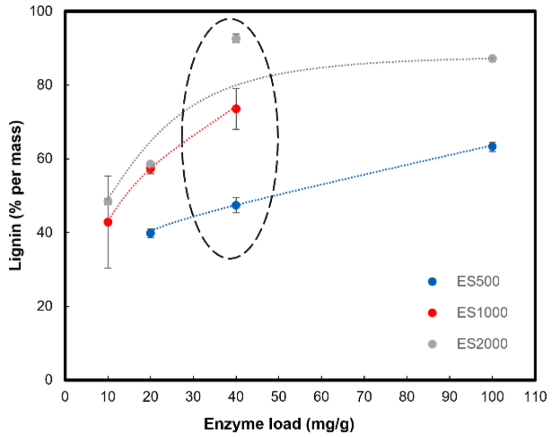

Figure 76. The effect of the enzyme load on the lignin content in enzymatic solids.

In Figure 77, the effect of the enzyme load on glucan yield in the solution is shown. As expected, the higher the enzyme load the higher the glucan yield in the solution: going from 10 mg/g to 40 mg/g enzyme load (ES2000) the glucan yield is increased by a factor of almost 2. Similar tendency is witnessed with P-factor 1000, where This is consistent with an increase on the accessibility for the enzymes to the solids as the P-factor increases (Borrega et al., 2013). At P-factor 2000 almost all glucan is hydrolyzed leaving pure lignin in the solids.

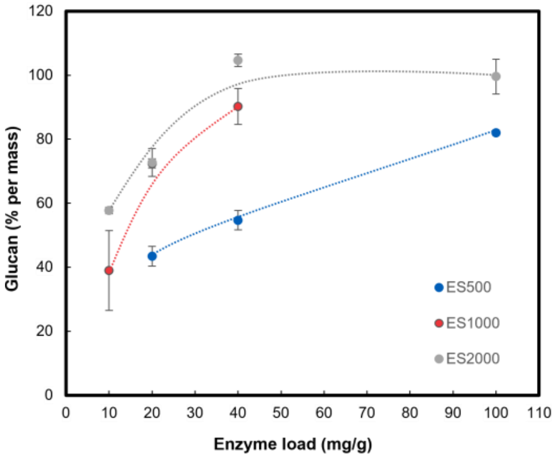

Figure 77. The effect of the enzyme load (10, 20, 40 and 100 mg/g) on the total glucan yield in enzymatic solids ES500, ES1000 and ES2000.

Application

Among the enzymatic solids obtained after enzymatic hydrolysis, specific samples were selected (*Table 24*) to be tested on ABES as a LCFH-PF blend, based on recently published results (Balakshin et al., 2021). It was found that CelloLignins with 50-20 % of residual cellulose were suitable in partial replacement of commercial PF wood adhesives.

Table 24. Samples selected for application as a replacement of PF wood adhesives.

Substrates	P-factor	Enzyme load, mg/g	Lignin, %	Carbohydrates, %
ES1000-40	1000	40	67	24
ES2000-20	2000	20	58	38

ABES tests was used to evaluate enzymatic solids for direct substitution of PF adhesives. The approach was used to track the development of adhesive bond strength as a function of temperature. It was evident (Figure 78) that the ES-PF blends showed a very similar performance as compared to the commercial PF control considering the experimental error.

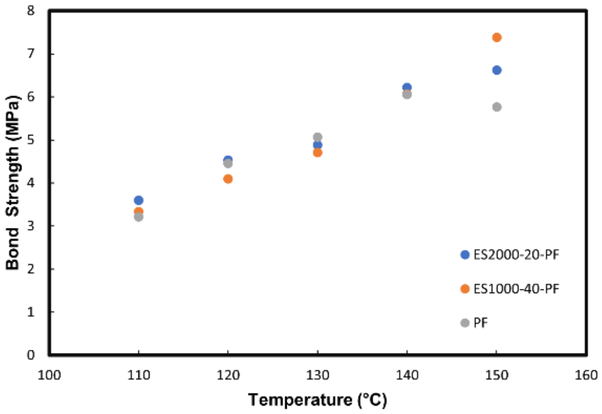

Figure 78. The effect of temperature on the bond strength of ES- PF blends.

Conclusions

Coupling AqSO process with enzymatic hydrolysis was successfully performed. By varying the P-factor and the enzyme load we were able to tune the lignin:carbohydrates ratio in a wide range (from 10 % to 90 %) present in the enzymatically treated solids. The most interesting spot for adhesive application was found in the range 50-70 %, obtained with an enzyme load of 20; 40 mg/g and P-factor of 1000; 2000. These samples were tested as replacement of PF wood adhesives. Generally, 30 % of a commercial PF resin was possible to replace with enzymatic solids. The process severity value and enzyme load lead to a slight increase to the bond. The results showed that the bonding strength of the LCH-PF blend was very close to that of the control PF resin indicating good potential of using AqSO LCH in replacing PF wood adhesive.

Acknowledgements

Academy of Finland for research grant (341596).

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Enzymatic upgrading of AqSO biorefinery Cellolignins for high value applications

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Introduction

One of promising directions in a new biorefinery approach is the focus on ligno-carbohydrate functional hybrids (LCFH) to take advantage of the synergism between lignin and carbohydrates in specific high-value applications. AquaSolv Omni (AqSO) Biorefinery developed in our group is a green integrated biorefinery allowing for efficient engineering of lignin and LCFHs in a wide range of composition, structure and properties (Tarasov et al., 2022). the goal of the enzymatic modification is the engineering of the resulted Cellolignins (lignins containing residual cellulose) rather than optimization of sugars yields.

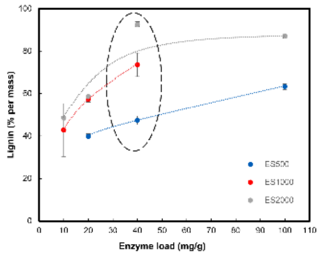
Methodology

- ✓ Phenol-formaldehyde resin is added
- ✓ ES-PF blend is tested on ABES

Results and Discussion

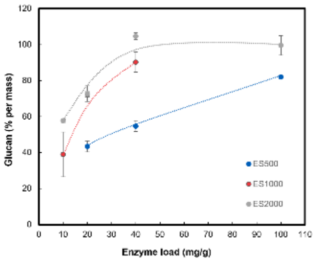
The effect of the enzyme load on the total lignin content in enzymatic solids

- ✓ Tunable lignin content
- ✓ Different material (different lignin:carbs ratio)
- ✓ At high enzyme load and high P-factor → almost pure lignin was obtained



The effect of the enzyme load on the total glucan yield in enzymatic solids

- ✓ High enzyme load and P-factor → complete glucose removal
- ✓ Carbohydrates yield at enzyme load 40 mg/g and 100mg/g differs insignificantly



Conclusion

- ✓ Depending on the AqSO process severity and enzyme (cellulase cocktail) load, LCFHs with lignin contents from 10 to 90%, different lignin structures and properties were obtained.
- ✓ They were tested in replacement of phenol-formaldehyde (PF) wood adhesive using the automatic bond evaluation systems (ABES).
- ✓ It was demonstrated that the Cellolignins containing 20–40% residual cellulose enhanced PF performance.
- ✓ The Cellolignins were also successfully tested in carbon foam applications.
- ✓ Their use in Ioncell carbon fibers is in process.
- ✓ The promising results of these application tests demonstrated a high potential of creating precursors for value-added products on the base of the AqSO biorefinery approach.

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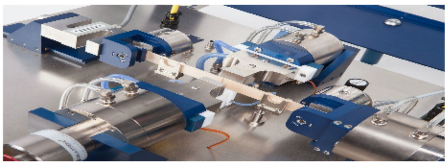
Applications

Recent studies (Balakshin et al., 2021) showed the good potential of lignocellulosic hybrids produced by a biorefinery process in replacement of PF wood adhesives. Therefore, among the enzymatic solids obtained after enzymatic hydrolysis, specific samples were selected to be tested on ABES as a LCFH-PF blend, based on recently published results (Tarasov et al., 2022).

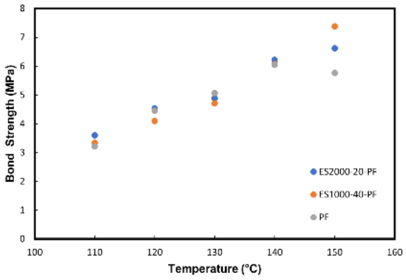
P-factor	Enzyme load, mg/g	Lignin, %	Carbohydrates, %	Label
1000	40	67	24	ES1000-40
2000	20	58	38	ES2000-20

- ➢ 50-70% lignin in composition
- ➢ T=110, 120, 130, 140, 150 °C
- ➢ Cure time 50 sec



Enzymatic solids as phenol-formaldehyde resin filler

- ✓ **30% of the resin** replaced with enzymatic solids
- ✓ A slight increase in bond strength



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Engineered Lignin Products

UV Spectrophotometry of Lignin Revisited - Exploring Solvents with Low Toxicity

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Abstract

UV spectrophotometry of lignin is a potent technique, as it can be used for both qualitative and quantitative analysis. For example, the absorptivity at 280 nm has been suggested to estimate the lignin content in solutions (Lin & Dence, 2012). Ionization difference spectrometry can further be used to quantify the content of phenolic hydroxyl groups. Such analysis may additionally provide information about the chemistry of the monomeric units, delineating types such as condensed and conjugated structures (Goldmann et al., 2017). To study the technical lignin by UV spectrophotometry, solvation in a good solvent is paramount. Traditional approaches use solvents such as formamide, 2-methoxyethanol or dioxane (Lin & Dence, 2012). These solvents exhibit carcinogenic or other detrimental effects on the human health. We therefore tested the solubility of technical lignin in solvents with low toxicity and studied their suitability for UV spectrophotometry. Several solvent systems were identified, such as dimethyl sulfoxide (DMSO), ethylene glycol, and blends of propylene carbonate with alcohols. For ionization difference spectrophotometry, blends of DMSO with water or ethanol were found the most practical. Our results hence facilitate UV spectrophotometry of technical lignin in a safe and sound manner.

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UV Spectrophotometry of Lignin Revisited – Exploring Solvents with Low Toxicity

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Introduction

UV-spectrophotometry of lignin is a potent technique, as it can be used for various types of analysis:

- Quantitative measurements of lignin concentration and purity.
- Determination of phenolic hydroxyl groups by ionization difference spectrophotometry.
- Bathochromic and hypochromic shifts can yield qualitative information on monomeric configuration and addition/substitution reactions on the phenolic moieties.

Established procedures utilize solvents such as formamide, 2-methoxyethanol or dioxane, which exhibit carcinogenicity and other detrimental effects on the human health. We therefore explored alternative solvents that are more benign.

Lignin Solubility in Organic Solvents

A screening with 30 different solvents was conducted to assess the solubility of lignin. The Hansen Solubility Parameters were calculated according to [1].

Lignin Sample	Dispersion forces (δ_d) in MPa$^{0.5}$	Polar interactions (δ_p) in MPa$^{0.5}$	Hydrogen bonding (δ_h) in MPa$^{0.5}$
Softwood Kraft Lignin (SKL1)	17.6	12.6	15.95
Arkansas/Straw Soda Lignin (ASL1)	17.6	9.1	15.95

Using the equation below, the distance Ra between the polymer (δ_{i1}) and the solvent (δ_{i2}) can be determined to test their compatibility ($Ra < R_0$) [2].

$$Ra^2 = 4(\delta_{d2} - \delta_{d1})^2 + \left(\delta_{p2} - \delta_{p1}\right)^2 + (\delta_{h2} - \delta_{h1})^2$$

As our results show, the UV absorptivity at 280 nm correlates with the distance Ra, i.e., a lower distance yielding a higher absorptivity (better solvent system).

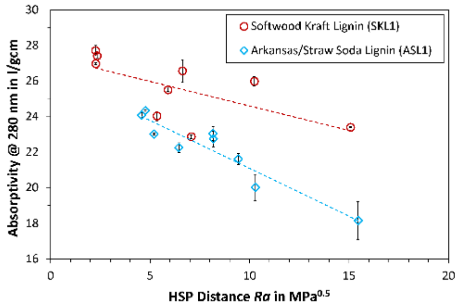

Figure 1. Relationship between distance Ra and absorptivity at 280 nm for various solvent. [3]

UV-Spectrophotometry of Lignin

It is well known that the botanical origin and the separation process greatly affect the absorbance spectra of lignin. In addition, our research shows that the solvent system also has a large effect.

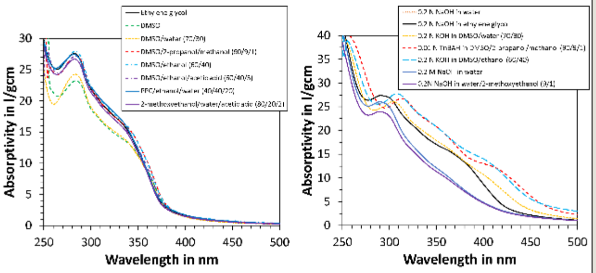

Figure 2. Absorptivity of softwood Kraft lignin in neutral (left) or alkali solvents (right). [3]

As can be seen in see Figure 2, alkali solvents induced both hyperchromic and bathochromic shifts at varying intensity. In case of neutral solvents, the qualitative changes to the UV spectrum were less pronounced. Here, the absorptivity was greater for better solvents (hyperchromic shift), as illustrated in Figure 1.

Phenolic Hydroxyl Groups

The ionization difference spectrum was calculated by subtracting the neutral from the alkali spectrum [4]. Based on this, the phenolic hydroxyl groups can be calculated according to published procedures [4-6]. A method comparison with non-aqueous potentiometric titration and FTIR revealed the following:

- The procedure by Chen et al. [6] calculated phenolic OH values that were in best agreement with other techniques.
- The solvents ethylene glycol or DMSO/water (70/30) showed the greatest potential.

Conclusion

Various solvents and solvent-blends were identified, which are benign and well-suited for UV spectrophotometry of lignin. For measuring neutral UV spectra, solvents based on DMSO, ethylene glycol, DMSO/ethanol blends, or propylene carbonate/ethanol/water blends showed good potential. Ethylene glycol or DMSO/water are furthermore recommended for recording alkali spectra.

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Engineered Lignin Products

Customized Catalytic Hydropyrolysis of Biomass to High-Quality Bio-Oil Suitable for Co-Processing in FCC Refining Unit

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Abstract

This study aims to investigate the critical elements of the biomass ex-situ catalytic hydropyrolysis concept to improve the quality of pyrolysis oil (bio-oil) for further co-processing in an FCC refining unit. Generally, the high oxygen and low hydrogen contents of biomass result in a bio-oil with low quality, necessitating its upgrading which can be performed as integrated in the pyrolysis process via in-situ or ex-situ configuration. In this work, the quality of stem wood-derived pyrolyzates (500 °C) was improved via ex-situ catalytic hydropyrolysis (400 °C) using a bench-scale drop tube furnace pyrolyzer, and then the produced bio-oil was co-processed with fossil oil using a lab-scale FCC unit (525 °C). Catalytic hydropyrolysis of stem wood was carried out using different metal-acid catalysts, such as Ni/HZSM-5, Ni/HBeta, Mo/TiO_2, and Pt/TiO_2 at atmospheric pressure. FCC runs were performed using Spent FCC catalyst and conventional fossil FCC feedstock co-fed with stem wood-derived bio-oil in a fluidized bed reactor. Co-feeding the non-upgraded bio-oil with fossil oil into the FCC unit increased the coke yield and decreased the yield of gasoline/naphta, indicating that bio-oil needs to be upgraded for further co-processing in the FCC unit. Experimental results showed that different catalysts significantly affected the products composition and yield; Ni based catalysts were strongly active tending to generate a high yield of gas, while Mo and Pt based catalysts seemed better for production of liquid with improved quality. The quality of bio-oil was improved by reducing the formation of reactive oxygenates through the atmospheric catalytic hydropyrolysis process. The composition of oil obtained from hydropyrolysis also showed that the yield of phenols and aromatic hydrocarbons was relatively improved.

CUSTOMIZED CATALYTIC HYDROPYROLYSIS OF BIOMASS TO HIGH-QUALITY BIO-OIL SUITABLE FOR CO-PROCESSING IN FCC REFINING UNIT

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[1]


INTRODUCTION

The 2050 global target of reaching negative CO_2 emissions necessitates a gradual transition to renewable fuels in the transport sector. In Sweden, one potential way to reach this target is to utilize the forest residual products (biomass) and convert them into transport fuels. So far, thermochemical technique of pyrolysis has been vastly and efficiently used for biomass conversion into the energy-valued product of pyrolysis oil. However, the high oxygen and low hydrogen contents of biomass result in a pyrolysis oil with low heating value, hindering the direct application of this oil as transportation fuel. Therefore, upgrading of the pyrolysis oil is needed before considering it as a fuel in the current transportation infrastructure. In one way, the quality of pyrolysis oil can be improved by integrating the pyrolysis process with a catalytic upgrading system. The catalyst can be used in both in-situ and ex-situ configurations, naming the whole process as in-situ pyrolysis and ex-situ pyrolysis, respectively [2]. The ex-situ configuration has the potential of optimizing the catalytic operation section as well as regenerating/reusing the catalyst, which is economically defensible. Besides the application of catalyst in the biomass pyrolysis process, introducing hydrogen into the system (hydropyrolysis process) enhances the hydrogen content of the hydrocarbon pool of the pyrolysis intermediates, causing the deoxygenation of the O-containing pyrolyzates to valuable chemicals in the range of transport fuel.

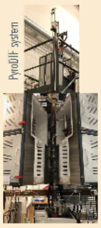
01 TECHNOLOGY

This study aims to investigate the critical elements of the biomass ex-situ catalytic hydropyrolysis concept to improve the quality of pyrolysis oil (bio-oil) for further co-processing in an FCC refining unit.

Hence, the quality of stem wood-derived pyrolyzates was improved via ex-situ catalytic hydropyrolysis using a bench-scale drop tube furnace pyrolyzer (PyroDTF). The produced bio-oil was co-processed with fossil oil using a lab-scale FCC unit.

Catalytic hydropyrolysis of stem wood was carried out using different metal-acid catalysts, such as 5Ni/HZSM-5 (5 wt% Ni), 5Ni/HBeta (5 wt% Ni), $7Mo/TiO_2$ (7 wt% Mo), $10Mo/TiO_2$ (10 wt% Mo), and $7Pt/TiO_2$ (7 wt% Pt) at atmospheric pressure. These metal-acid bifunctional catalysts, containing strong hydrogenation and hydrogenolysis functionalities, were selected to enhance the production of O-free compounds during the hydropyrolysis process under an atmospheric pressure of hydrogen.

FCC runs were performed using Spent FCC catalyst and conventional fossil FCC feedstock co-fed with stem wood-derived bio-oil in a fluidized bed reactor.


PyroDTF system

FCC system


MATERIALS / METHODS

Feedstock and catalysts :

Stem wood was used as feedstock in hydropyrolysis experiments. The bifunctional metal-acid catalysts of Ni/HZSM-5, Ni/HBeta, Mo/TiO_2, and Pt/TiO_2 were prepared by wet impregnation method.

Catalytic hydropyrolysis runs :

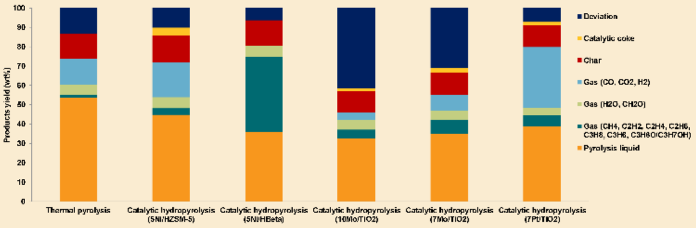
Atmospheric pressure; gas (N_2 and N_2/H_2) flow rate 15 l/min; feedstock moisture content < 5 wt%; feeding rate 60 g/h; pyrolysis temperature 500 °C; catalysis temperature 350-400 °C.

FCC runs :

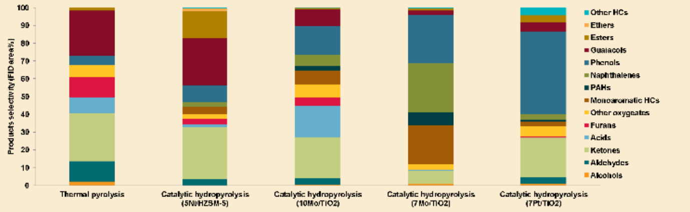
Conventional fossil FCC feedstock co-fed with a reference bio-oil and stem wood-derived thermal pyrolysis oil (20/80 w/w). Fluidized bed reactor (525 °C) and Spent FCC catalyst were used.

02 RESULTS

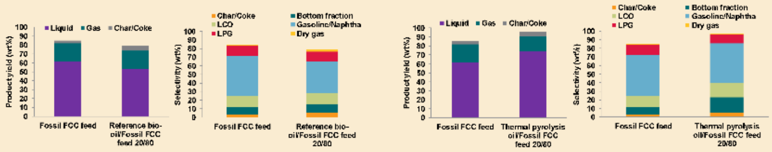
Mass balance for the pyrolysis and catalytic hydropyrolysis of stem wood



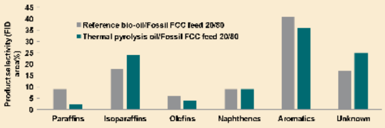
Chemical distribution in the liquid organic products obtained from stem wood pyrolysis and catalytic hydropyrolysis



Product yields for FCC tests on conventional fossil FCC feed mixed with a reference bio-oil and thermal pyrolysis oil from stem wood
***Gas**: dry gas fraction containing H_2, CO, CO_2, CH_4, C_2H_6/C_2H_4 and liquified petroleum gas (LPG) fraction containing C_3 and C_4 hydrocarbons*
***Liquid**: bottom fraction (>360 °C), light cycle oil (LCO, 221-360 °C), gasoline/naphtha (IBP-221 °C)*



Product selectivity: GC-MS/FID analysis results for the liquid products obtained from co-processing of FCC fossil oil with a reference bio-oil and stem wood thermal pyrolysis oil



03 DISCUSSION

➔ The decarbonylation and decarboxylation mechanisms, forming CO and CO_2, occurred during the stem wood hydropyrolysis over the catalysts of 5Ni/HZSM-5 and $7Pt/TiO_2$.

➔ Although CO and CO_2 were the main gas products when 5Ni/HZSM-5 and $7Pt/TiO_2$ were used as catalyst, light hydrocarbons, mainly methane, were the main products of stem wood hydropyrolysis using 5Ni/HBeta.

➔ A higher selectivity to oxygen-free compounds was acheived using the $7Mo/TiO_2$ catalyst.

➔ $7Pt/TiO_2$ and $7Mo/TiO_2$ resulted in a selective production of phenolics and phenolics together with aromatic HCs (mono- and polycyclic aromatic HCs), respectively.

➔ An increase in the bottom fraction yield was observed by co-feeding pyrolysis oil with the fossil oil in the FCC unit [3].

➔ A decrease in hydrogen formation together with an increase in char/coke and CO/CO_2 formation were observed during the FCC co-feeding runs.

➔ The liquid product of FCC runs composed of main groups of hydrocarbon compounds, including paraffins, iso-paraffins, olefins, naphthenes, and aromatics.

04 CONCLUSION

Co-feeding the non-upgraded reference bio-oil (20 wt%) with fossil oil into the FCC unit increased the coke yield and decreased the yield of gasoline/naphtha. However, co-processing of the stem wood pyrolysis oil with the fossil oil did not change the selectivity to gasoline/naphtha.

To be able to increase the bio-oil ratio for an efficient FCC co-processing, it is of great interest to improve the quality of bio-oil by deoxygenation via catalytic hydropyrolysis.

Experimental results showed that different catalysts significantly affected the products composition and yield; Ni based catalysts were strongly active tending to generate a high yield of gas (mainly light hydrocarbons), while Mo and Pt based catalysts seemed better for production of liquid with improved quality.

Carrier material of the metal catalysts also affected the results obtained from hydropyrolysis of stem wood; HBeta zeolite resulted in higher yields of gas products than HZSM5 zeolite.

The quality of bio-oil was improved by reducing the formation of reactive oxygenates through the atmospheric catalytic hydropyrolysis process.

The composition of oil obtained from hydropyrolysis also showed that the yield of phenols and aromatic hydrocarbons was relatively improved.

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High Performing Wood Based Products for Industrial Scale

Reconstructing Lignocellulose Biomass Wastes into Construction Materials

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Abstract

Wood is one of the oldest construction materials, though largely neglected in the post-industrial society. For most of the buildings build in the last century wood was substituted by steel, cement and bricks, all being non-renewable materials with heavy CO_2 footprint. While this substitution was largely driven by the fear of fire, the non-combustible materials may actually perform worse in the case of fire. To add to the benefits of wood, it is lighter and has a better strength-to-weight ratio, performs well in seismic zones and has a good predictability in case of fire.

Driven by the sustainability and low impact of wood on environment, the beginning of this century revive wood as a construction material, and particularly it was demonstrated that wood can be used for tall buildings. The bottleneck of using wood as construction material is its relative inhomogeneity and restriction of the sized of building blocks by the sizes of trees. New opportunities to use wood as a construction material in modern architecture with its demands for creative design can open when wood is brought to the processability of cement. The components of the lignocellulose biomass can be separated and brought to the nanoscale with subsequent re-combination into the processable clay-like precursor for molding or hot-pressing. The feasibility of this process is achieved due to the sustainable and cheaper procedure for nanocellulose isolation. Novel approach for lignin re-polymerization and use of hemicellulose to mediate the lignin-cellulose interaction in the composite are fundamental for wood nano-reconstruction.

Wood based construction materials

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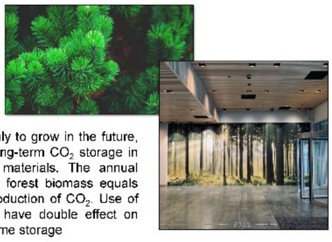
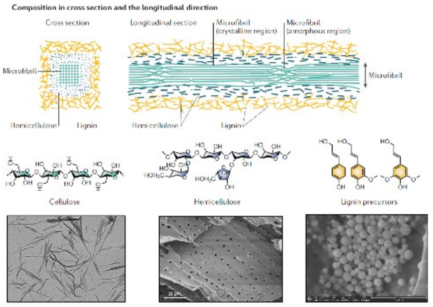
Introduction



The construction sector is a hard-to-abate CO_2 intensive sector with 8% of the CO_2-eq emissions world-wide, mainly due to the abundant use of concrete and steel.

It has large scales, that are expected only to grow in the future, and this lever can be used for useful long-term CO_2 storage in the form of wood-based construction materials. The annual transformation of atmospheric CO_2 into forest biomass equals 700 Gt and is about the net primary production of CO_2. Use of wood-based construction materials will have double effect on CO_2 – decrease the evolution and long-time storage

Wood structure

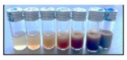


(adapted from Chen Chen et al., Nature review materials, 2020)

Wood has many advantages as a construction material: light weight, higher strength-to-weight ratio, predictable behavior in fire and good performance in seismic zones. It also has good heat and sound insulating properties granted by its anisotropy.

Wide range of wood types, from cork oak to ironwoods, fulfills broad range of properties for construction applications. This natural diversity is also a straightforward recipe to tailor the properties of wood-based materials by changing the composition of main components and the density of packing.

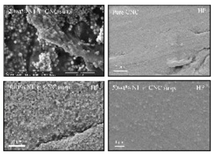
Reconstructing wood



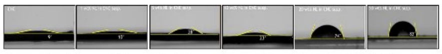
Isolating cellulose and lignin as nanoparticles allows broad range of their ratios and packing from light-weight foams to compact dense materials.

Mixing CNC and nanolignin from 1wt% to 50wt%

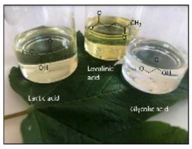
Freeze drying the colloids



Hot-pressing the dry foams

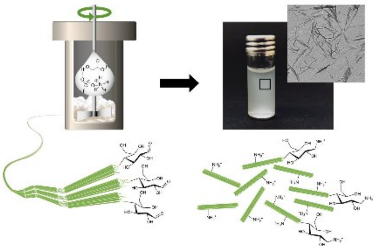


The anisotropy of the material can be achieved by directional freezing. Pressure/heat treatment introduces improved strength and consistency of the material. Increase of lignin content tailors hydrophobicity.

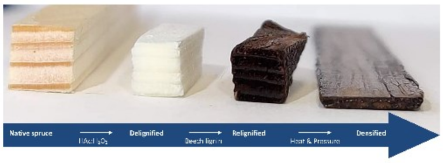


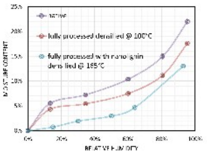
Any use of wood or biomass a source of sustainable materials requires also sustainable and safe processing procedures. Proposed method to isolate nanocellulose is based on the use of eutectics composed of organic acids that can be obtained from biomass[1-3]

CNC isolation in eutectics



Densified wood



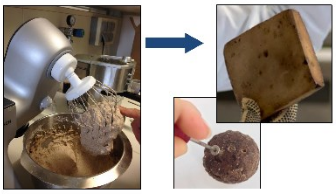


To complement the advantages properties of wood with the better moisture resistance and fire retardancy simultaneously improving mechanical properties, we liberate cellulose scaffold to enable modified lignin containing mixtures for impregnation formulations and further densification.

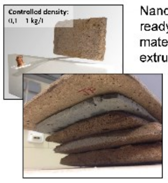
Superligna

Wood waste and low-quality wood are not valorized at their best in paper-making, construction or any other sector.

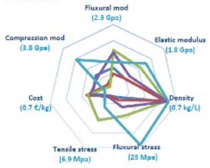
Only 30-40% of harvested wood is used in the form of boards or plank products

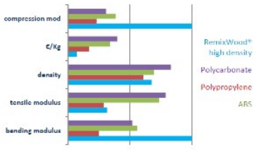


Re-mixing and processing wood



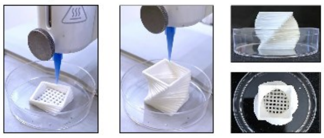
Nanostructured wood components are ready to be recombined into a clay-like material ready for hot-pressing and extrusion into competitive construction materials.





Wood for additive manufacturing

Additive manufacturing persistently penetrates industrial and biomedical applications and gains its importance in the construction. For the bio-based materials to be used as 3D printing ink certain rheology has to be achieved. We showed excellent printability of CNC-stabilized Pickering emulsions – a sustainable tool to combine water and oil-based phases in one ink[4]

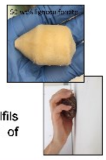


Excellent printability of the CNC-stabilized Pickering emulsions paves the way for wood-based materials into arising technology of 3D printed houses

Conclusions

Broad substitution of concreate and metal by wood and wood-based materials in construction sector has a potential to turn cities into carbon sinks and scale enough to cover primary CO_2 production

Isolation of nanocellulose in eutectic media fulfils sustainability criteria for raw starting material and use of renewable chemicals in processing



Separating main wood components in their nanoscale form opens more pathways for their recombination to result in families of materials able to satisfy demanding modern architecture, constantly increasing scales of construction sector and necessity of circular and minimal-waste technologies.

Wood-based materials propose variability of processing from traditional for construction sector extrusion and hot-pressing to newly implemented additive manufacturing.

Acknowledgements

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High Performing Wood Based Products for Industrial Scale

High-Performing Functionalized Cellulose Materials via High Consistency Processing

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Abstract

Modification and derivatization of cellulose is typically either surface or diffusion limited, many cases both. Consequently, chemists tend to perform their esterification and esterification reactions in homogeneous systems, which means utilization of waist volumes of solvents, necessary to be recycled. Unlike biotechnologists apply enzymes for cellulose hydrolysis and oxidation, which are slow surface dependent reactions due size of the enzyme proteins.

In order to intensify these and other reactions, it has become essential to overcome either diffusion limitation or formation of new reactive surfaces. Even if these are considerably different approaches, they are possible be solve markedly similarly by means of high consistency processing under intensive mixing.

Kneading and compounding technologies enable handing of high viscous fluids with high dissipative or dispersive mixing providing benefit in compact equipment, low mass inventory in process and high flexibility. Further, certain configurations with positive displacement enable continuous operation mode. The technologies are typically for other polymers, dominantly synthetic plastics and rubbers, but they are universal also for natural polymers including celluloses.

Scientifically the phenomena is reduction of reactant diffusion limitations and therefore improved reaction rates and stoichiometry efficiency. Intensive mixing enables continuous renew of reactive surfaces and prevent forming of diffusion restricted films. In this paper, we provide some examples cellulose modification in high consistency environments enabling lucrative reductions in both processing time times and reactant consumptions.

Keywords: materials, functionalized cellulose, high consistency, processing

High-performing functionalized cellulose materials via high consistency processing

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Why high consistency processing?

- High consistency with intensive mixing intensifies diffusion limited chemical reactions by preventing the formation of diffusion restricted films and enables continuous renewal of reactive surfaces. These actions are beneficial in enzymatic and chemical modification of cellulose as well as in chemical derivatization.
- Expected benefits are compact process with smaller reactors, lower chemical dosages, shorter reaction times and less waste chemicals and effluents.

High consistency allylation of chemical pulp with allylglycidyl ether (AGE)

- Chemical modification of cellulose pulp with 3-allyloxy-2-hydroxypropyl substituents (allyl) provides reactive double bonds in cellulose structure. The reactive allyl groups can be used for many kinds of post-treatments and modifications of cellulose materials such as dihydroxylation, epoxidation, coupling with thiol reagents by thiol-ene chemistry or grafting reaction (Figure 1).

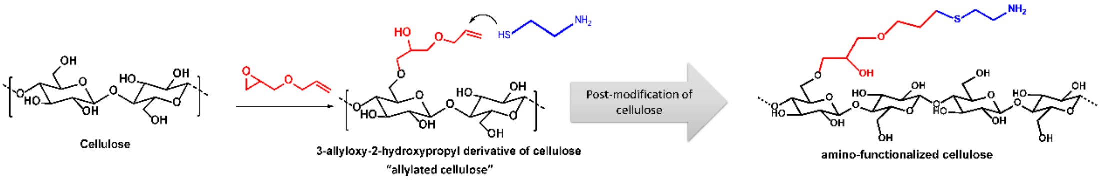

Figure 1. Example for chemical modification by allylation and then functionalization with thiol reagents such as cysteamine.

- In order to intensify allylation treatment in terms of reaction efficiency, treatment consistency was increased from LC (4-5 wt%) to HC (15-22 wt%) in tandem with decreasing chemical dosages and reaction time.
- High consistency with intensive mixing resulted higher degree of substitution (allyl) with lower chemical dosage (Figure 2). Reaction time was reduced by 20 hours Reaction efficiency become 3-6 times more efficient (Figure 3).

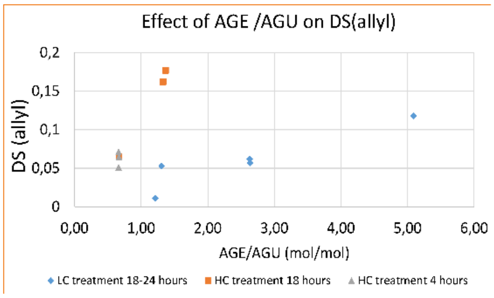

Figure 2. Influence of treatment consistency and chemical dosage on the degree of substitution.

DS, degree of substitution; AGE, allyl glycidyl ether (mol); AGU, anhydroglucose unit (mol)

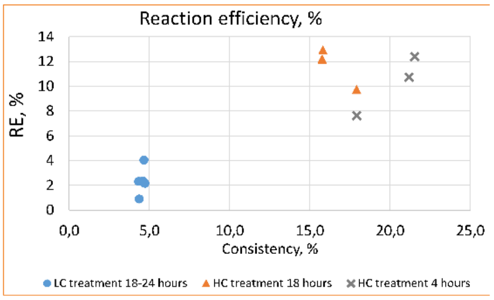

Figure 3. Influence of treatment consistency on reaction efficiency.

RE, % = DS x100% / (AGE / AGU)

Conclusion

- **High consistency with intensive mixing intensifies chemical reactions and enzymatic treatments**

- **Benefits are:**
  - **higher degree of substitution, more efficient reaction result**
  - **less chemicals / enzymes**
  - **shorter reaction times**
  - **smaller reactors**
  - **less waste chemicals and effluents**

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beyond the obvious

Purification of Organic Solvents Contaminated with Wood Extractives: a Liquid-Liquid Extraction Process Using Fully Recyclable Biomimetic Solvents

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Abstract

The production of carboxylic acids from sustainable feedstock is a rapidly developing field of research. Existing non-fossil production routes are mainly based on alcoholic, acido- and acetogenic fermentation, chemocatalytic conversion, hydrothermal treatment, or isolation from biomass hydrolysates. Reactive extraction with organic solvents is an efficient separation technique to recover carboxylic acids from such aqueous solutions. However, after thermal stripping of the carboxylic acid, non-volatile contaminations may remain in the solvent and deteriorate the process efficiency.

We show that various long chain carboxylic acids contained in wood extractives accumulate during solvent recycling of a commercial scale acetic acid extraction plant due to their lipophilic character and high boiling points. Increasing concentrations of palmitic acid decreased the partition coefficient of acetic acid between the undecane/trioctyl phosphine oxide (TOPO) solvent and aqueous acetic acid, mimicking the commercial scale biorefinery process. The extraction efficiency was found to be proportional to the amount of “free TOPO”, meaning the concentration of TOPO that is not bound by fatty acids. We show that various alkanolamines can be used to remove more than 99 % of the fatty acids contained in the biorefinery solvent in a cross current extraction. The superior capability of these amines is related to structural and physical properties. After washing the purified solvent with water or mild acid, the ability of the solvent to extract additional acetic acid is restored and amines may be recovered by distillation.

We describe a technique to purify extraction solvents used for the recovery of carboxylic acids from biomass hydrolysates or fermentation broths. Process efficiency can be increased by extraction of contaminated solvents with fully recyclable and readily biodegradable amines with close structural similarity to choline.

Purification of organic solvents contaminated with wood extractives: A liquid-liquid extraction process using fully recyclable biomimetic solvents

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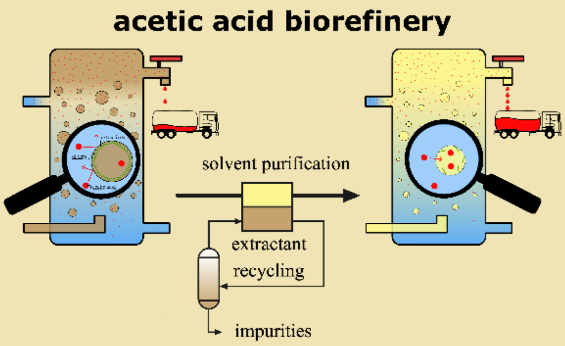
Introduction 1.

Background

Carboxylic acids are large scale chemical products and can be produced from renewable resources by chemocatalytic conversion, fermentation processes or biomass hydrolysis. In the downstream processing, reactive extraction is commonly applied to recover carboxylic acids from aqueous solutions. However, contaminations of the organic solvent may impair the process efficiency, cause fouling problems and thus need to be removed.


acetic acid biorefinery

solvent purification

extractant recycling

impurities

Objectives 2.

- characterization of a contaminated acetic acid biorefinery solvent
- quantification of impurities
- investigation of the influence on the biorefinery efficiency
- solvent purification using liquid-liquid extraction

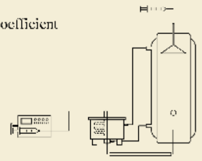
Methods 3.

Single drop extractions

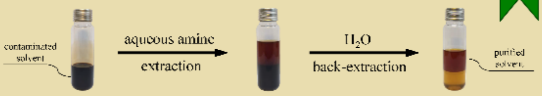
- model solutions (70 wt.% undecane, 30 wt.% TOPO + x palmitic acid)
- Influence of lipophilic acids on drop size
- influence of lipophilic acids on mass transfer coefficient

Cross-current batch extractions

- screening of aqueous extractants (inorganic & organic bases)
- multi-stage extraction & back-extraction
- optimization of extraction conditions

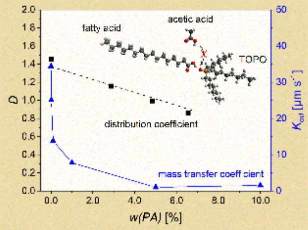


Results 4.



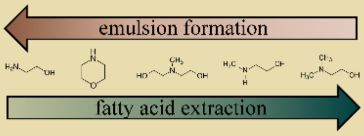
Biorefinery solvent characterization

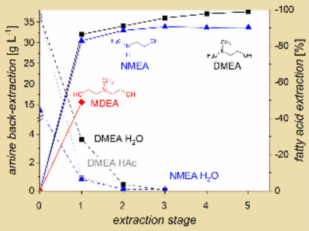
- solvent contains around 10 wt.% impurities
- high amounts of lipophilic wood extractives (especially fatty acids & resin acids)
- solid sugar degradation products



Influence of impurities on efficiency

- solid impurities cause fouling
- dissolved impurities increase drop size
- lipophilic acids bind to TOPO from solvent
- reduced distribution coefficient for acetic acid
- sharp decrease in mass transfer of acetic acid





Screening of aqueous extractants

- inorganic bases (NaOH, KOH, NH_3) inefficient
- formation of stable emulsions
- extraction efficiency follows law of matching water affinities
- chaotropic cations favour fatty acid dissolution in aqueous phase
- high extraction efficiency for alkanolamines
- basicity and steric demand also influence the extraction efficiency
- solid particles are co-extracted

Conclusions 5.

- ❖ high levels of lipophilic wood extractives identified in industrial biorefinery solvent
- ❖ fatty & resin acids decrease distribution and mass transfer coefficient of acetic acid
- ❖ LLE with aqueous amines removes lipophilic wood extractives and particles
- ❖ back-extraction with water or dilute acid removes amines from the organic phase
- ❖ DMEA removes 99% of wood extractives and is fully recyclable

Acknowledgements Financial support was provided by the Austrian government, the provinces of Lower Austria, Upper Austria, and Carinthia as well as by Lenzing AG. We also express our gratitude to the Johannes Kepler University, Linz, the University of Natural Resources and Life Sciences (BOKU), Vienna, and Lenzing AG for their in-kind contributions.

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Recovery and Characterization of Low-Molecular-Weight Lignin from Ultrafiltered Kraft Black Liquor

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Abstract

Kraft lignin is an aromatic polymer found in black liquor, a side stream of the kraft pulping industry. Usually, lignin is burned in the recovery boiler of the pulp mill as a fuel for energy generation. However, lignin has great potential as a raw material for the production of fossil-free fuels, chemicals, and materials. Membrane filtration has been studied in the last decades as a key separation method to recover lignin from black liquor. Further studies to concentrate lignin using membrane filtration are required, as well as characterization of the resulting lignin fractions for the development of molecular tailored lignin-based applications.

In the present work, nanofiltration (NF) was used to concentrate and recover the low-molecular-weight lignin obtained from the permeate of ultrafiltration of kraft black liquor. The concentration was performed using a NF090801 polymeric NF membrane (SolSep) with a molecular weight cut-off of 350 Da. A transmembrane pressure of 25 bar and 50 °C during the filtration increased the lignin content from 27 to 52 g/l, whereas a transmembrane pressure of 15 bar and 70 °C gave an increase from 18 to 45 g/l in lignin content. The lignin fraction recovered in the retentate of the NF step was analyzed by size-exclusion chromatography to ascertain the molecular weight of the lignin. Moreover, Fourier transform infrared spectroscopy and thermogravimetric analysis were carried out to evaluate the thermal properties and functionalities of the obtained fractions.

Battestini Vives, M., Abdelaziz, O., Thuvander, J., Arkell, A., Hulteberg, C., & Lipnizki, F.
Recovery and Characterization of Low-Molecular-Weight Lignin from Ultrafiltered Kraft Black Liquor

Recovery and characterization of low-molecular-weight lignin from ultrafiltered kraft black liquor

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Introduction

Kraft lignin is an aromatic polymer found in black liquor, which is usually burned in the recovery boiler for energy generation. Lignin has great potential as a raw material for the production of fossil-free fuels and chemicals. Membrane filtration is a key separation method to recover different lignin fractions.

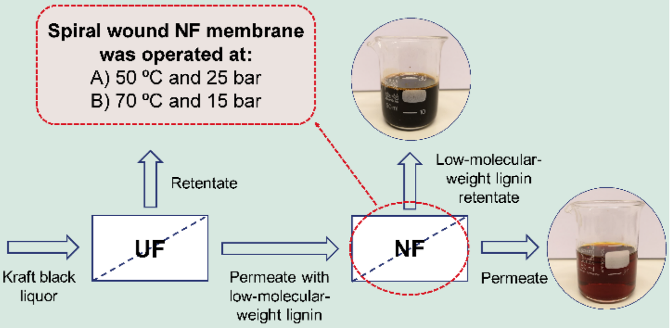
Further studies to scale up the concentration of lignin using membrane filtration are required, as well as characterization of the lignin fractions.

Aim

Concentrate ultrafiltered kraft black liquor by nanofiltration at pilot scale, and characterize the resulting lignin fractions.

Materials and methods

- The membrane used was a NF090801 (SolSep BV) in spiral wound configuration with a molecular weight cut-off of 350 Da.
- The membrane area was 1.8 m^2.
- The filtration was run at a pulp mill with a 400 L initial volume of ultrafiltered kraft black liquor.



Spiral wound NF membrane was operated at:
A) 50 ºC and 25 bar
B) 70 ºC and 15 bar

Results

- A volume reduction (VR) of 80% and a lignin retention of 82% was achieved for both conditions *(Figure 1)*.
- Condition *B* had a higher average flux, 47 L/m^{2}h, compared to *A*, 35 L/m^{2}h.
- As expected, the lignin content increased, due to the feed being concentrated by recycling it over the membrane *(Table 1)*.

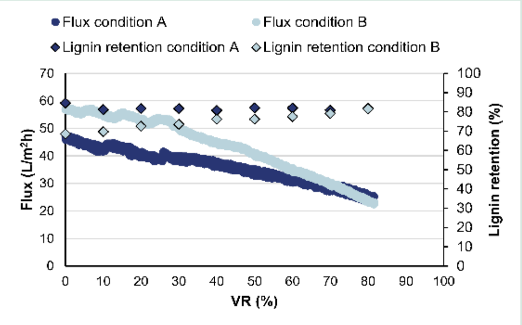


Figure 1: Flux and lignin retention vs VR for spiral wound membrane at conditions *A* and *B*.

Table 1: Lignin content for initial and final VR at conditions *A* and *B*.

Lignin content	VR 0%	VR 80%
Condition A	27 g/L	52 g/L
Condition B	18 g/L	45 g/L

- Lignin was separated between 100 to 1000 Da, and 1000 Da to 10 kDa, with condition *B* showing a more clear division compared to condition *A (Figure 2)*.

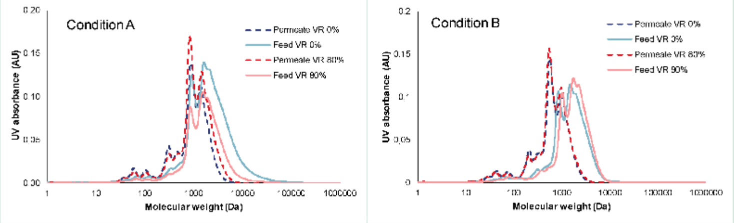


Figure 2: Molecular weight distribution for the permeate and feed samples taken at VR 0% and VR 80% at conditions *A* and *B*.

Conclusions

- The spiral wound NF membrane used in this study can successfully separate the low-molecular-weight lignin fractions.
- Lignin was similarly concentrated under both operating conditions due to a high membrane retention.

This research was possible thanks to the funding provided by the Swedish Energy Agency.

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Microbial Expansin Related Proteins for Improved Enzymatic Action for Conversion of Lignocellulose to Platform Sugars

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Abstract

Cost effective enzymatic deconstruction of cellulosic materials for the production of renewable fuels and chemicals is challenged by the limited accessibility of enzymes to cellulose substrates. Recently identified loosenin-like proteins (PcaLOOLs from Phanerochaete carnosa) can promote amorphogenesis and disrupt noncovalent binding between cellulose fibrils, thus promoting cell wall loosening and increasing surface accessibility for enzymatic hydrolysis. Like other microbial expansin-related proteins characterized to date, loosenins do not display hydrolytic activity; instead, they reportedly boost hydrolysis by cellulolytic enzymes although the impact of expansin-related proteins on cellulolytic activity is substrate dependent (Liu et al., 2015).

Herein, the impact of four PcaLOOLs on the activity of different cellulolytic enzymes was evaluated using a lignocellulosic substrate from softwood fiber. The PcaLOOLs were heterologously produced in *Pichia pastoris* in shake-flask and 5-L bioreactor systems, and then purified by affinity chromatography. Notably, the bioreactor production increased PcaLOOL yield over 10-times. Each PcaLOOL was used to pretreat the lignocellulosic material prior to the addition of cellulolytic enzyme; alternatively, each PcaLOOL was added directly with the cellulolytic enzyme to the lignocellulosic substrate. The release of soluble sugars was quantified at regular time points over 24-hours using the 4-hydroxybenzoic acid hydrazide (PAHBAH) assay and by high-performance anion exchange chromatography/pulsed amperometric detection (HPAEC-PAD). The hydrolysis reactions were performed at 40 °C and 50 °C to evaluate the impact of temperature on the boosting performance of PcaLOOLs. Briefly, all PcaLOOLs increased the enzymatic release of soluble sugars from the lignocellulosic substrate. On-going HPAEC analyses will evaluate the impact of PcaLOOLs on the profile of sugars released from the lignocellulosic substrate. In addition to lignocellulose deconstruction, the potential of PcaLOOLs to promote fiber defibrillation will be investigated.

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Microbial expansin related proteins for improved enzymatic action processing of lignocelluloses

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[b]Solid Biomass Refining Business Development and Production, St1 Oy, Finland
[c]Department of Chemical Engineering and Applied Chemistry, University of Toronto, Canada

What are expansins and how are they produced?

- Expansins are low molecular weight proteins found in plants , bacteria and fungi[1]
- Loosenins, resembling the N-terminal domain of plant expansins[2] ,are reported to weaken cellulose networks through a hydrolytic mode of action
- The *Pca*LOOLs studied herein were selected from transcriptome analysis of *P. carnosa*[3,5] and were expressed in *Pichia pastoris*

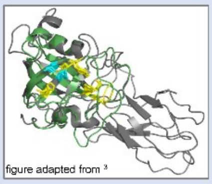
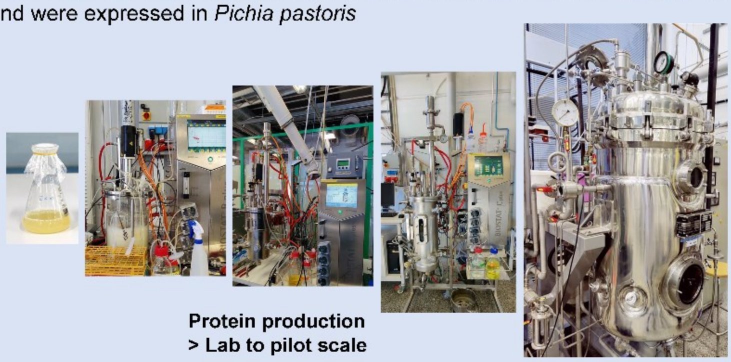


figure adapted from [3]



Protein production
> Lab to pilot scale

- To obtain fermentable sugars in lignocellulose, accessibility to cellulose remains a challenge
- To improve the efficiency of enzymes and development of cost-effective 'greener' processes for obtaining sugars, PcaLOOLs can be used

Action of PcaLOOLs on lignocellulose processing

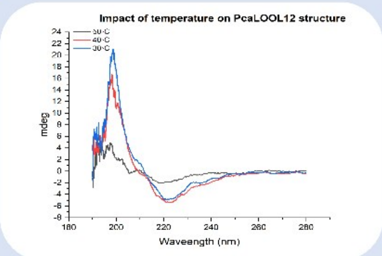


Figure 1. β sheet rich protein folding for PcaLOOl12 secondary structure at different temperatures at a loading of 0.3mg/ml at 25°C

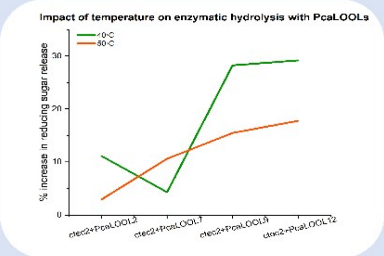


Figure 2. Effect of temperature on activity of PcaLOOLs during enzymatic hydrolysis.

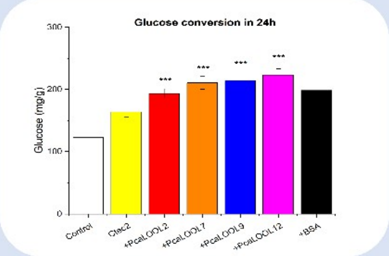
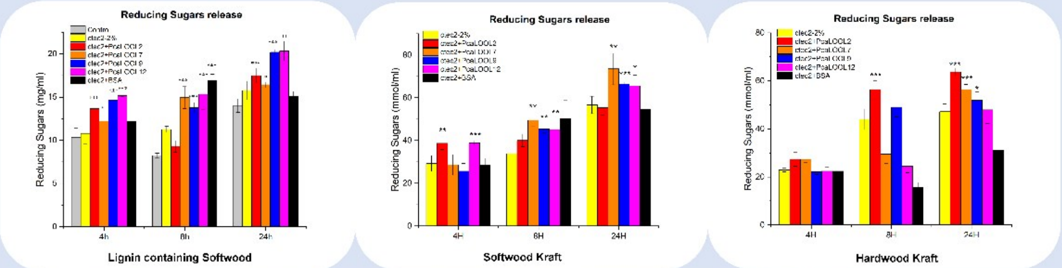


Figure 3. Glucose release (using HPAEC-PAD) from pretreated softwood by Ctec2 with and without the addition of *Pca*LOOL.



Lignin containing Softwood

Softwood Kraft

Hardwood Kraft

Figure 4. Total reducing sugars release from different pulps by Ctec2 with and without the addition of *Pca*LOOL measured using PAHBAH assay after 4h, 8h and 24h of reaction.
All reading were measured in triplicates

Conclusions

- All PcaLOOLs boost the glucose release from lignocellulose substrates
- Lowering the temperature boosted the sugar release, thus leading to cost reduction
- PcaLOOLs might help in increasing the cellulose accessibility by binding to lignin

Further work

- Study impact of PcaLOOLs on fiber morphology and pore size distribution
- Investigate the potential of PcaLOOLs to boost chitinases
- Evaluate the impact of PcaLOOLs on fungal substrates

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This work made use of the Aalto University's Bio-economy facilities. This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 964764.

Low Emission Biorefineries and Side-Stream Valorization

Adaptive Bayesian Optimization for Alkaline Oxidation of Birch Wood

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Abstract

Bayesian optimization provides a tool for adaptive design of experiments when the goal is to improve process performance. The aim is to use the information from earlier experiments to focus on experimental conditions that are likely to improve process performance. Bayesian optimization uses a non-parametric model which is updated based on adaptive sampling of the experimental domain. This combines modelling and optimization into a single process and can potentially reduce the number of experiments which are required to reach optimal process conditions.

Bayesian optimization was used to optimize the conditions of the AlkOx process, which is a two-stage biorefinery concept based on prehydrolysis and alkaline oxidation. The process utilizes biomass efficiently and is sulphur free. The conditions can be adjusted for different biomass materials and fraction properties. The focus was on the alkaline oxidation stage using prehydrolysed and defibrated birch wood as feed material. The oxidation was performed in Na_2CO_3 solution in a 43 L reactor under pressurized oxygen using different temperatures, reaction times and liquor to wood ratios. The aim was to find the process conditions which maximized cellulose yield constrained by defined target ranges for kappa number (0-6.57) and pulp viscosity (400-600 ml/g).

Five predefined experiments were performed, after which the experiments suggested by Bayesian optimization were initialized. Based on 10 iterations, maximum cellulose yield quickly converged at 53-54 % with target kappa number and pulp viscosity. The results were compared with a traditional approach using a Box Behnken design with 15 experiments. The two methods produced comparable results and indicated similar process conditions for fulfilling the experimental objective. Bayesian optimization could thus be a useful tool for optimizing a range of biorefinery processes efficiently and reliably

Adaptive Bayesian optimization for alkaline oxidation of birch wood

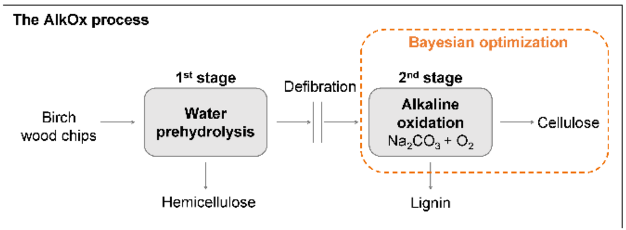
Hanna Hörhammer, Hannu Rummukainen, Jari Sirviö, Jorma Kilpi, Pirkko Kuusela, Mikko Mäkelä
VTT, FINLAND

Introduction

Bayesian optimization provides a tool for adaptive design of experiments (DOE) when the goal is to improve process performance. The aim is to use the information from earlier experiments to focus on experimental conditions that are likely to improve process performance. Bayesian optimization uses a non-parametric model which is updated based on adaptive sampling of the experimental domain. This combines modelling and optimization into a single process and can potentially reduce the number of experiments which are required to reach optimal process conditions. Bayesian optimization was used to optimize the conditions of the AlkOx process, which is a two-stage biorefinery concept based on prehydrolysis and alkaline oxidation. The focus was on the alkaline oxidation stage using prehydrolysed and defibrated birch wood as feed material.

Experimental

The oxidation was performed in alkaline solution in a 43 L reactor under pressurized oxygen using different temperatures, reaction times and liquor to wood ratios. Five predefined experiments were performed, after which the experiments suggested by Bayesian optimization were initialized. For comparison a traditional DOE with 15 experiments was conducted. The aim was to find the process conditions which maximized cellulose yield constrained by defined target ranges for kappa number (0-7) and pulp viscosity (400-600 mL/g).



The AlkOx process

Birch wood chips

1st stage

Water prehydrolysis

Hemicellulose

Defibration

Bayesian optimization

2nd stage

Alkaline oxidation
$Na_2CO_3 + O_2$

Lignin

Cellulose

Fig 1. Adaptive Bayesian optimization was used to maximize cellulose yield in the AlkOx biorefinery based on alkaline oxidation of birch wood.

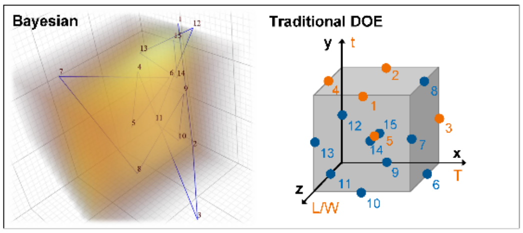


Fig 2. In Bayesian optimization the model suggests the next trial point, whereas in the traditional DOE the trial points were defined in advance.

Results

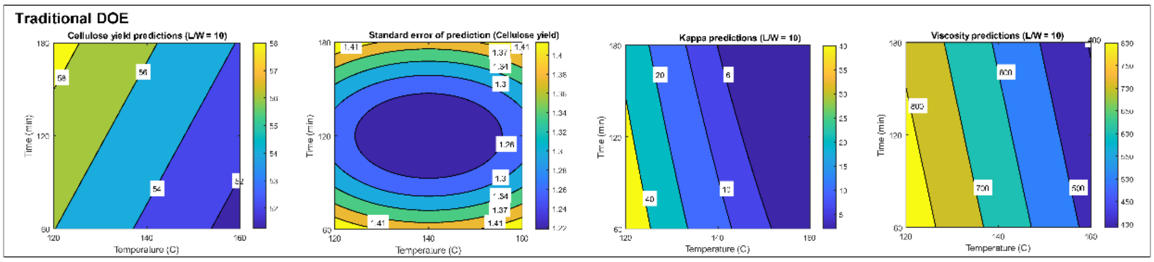


Fig 3. Cellulose yield, kappa number and viscosity model using traditional DOE with 15 experiments (L/W=10).

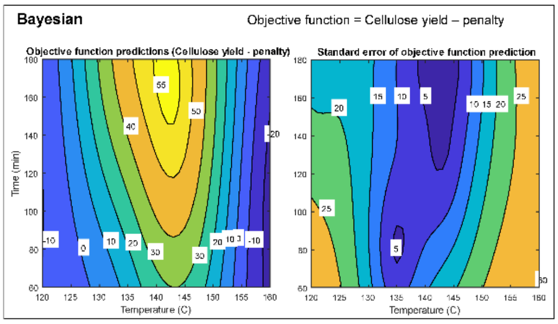


Fig 4. Bayesian optimization response surface after 15 experiments (L/W=10).

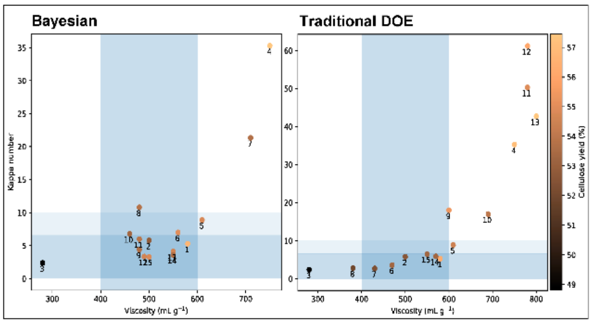


Fig 5. Cellulose yield, kappa number and viscosity of birch pulps.

Conclusions

Based on 10 Bayesian iterations, maximum cellulose yield quickly converged at 53-54% with target kappa number and pulp viscosity. The Bayesian and the traditional DOE methods produced comparable results and indicated similar process conditions for fulfilling the experimental objective. However, in Bayesian optimization a large number of trials were close to optimal conditions providing more accurate knowledge for optimizing a range of biorefinery processes efficiently and reliably.

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beyond the obvious

Low Emission Biorefineries and Side-Stream Valorization

Production of Water-Soluble Carbohydrates from Aspen Wood Flour with Hydrogen Chloride Gas

Antti Topias Kilpinen, and Eero Kontturi

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Abstract

The overall aim of this study was to optimize the reaction conditions for concentrated acid hydrolysis of aspen wood flour by employing anhydrous hydrogen chloride gas to produce fermentable sugars. Gas hydrolysis with HCl was conducted both with and without temperature control during the hydrolysis under relatively low pressure of 1 bar. Process parameters for HCl gas hydrolysis included the moisture content of aspen wood flour (0.7-50 %) and reaction time under pressure (30 minutes to 24 hours). Temperature control during gas hydrolysis was used to prevent excess degradation of C5-sugars during the gas application phase via cooling in ice bath and to speed up the hydrolysis reaction during the last 10 minutes via heating to 50 °C. This enabled the hydrolysis to proceed in comparably mild temperature conditions, resulting in higher yields of water-soluble carbohydrates. In addition, liquid-phase hydrolysis with concentrated hydrochloric acid was conducted in concentrations of 32-42 % and 15 minutes to 24 hours reaction times for comparison with gas-phase process. Highest yield for water-soluble carbohydrates from aspen wood flour (92 % of available glucan and 91 % of available xylan) was achieved with temperature-controlled gas hydrolysis using 50 % moisture content and 2 h total reaction time, which is in line with previous research and comparable to hydrolysis with concentrated (42 %) hydrochloric acid.

Introduction

Anhydrous HCl gas has been utilized for concentrated acid hydrolysis to break down lignocellulosic biomass into fermentable sugars with high yields (>80 %) in various laboratory and pilot scale trials. (Blanch et al., 2011; Wenzl 1970; Higgins & Ho 1982; Kauko 1921) However, in previous studies the used HCl gas pressure has either been relatively high (5–42 bars) (Sharkov et al., 1971; Antonoplis et al., 1983; Wenzl 1970) or the wet biomass has been merely exposed to HCl gas without pressurizing in fluidized bed reactor (Hawley et al., 1983; Wenzl 1970; Higgins & Ho 1982) or blown through the hydrolysis feedstock in a blow through reactor (Higgins & Ho 1982).

In this study, wood flour from aspen (Populus Tremula) was hydrolyzed both with concentrated hydrochloric acid and gas-phase HCl by employing the gas hydrolysis reactor used by Pääkkönen et al., in 2018. The aim is to find optimal parameters to produce fermentable sugars using the relatively low HCl gas pressure of 1 bar.

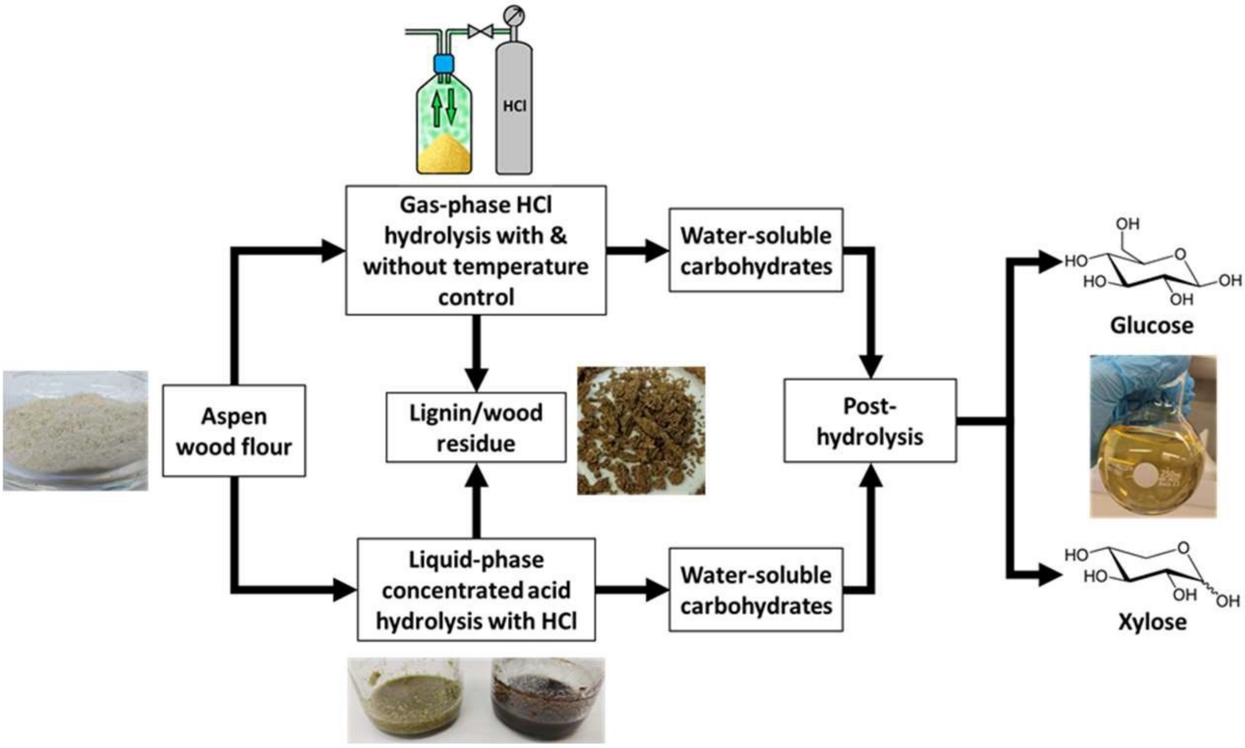

Figure 79. Visual abstract

Experimental

Hydrochloric acid stock solutions in concentrations of 32 % and 36.1 % were purchased from VWR. Aspen (*Populus Tremula*) wood chips were provided by Avantium and milled with Wiley mill M02 through a 1.9 mm screen. Reactor used by Pääkkönen et al., in 2018 was utilized for gas hydrolysis and for the concentration of hydrochloric acid to 39 % and 42 %.

Anhydrous HCl gas hydrolysis was conducted both with and without temperature control during the hydrolysis under the relatively low pressure of 1 bar. Process parameters for HCl gas hydrolysis included the moisture content of aspen wood flour (0.7-50 %) and reaction time under pressure (30 minutes, 2 h, 6 h, & 24 h). Temperature control during gas hydrolysis was used to prevent excess degradation of C5-sugars during the gas application phase via cooling in ice bath and to speed up the hydrolysis reaction during the last 10 minutes via heating to 50 °C. Liquid- phase hydrolysis with concentrated hydrochloric acid was conducted in concentrations of 32 %, 36 %, 39 % and 42 % and reaction times of 15 min, 30 min, 1 h, 2 h, 4 h, 6 h, 8 h, 16 h and 24 h for comparison with gas-phase process.

Hydrolyzed carbohydrates in hydrolysis filtrates and carbohydrate composition of aspen were quantified according to analytical methods NREL/TP-510-42618 and NREL/TP-510-42623 by employing high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) under the Dionex ICS-3000 system (Sunnyvale, CA, USA). MilliQ water was used as the mobile phase at a flow rate of 0.38 mL/min with a CarboPac PA20 column. Furfural and hydroxymethylfurfural (HMF) were determined from hydrolysis filtrates via high-performance liquid chromatography (HPLC) by using Dionex UltiMate 3000 HPLC (Dionex, Sunnyvale, CA, USA) equipment outfitted with ultraviolet (UV) detector and Rezex ROA-Organic Acid column (Phenomenex). Sulfuric acid solution (0.0025 mol/l) was used as the eluent at a flow rate of 0.5 ml/min. The column temperature was 55 °C. Furfural and HMF concentrations in the liquid samples were determined by the UV detector at wavelengths of 210 and 280 nm.

Results and discussion

Hydrolysis with concentrated hydrochloric acid

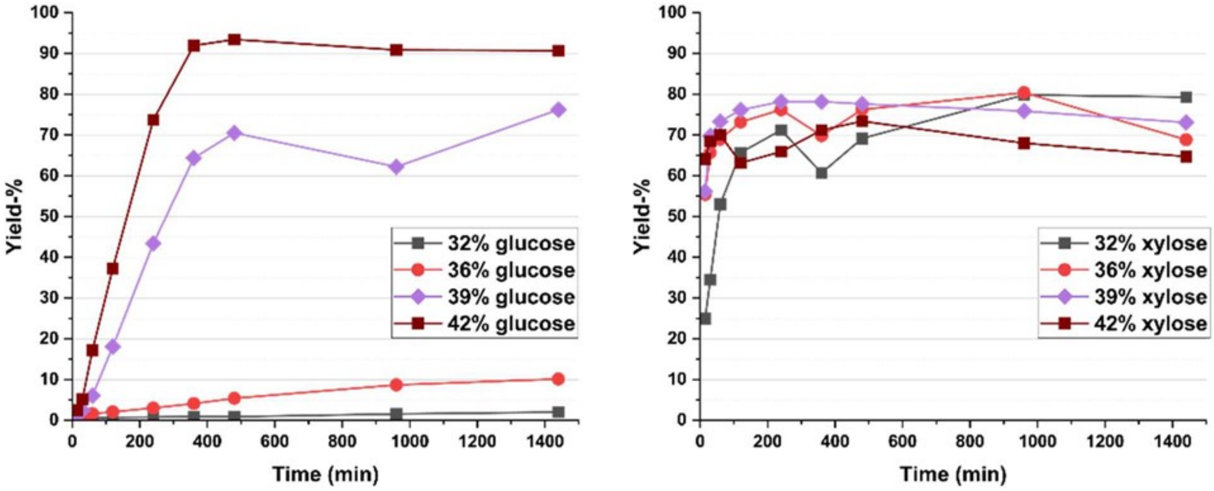

Figure 80. Yields of glucose and xylose (water-soluble carbohydrates) from aspen wood flour in hydrolysis with liquid hydrochloric acid at different acid concentrations over time in 21 °C.

From the Figure 80 it can be observed that with HCl concentrations of 32 % and 36 % mainly the hemicellulose fraction is hydrolyzed along with some degradation of disordered regions of cellulose. When the HCl concentration is increased to 39 %, around 70 % of the cellulose is hydrolyzed to water-soluble oligosaccharides after 6 hours. After the HCl concentration is further increased to 42 %, the yield of glucose rises to over 90 % after 6 h. This indicates that almost all crystalline cellulose has dissolved and broken down to water-soluble mono- and oligosaccharides during the hydrolysis.

From the yield of xylose, we can see that with all employed acid concentrations the maximum yield of xylose eventually plateaus to 60-80 % after 2 hours of hydrolysis. This might indicate that in such high acid concentrations xylose degrades to furfural and other degradation products as the hydrolysis progresses. However, according to HPLC results, the amount of furfurals formed during the concentrated acid hydrolysis was quite negligible unless they turn immediately to humins.

Hydrolysis with anhydrous HCl gas

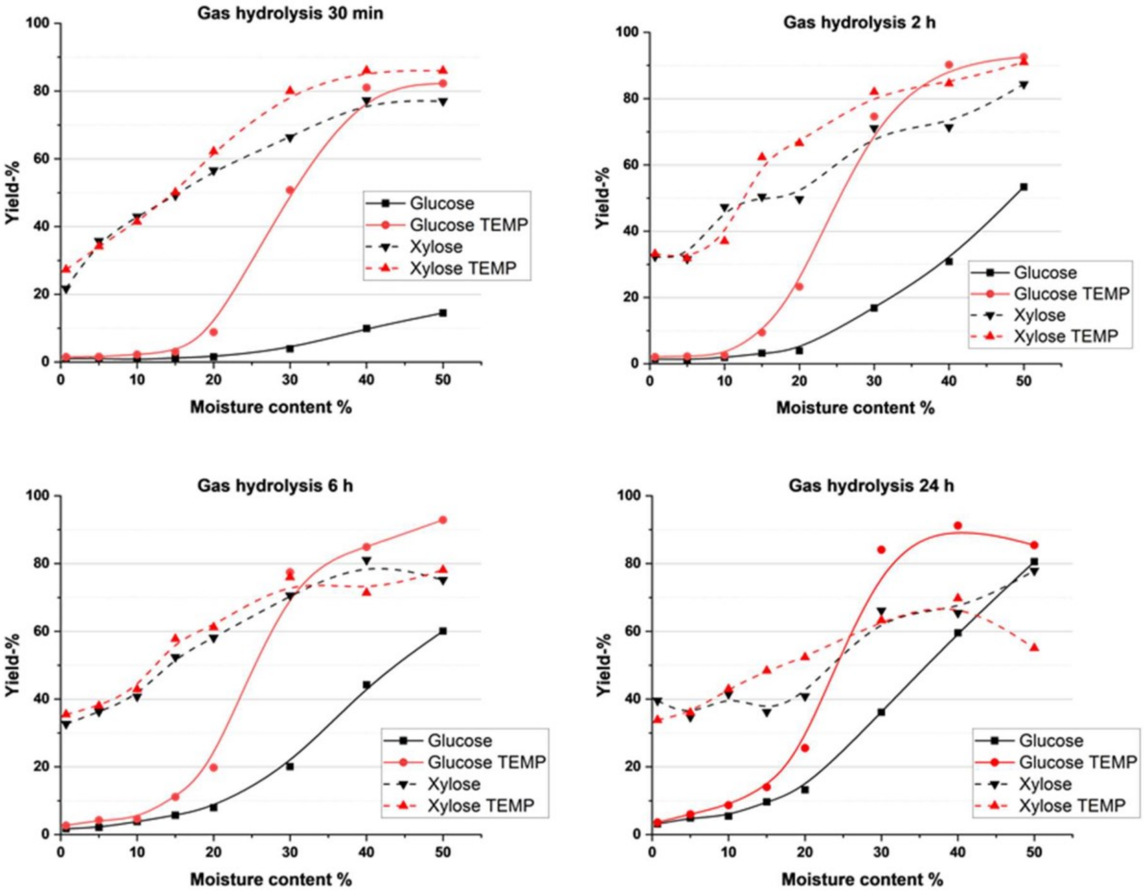

Figure 81. Yields of glucose and xylose from aspen wood flour in gas hydrolysis. TEMP refers to gas hydrolysis with temperature control.

Conclusions

It was possible to gain high yields of water-soluble carbohydrates from aspen wood flour both with liquid and gaseous HCl hydrolyses. Temperature-controlled gas hydrolysis produced high yields for both xylose and glucose without pre-hydrolysis step, even with relatively low pressure of 1 bar. The highest water-soluble carbohydrate yield from available xylan and glucan were 91 % and 92 % respectively. These yields were achieved with temperature-controlled gas hydrolysis at 50 % moisture content using 2 h reaction time. Results are in line with previous research employing anhydrous HCl gas for hydrolysis.

Acknowledgements

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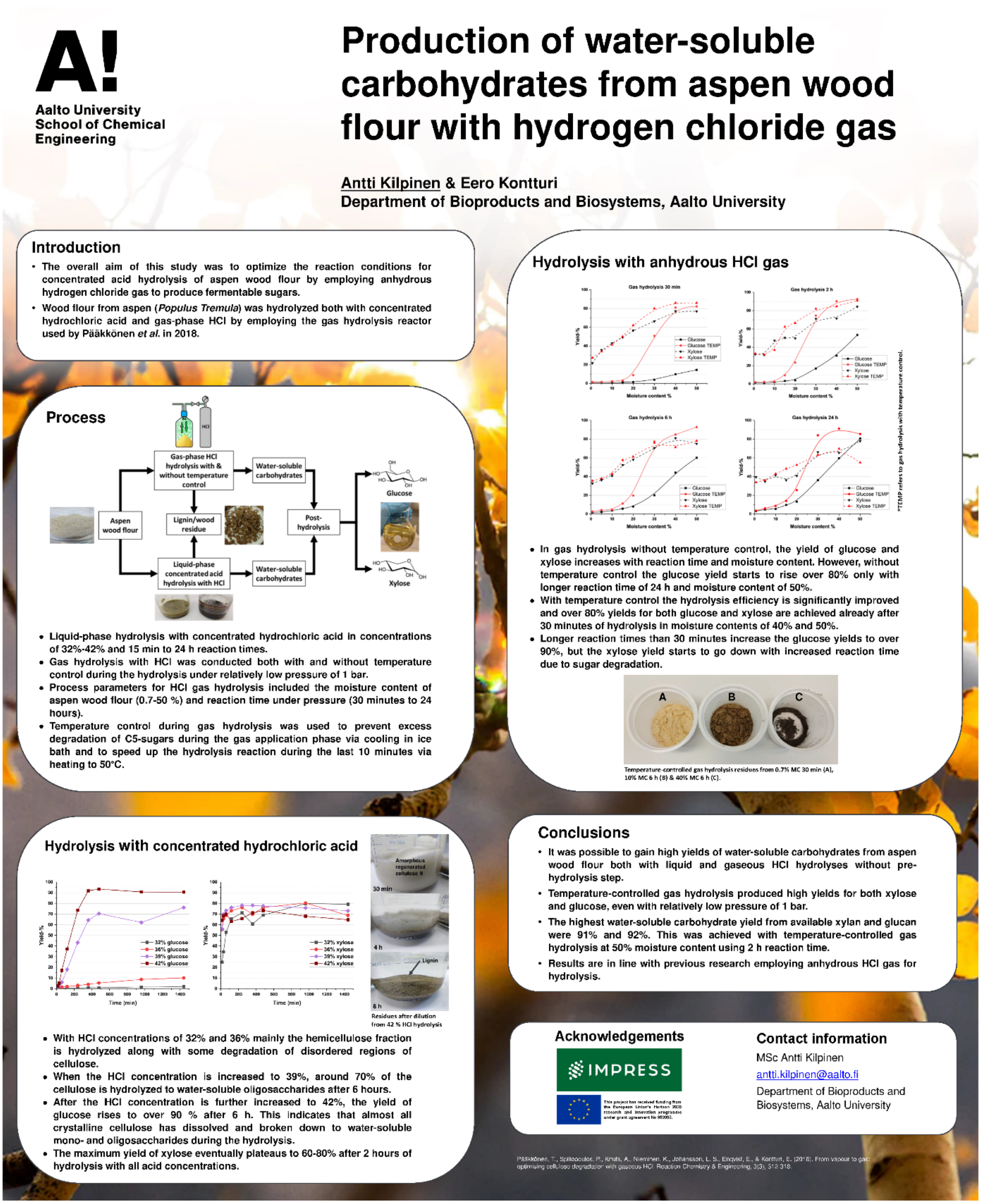

Aalto University
School of Chemical Engineering

Production of water-soluble carbohydrates from aspen wood flour with hydrogen chloride gas

Antti Kilpinen & **Eero Kontturi**
Department of Bioproducts and Biosystems, Aalto University

Introduction

- The overall aim of this study was to optimize the reaction conditions for concentrated acid hydrolysis of aspen wood flour by employing anhydrous hydrogen chloride gas to produce fermentable sugars.
- Wood flour from aspen (*Populus Tremula*) was hydrolyzed both with concentrated hydrochloric acid and gas-phase HCl by employing the gas hydrolysis reactor used by Pääkkönen *et al.* in 2018.

Process

- Liquid-phase hydrolysis with concentrated hydrochloric acid in concentrations of 32%-42% and 15 min to 24 h reaction times.
- Gas hydrolysis with HCl was conducted both with and without temperature control during the hydrolysis under relatively low pressure of 1 bar.
- Process parameters for HCl gas hydrolysis included the moisture content of aspen wood flour (0.7-50 %) and reaction time under pressure (30 minutes to 24 hours).
- Temperature control during gas hydrolysis was used to prevent excess degradation of C5-sugars during the gas application phase via cooling in ice bath and to speed up the hydrolysis reaction during the last 10 minutes via heating to 50°C.

Hydrolysis with concentrated hydrochloric acid

Residues after dilution from 42 % HCl hydrolysis

- With HCl concentrations of 32% and 36% mainly the hemicellulose fraction is hydrolyzed along with some degradation of disordered regions of cellulose.
- When the HCl concentration is increased to 39%, around 70% of the cellulose is hydrolyzed to water-soluble oligosaccharides after 6 hours.
- After the HCl concentration is further increased to 42%, the yield of glucose rises to over 90 % after 6 h. This indicates that almost all crystalline cellulose has dissolved and broken down to water-soluble mono- and oligosaccharides during the hydrolysis.
- The maximum yield of xylose eventually plateaus to 60-80% after 2 hours of hydrolysis with all acid concentrations.

Hydrolysis with anhydrous HCl gas

- In gas hydrolysis without temperature control, the yield of glucose and xylose increases with reaction time and moisture content. However, without temperature control the glucose yield starts to rise over 80% only with longer reaction time of 24 h and moisture content of 50%.
- With temperature control the hydrolysis efficiency is significantly improved and over 80% yields for both glucose and xylose are achieved already after 30 minutes of hydrolysis in moisture contents of 40% and 50%.
- Longer reaction times than 30 minutes increase the glucose yields to over 90%, but the xylose yield starts to go down with increased reaction time due to sugar degradation.

Temperature-controlled gas hydrolysis residues from 0.7% MC 30 min (A), 10% MC 6 h (B) & 40% MC 6 h (C).

Conclusions

- It was possible to gain high yields of water-soluble carbohydrates from aspen wood flour both with liquid and gaseous HCl hydrolyses without pre-hydrolysis step.
- Temperature-controlled gas hydrolysis produced high yields for both xylose and glucose, even with relatively low pressure of 1 bar.
- The highest water-soluble carbohydrate yield from available xylan and glucan were 91% and 92%. This was achieved with temperature-controlled gas hydrolysis at 50% moisture content using 2 h reaction time.
- Results are in line with previous research employing anhydrous HCl gas for hydrolysis.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869993.

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Hydrodeoxygenation of Black Liquor HTL-Oil Model Compounds in Supercritical Water

Sari Rautiainen[1], Felix Hyppönen[1], Tyko Viertiö[1], Juha Lehtonen[1], Luděk Meca[2], and Pavel Kukula[2]

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Corresponding author: Sari Rautiainen <sari.rautiainen@vtt.fi>

Abstract

A very promising and currently underutilized abundant non-food feedstock for biofuels is black liquor (BL), a side stream of chemical pulping industry. The lignin and other organics present in black liquor contain circa half of the energy of wood chips, and currently most of it is burnt in pulp mills. EU project Black Liquor to Fuel (BL2F) aims to develop a feasible route from black liquor to drop-in biofuels for aviation and shipping. In the first step, black liquor is treated under hydrothermal conditions to separate the cooking chemicals and produce HTL-oil from the organics. The HTL-oil is then further upgraded using catalytic hydrotreating using an integrated hydrothermal hydrodeoxygenation process. The aim of the hydrothermal HDO is to remove most of the oxygen and sulfur present in the feed and to stabilise the oil for easier transport and further upgrading at oil refineries.

In this work, we have studied hydrodeoxygenation of HTL-oil model compounds in aqueous conditions in a batch reactor. Isoeugenol, 4-methylcatechol and diphenylmethane were selected as model compounds representing different functionalities in HTL-oil. The studied catalysts were selected based on stability of the catalysts and support materials under supercritical water conditions. The HDO experiments were carried out both in subcritical and supercritical conditions using hydrogen gas; the effect of the catalyst and reaction conditions on the product distribution will be discussed in detail.

Hydrodeoxygenation of black liquor HTL-oil model compounds in supercritical water

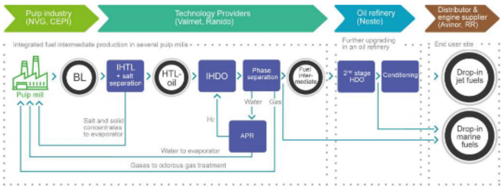
Sari Rautiainen,[1*] Felix Hyppönen,[1] Tyko Viertiö,[1] Niko Vuorio,[1] Saravanan Kasipandi,[1] Juha Lehtonen,[1] Luděk Meca,[2] Pavel Kukula[2]

Introduction

Black liquor (BL), a side stream of chemical pulping industry, is a very promising and currently underutilized abundant non-food feedstock for biofuels. The lignin and other organics present in black liquor contain circa half of the energy of wood chips, and currently most BL is burnt in pulp mills. EU project Black Liquor to Fuel (BL2F) aims to develop a feasible route from black liquor to drop-in biofuels for aviation and shipping.

BL2F Process

In the first step of BL2F process, black liquor is treated under supercritical conditions to separate the cooking chemicals and produce HTL-oil from the organics. The HTL-oil is then further upgraded using catalytic hydrotreating using an integrated hydrothermal HDO process. The aim of the hydrothermal HDO is to remove most of the oxygen and sulfur present in the feed and to stabilise the oil for easier transport and further upgrading at oil refineries. Herein, the hydrodeoxygenation (HDO) of model BL HTL-oil is studied in supercritical water (SCW) using sulfided catalysts.



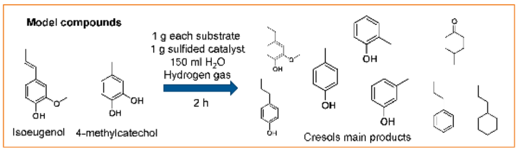
Process scheme of the Black Liquor to Fuel –process developed in BL2F EU project.

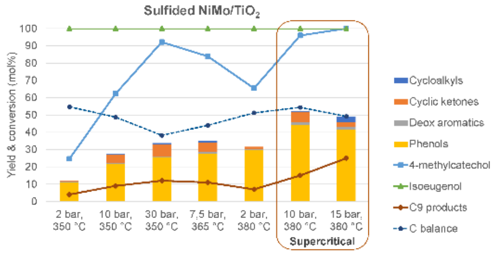
Stability tests

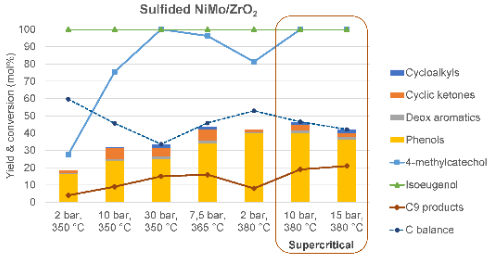
The supports were tested for stability in SCW by treatment at 380 °C for 2 hours under nitrogen atmosphere.

	BET (m^2/g)		Desorp. Pore vol. mm^3/g	
Material	fresh	used	fresh	used
α-Al_2O_3 corundum	1.81	2.22	4.7	4.8
TiO_2 rutile	3.57	3.71	7.4	7.0
ZrO_2 monoclinic	56.4	47.2	261	255
Activated carbon	890	798	368	403

HDO experiments







Conclusions

- **Hydrodeoxygenation of BL HTL-oil model compounds in sub- and supercritical water was studied using sulfided NiMo catalysts**
  - **Isoeugenol was easily converted but 4-methylcatechol required harsher conditions**
  - **Cresols were detected as main products**
  - **Increase of hydrogen pressure supressed cracking reactions**
  - **Cyclic ketones were produced by hydrogenation of the aromatic ring**
- **Based on the results, availability of hydrogen is more crucial on the HDO than temperature**

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This project has received funding from the European Union Grant Number 884111

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Low Emission Biorefineries and Side-Stream Valorization

Electrochemical Reduction of Aldonic Acids into the Corresponding Aldoses in the Presence of Electrolytes Reflecting SSL Composition

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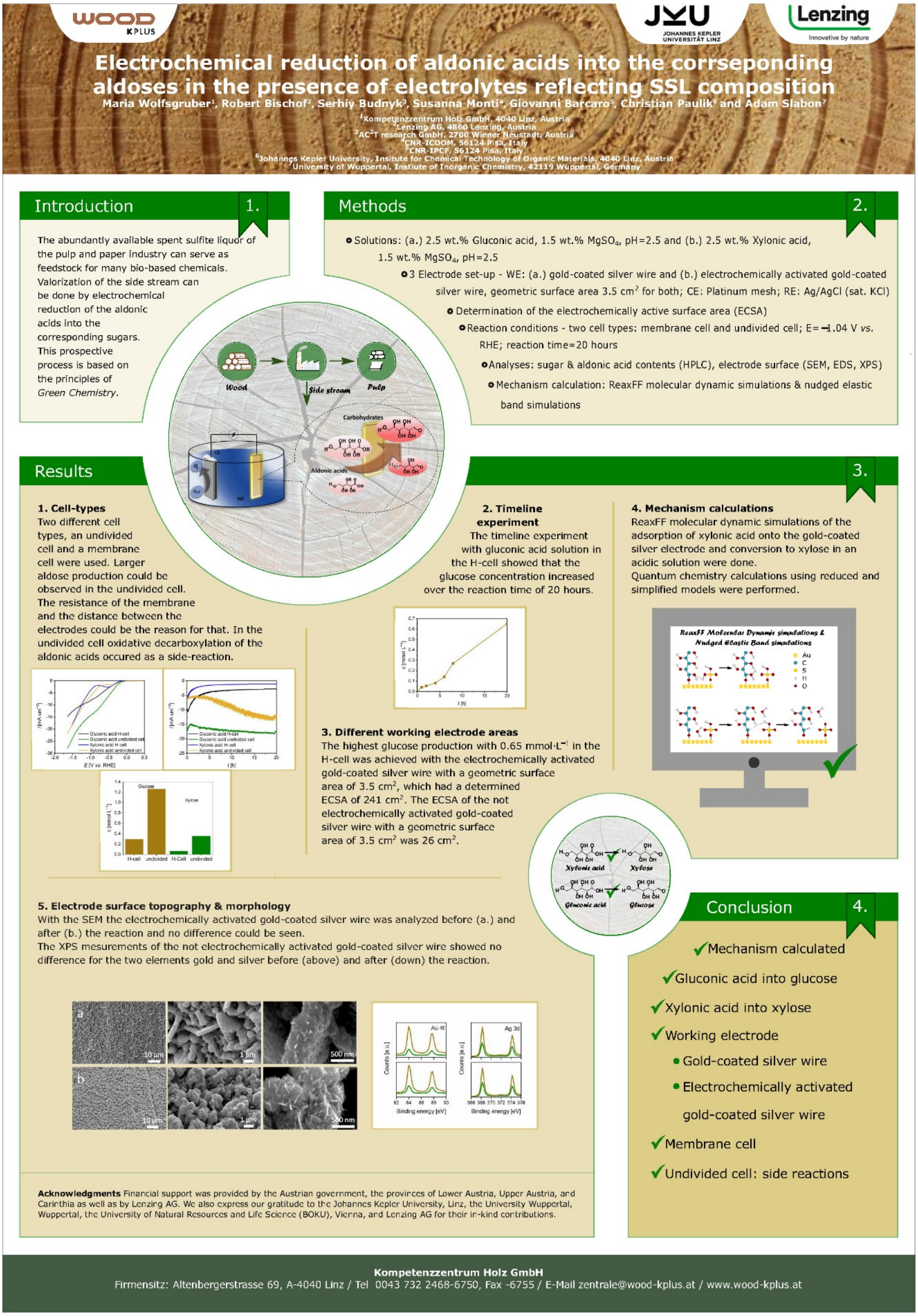
Abstract

Spent sulfite liquor (SSL) is an abundantly available side stream in the pulp and paper industry. Since it is rich in different carbon sources, it can serve as feedstock for many bio-based platform chemicals. SSL mainly consists of different wood degradation products such as sugars, lignosulfonates and aldonic acids. The biotechnological valorization of the side stream in biorefineries is hampered by the inability of many microorganisms to metabolize the aldonic acids, leading to complications of fermentation downstream operations and reduced yields. The aldonic acids are formed during the reaction of aldoses in the oxidative environment of the sulfite process. Since the separation of the aldonic acids from the SSL is very challenging, a conversion of these acids into fermentable carbohydrates is desirable. We therefore propose to reduce aldonic acids into their corresponding biomass sugars.

Within this respect, electrochemical reduction is a prospective process and based on the principles of Green Chemistry. In our study, the electrochemical reduction of gluconic acid into glucose and xylonic acid into xylose was demonstrated. Various electrodes at different potentials were tested, with the best conversion achieved with a gold-coated silver wire as working electrode. Different model solutions with aldonic acid concentrations between 2.5 and 15.0 w.-% were prepared for the experiments.

Aiming a side stream valorization, it could be shown that the electrochemical reduction of aldonic acids to the corresponding aldoses in model solutions is possible.



Electrochemical reduction of aldonic acids into the corrseponding aldoses in the presence of electrolytes reflecting SSL composition

Maria Wolfsgruber[1], Robert Bischof[2], Serhiy Budnyk[3], Susanna Monti[4], Giovanni Barcaro[5], Christian Paulik[6] and Adam Slabon[7]

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Introduction 1.

The abundantly available spent sulfite liquor of the pulp and paper industry can serve as feedstock for many bio-based chemicals. Valorization of the side stream can be done by electrochemical reduction of the aldonic acids into the corresponding sugars. This prospective process is based on the principles of *Green Chemistry*.

Methods 2.

- Solutions: (a.) 2.5 wt.% Gluconic acid, 1.5 wt.% $MgSO_4$, pH=2.5 and (b.) 2.5 wt.% Xylonic acid, 1.5 wt.% $MgSO_4$, pH=2.5
- 3 Electrode set-up - WE: (a.) gold-coated silver wire and (b.) electrochemically activated gold-coated silver wire, geometric surface area 3.5 cm^2 for both; CE: Platinum mesh; RE: Ag/AgCl (sat. KCl)
- Determination of the electrochemically active surface area (ECSA)
- Reaction conditions - two cell types: membrane cell and undivided cell; E=−1.04 V *vs.* RHE; reaction time=20 hours
- Analyses: sugar & aldonic acid contents (HPLC), electrode surface (SEM, EDS, XPS)
- Mechanism calculation: ReaxFF molecular dynamic simulations & nudged elastic band simulations

Results 3.

1. Cell-types

Two different cell types, an undivided cell and a membrane cell were used. Larger aldose production could be observed in the undivided cell. The resistance of the membrane and the distance between the electrodes could be the reason for that. In the undivided cell oxidative decarboxylation of the aldonic acids occured as a side-reaction.

2. Timeline experiment

The timeline experiment with gluconic acid solution in the H-cell showed that the glucose concentration increased over the reaction time of 20 hours.

3. Different working electrode areas

The highest glucose production with 0.65 mmol·L⁻¹ in the H-cell was achieved with the electrochemically activated gold-coated silver wire with a geometric surface area of 3.5 cm^2, which had a determined ECSA of 241 cm^2. The ECSA of the not electrochemically activated gold-coated silver wire with a geometric surface area of 3.5 cm^2 was 26 cm^2.

4. Mechanism calculations

ReaxFF molecular dynamic simulations of the adsorption of xylonic acid onto the gold-coated silver electrode and conversion to xylose in an acidic solution were done.
Quantum chemistry calculations using reduced and simplified models were performed.

5. Electrode surface topography & morphology

With the SEM the electrochemically activated gold-coated silver wire was analyzed before (a.) and after (b.) the reaction and no difference could be seen.
The XPS mesurements of the not electrochemically activated gold-coated silver wire showed no difference for the two elements gold and silver before (above) and after (down) the reaction.

Conclusion 4.

- ✓Mechanism calculated
- ✓Gluconic acid into glucose
- ✓Xylonic acid into xylose
- ✓Working electrode
  - Gold-coated silver wire
  - Electrochemically activated gold-coated silver wire
- ✓Membrane cell
- ✓Undivided cell: side reactions

Acknowledgments Financial support was provided by the Austrian government, the provinces of Lower Austria, Upper Austria, and Carinthia as well as by Lenzing AG. We also express our gratitude to the Johannes Kepler University, Linz, the University Wuppertal, Wuppertal, the University of Natural Resources and Life Science (BOKU), Vienna, and Lenzing AG for their in-kind contributions.

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Thermochemical Process Wastes as Carbon Material Sources

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Abstract

Wood biorefinery includes multitude of various processes devoted to the complete utilization of the main and side products. The complete separation of C5 and C6 sugars from wood and their further application attracts a widespread attention nowadays. C5 sugars can be as such catalytically converted into the furfural or as monosaccharides transferred into water solution for the further conversion using hydrolysis. The obtained lignocellulose can be used in thermochemical pyrolysis (350–400 °C) to synthesize levoglucosan from the cellulose part (~40 %), while the cellulose residues can be hydrolyzed to produce glucose and lignin part can be used for biochar. In the process of pyrolysis evolves mixture of various condensable products (furans, aldehydes, phenolic derivatives), which can be used directly. The aim of our research was to demonstrate, that these side products, using conventional or hydrothermal carbonization, can be utilized as precursors for the high value products – activated carbons with the specific meso- and micropores distribution, which can be used as electrodes in supercapacitors and fuel cells. The results of the research demonstrate the high efficiency of the synthesized activated carbon materials in the electric devices for the accumulation and transfer of energy.

Advantage of this approach is the possibility to include the production of the carbon materials into the biorefinery cycle, since the implementation of sustainable strategies based on the integral valorization of residues is the most efficient way to achieve a profitable circular economy.

LATVIAN STATE INSTITUTE OF WOOD CHEMISTRY

Thermochemical process wastes as carbon material sources

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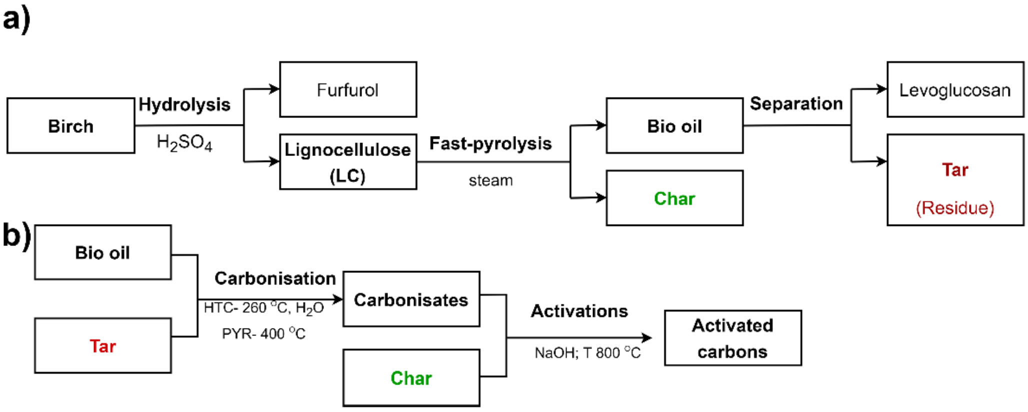


a)

Birch → **Hydrolysis** H_2SO_4 → Furfurol; Lignocellulose (LC)

Lignocellulose (LC) → **Fast-pyrolysis** steam → Bio oil; Char

Bio oil → **Separation** → Levoglucosan; Tar (Residue)

b)

Bio oil; Tar → **Carbonisation** HTC- 260 °C, H_2O PYR- 400 °C → Carbonisates

Carbonisates; Char → **Activations** NaOH; T 800 °C → Activated carbons

INTRODUCTION

Wood biorefinery includes multitude of various processes devoted to the complete utilization of the main and side products. The complete separation of C5 and C6 sugars from wood and their further application attracts a widespread attention nowadays. C5 sugars can be as such catalytically converted into the furfural or as monosaccharides transferred into water solution for the further conversion using hydrolysis. The obtained lignocellulose (LC) can be used in thermochemical pyrolysis (350–400 °C) to producing biooil containing levoglucosan and sugars (~40%) from the cellulose part, what can be hydrolyzed to produce glucose, as well as others condensable products. Conversely lignin mainly forming biochar. In the process of pyrolysis evolves mixture of various condensable products (furans, aldehydes, phenolic derivatives), which can be not used directly. The aim of our research was to demonstrate, that these side products with low ash content, using conventional (PYR) or hydrothermal carbonization (HTC), can be utilized as precursors for the high value products – activated carbons with the specific meso- and micropores distribution, which can be used as electrodes in supercapacitors and fuel cells. The results of the research demonstrate the high efficiency of the synthesized activated carbon materials in the electric devices for the accumulation and transfer of energy.

MATERIAL YIELD

Sample	Yield, %
Char (from LC)	23.4
Biooil (from LC)	41.6
Levoglucosan (from biooil)	33.5
Tar (from biooil)	66.5
Activated carbon (from Char, biooil, tar)	~30

CONCLUSIONS

Advantage of this approach is the possibility to include the production of the carbon materials into the biorefinery cycle, since the implementation of sustainable strategies based on the integral valorization of residues is the most efficient way to achieve a profitable circular economy.

The resulting materials have a large surface area (from 2665-3108 m^2g^{-1}) and an adjustable micro-meso pore structure with a mesopore volume of 37-54% of the total pore volume.

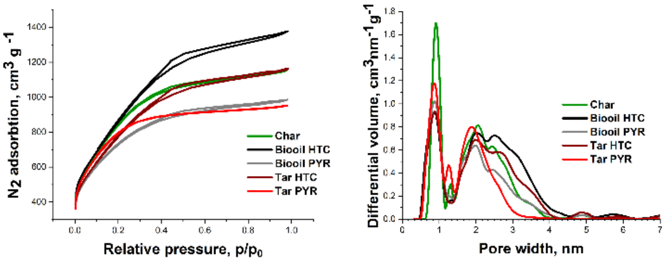
ACKNOWLEDGMENTS

The research was funded by ERAF project Nr. 1.1.1.1/20/A/027 "Improvement of wood- based biorefinery by innovative conversion of residues to nanoporous carbon materials (BiReMa)"

ELEMENTAL COMPOSITION OF ACTIVATED CARBON BASED ON FAST-PYROLYSIS CHAR, BIOOIL AND TAR.

	Carbonisated samples				Activated samples			
	N, %	C, %	H, %	O, %	N, %	C, %	H, %	O, %
Char	0.33	75.25	3.66	20.77	0.78	93.03	0.38	5.81
Biooil HTC	0.12	70.85	4.34	24.69	0.99	94.43	0.70	3.88
Biooil PYR	0.15	70.81	3.90	25.14	0.90	93.35	1.00	4.74
Tar HTC	0.10	71.12	4.56	24.23	1.11	93.05	1.52	4.32
Tar PYR	0.84	76.52	3.95	18.68	0.68	92.60	0.58	6.14

(A) N2 ADSORPTION-DESORPTION ISOTHERMS AND (B) PORE SIZE DISTRIBUTION OF ACTIVATED CARBON BASED ON FAST-PYROLYSIS CHAR, BIOOIL AND TAR.



POROUS STRUCTURE PARAMETERS OF ACTIVATED CARBON BASED ON FAST-PYROLYSIS CHAR, BIOOIL AND TAR.

Sample	Specific surface area, m^2 g^{-1}			Pore volume (V), cm^3 g^{-1}			Average pore width, nm	Mesopores from Vtotal, %
	BET	DR	DFT	total	micro	meso		
Char	3108	2732	1907	1.8	1.0	0.8	2.3	45.7
Biooil HTC	3183	2712	2100	2.1	1.0	1.1	2.7	54.8
Biooil PYR	2665	2363	1802	1.5	0.8	0.7	2.3	44.9
Tar HTC	2858	2454	1898	1.8	0.9	0.9	2.5	51.6
Tar PYR	2914	2609	1757	1.4	0.9	0.5	2.0	37.1

Novel Cellulose Modifications

Wood Derived Natural Microcrystalline Cellulose with the Functionality of Nanocellulose - New Perspective for Industry

Gert Preegel

Oü Fibenol, Tallinn, Estonia

Corresponding author: Gert Preedel <gert.preegel@fibenol.com>

OÜ Fibenol is a spin-off from Graanul Group, a leading EU wood pellets producer. Fibenol has built a new of a kind flagship biorefinery based on a novel pre-treatment technology to fully convert residual woody biomass into sustainable renewable feedstocks for the chemicals, materials, and fuels industries.

From our flagship plant in Imavere, Estonia we are introducing to the market a new quality of hydrolysis lignin, high purity cellulosic sugars and a unique characteristic micro crystalline cellulose (MCC).

Our hydrolysis lignin has been successfully used in different application areas such as bio composites, phenol replacement in resins and is an excellent starting point for further chemical and biological modification steps.

The cellulosic sugars on the other hand can be produced in very high purity and therefore are excellent substitution for conventional sugar sources with added benefit of reduced environmental footprint.

Micro crystalline cellulose production process is totally different compared to conventional Kraft fiber based MCC`s or nanoscale celluloses which opens new perspective for the end use cases. MCC can be used in different applications i.e. papermaking, film formation, viscosity modification agent etc.

Fibenol flagship plant can deliver samples at ton scale and industrial production is planned to be commissioned in Q1 2023.

Fibenol

Helping industries do more with less

We're using cutting-edge processes to develop a new generation of sugars, high purity hydrolysis lignin, and unique microcrystalline cellulose from hardwood. Our work opens a new era of biomaterials and bioproducts, helping industries do more with less.

Over 90% of biomass is turned into valuable products.

Residual birch
Fibenol flagship plant
Lignova™ lignin grades
Microcrystalline celluloses (under development)
C5, C6 cellulosic sugars

fibenol.com

LIGNOVA™

LIGNOVA™ is used as a drop-in substitute to fossil chemicals in many industrial applications like biocomposites, phenolic resins, polyols, and polyurethanes.

LIGNOVA™ Crude

Our hydrolysis lignin product LIGNOVA™ Crude retains its native properties with a mild extraction process without a sulfuric smell. It can be used as a binder for thermosetting and thermoplastic materials, plywoods or floral foams.

LIGNOVA™ Pure

LIGNOVA™ Pure has high functionality, reactivity, and good solubility in many solvents with the salts and cellulosic residues removed. Polyols, polyurethanes, and carbon fibres are just a few potential areas of application for such high purity material.

SPECIALTY CELLULOSES

Natural microcrystalline cellulose (MCC)

With our unique fractionation process, we break down wood into micro-scale particles. Fractionation solubilizes amorphous regions of the cellulose and allows us to produce crystalline cellulose particles.

Refined MCC

With bleaching and purification, we remove any residual lignin from the microcrystalline cellulose to produce a white product suitable for emulsification of food, cosmetics and other applications.

CRYSTAL STRUCTURE:	NATIVE CELLULOSE I
CONCENTRATION WT%:	10-20
DEGREE OF POLYMERIZATION:	<100
CRYSTALLINITY:	HIGH
SHAPE:	ROD LIKE

CELLULOSIC SUGARS

Our fractionation plant enables to produce environmentally friendly wood sugars – C5 and C6.

C5 Sugars

Our pretreatment process liberates most xylose present in wood in 20 seconds. After purification, the C5 sugar xylose is processed into low-calorie sweetener for food and beverages and is also applicable in the animal feed industry, pet food production, and even pharmaceuticals.

C6 Sugars

The main carbohydrate in hardwood is glucose. After our proprietary pretreatment process, we liberate the C6 sugars with a biological enzymatic process. The resulting product is the most versatile as it is an ideal substitute for common agricultural sugars.

SWEETWOODS

SWEETWOODS.EU

CREATING THE FUTURE FOR WOOD INDUSTRY

We turn wood into high purity lignin and wood sugars to industrialize innovative biomaterials and bioproducts.

THE PROJECT

Nine European companies have joined forces in the SWEETWOODS flagship project to change the way we perceive wood industry and to reduce global dependence on fossil resources.

Traditional wood industry is focused on a certain end product while using by-products for low-value energy solutions. Our game changing technology will **convert almost all** (over 90%) of the hardwood into usable high value biomaterials and bioproducts. This breakthrough enables us to produce a diversity of products and establish novel bio-based value chains with low ecological footprint.

Almost everything that is made from oil today could alternatively be made from wood in the future.

– OVER 90 % OF THE CARBON CONTENT OF WOOD CAN BE FURTHER REFINED

Our objective is to implement pilot scale demonstrated technology on a full industrial scale in four years. We will create industry-changing new value chains, where wood as sustainable raw material plays a vital role.

PRODUCTS FROM THE SWEETWOODS PROJECT

Lignin / sugars
Biochemicals
Insulation foams
Biocomposites
Elastomeric foams

PROJECT GOALS

- Show the successful and profitable production – on an industrial scale – of high-purity lignin from hardwood
- Use all main components of the biomass feedstock while minimizing any diversion of carbon content streams to low-value uses
- Produce high-purity lignin for a range of novel applications, namely elastomeric foams for tube insulation, rigid polyurethane foam panels for insulation and polymer compounds intended for injection molding
- Produce high-purity sugars – glucose, fructose, xylose and glucosone – for novel end-use cases, namely producing bio-IBN
- Establish markets for lignin and novel sugar-based platform chemicals

5	4	80 %
New bio-based value chains	Novel bio-based materials in the areas of insulation and elastomeric foams, injection molding, biofuels and biochemicals	Less waste from biorefining process over the current industrial state-of-the-art

OUR PARTNERS

The SWEETWOODS consortium brings together **9 European innovation oriented companies.**

Fibenol
Global Bioenergies
Vertech
armacell
TECNARO
METGEN
RECTICEL
2B
SPINVERSE

PROJECT IN NUMBERS

43,2	4	9
Million € total budget	Years	Partners

youtu.be/asRGF4PSsxE
What is SWEETWOODS? - watch the project description on YouTube

Horizon 2020
European Union Funding
for Research & Innovation

BBI JU

Bio-based Industries Consortium

Fibenol is currently the leading partner in the SWEETWOODS project and also consortium member in the projects REWOFUEL, VEHICLE and VIOBOND. These projects have received funding from the Bio-based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreements No 792061; 792104; 837866; 101022967, respectively.

Structure – Function – Performance Interrelations in Materials Engineering

Mapping The Properties and Performance of Nanocellulose- and Alginate-Based Cell Factory Matrices for Sustainable Photosynthetic Chemicals Production

Ville Rissanen[1], Vilja Siitonen[2], Tuukka Levä[1], Lauri Nikkanen[2], Sergey Kosourov[2], Maria Heilala[3], Josphat Phiri[3], Thaddeus Maloney[3], Mikko Mäkelä[1], Yagut Allahverdiyeva[2], and Tekla Tammelin[1]

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Author

Whole-cell immobilization in carrier matrices based on nanocellulosic hydrogels can be utilized in a range of application fields including biomedicine and biotechnology. One such emerging application is the so-called solid-state photosynthetic cell factory (SSFCF) aiming at sustainable biocatalytic chemicals production that contributes to circular bioeconomy. In the SSPCFs, immobilization has the potential to greatly improve the light-to-product ratio while reducing water and energy demands, but the efficiency of the system is integrally linked to the structure-property-performance interrelations of the nanocellulosic matrix. Thus, it is vital to employ interdisciplinary efforts based on materials, cell and bioprocess engineering to optimize the very distinct interplay between mechanical strength, mass transfer properties and biological performance of an efficient SSPCF. Here, we present a multidisciplinary experimental toolbox to investigate these properties from cross-linked matrix structures based on TEMPO-oxidized cellulose nanofibers (TCNF) and alginate. We use a combination of methods including rheology, multivariate data analyses, matrix structure investigations, and monitoring of gas exchange and biological operations of the immobilized photosynthetic cells. The obtained results give us new insight towards creating tailored cell factories – and immobilized systems in general – that can support the specific needs of the biological host and operational conditions.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 899576

MAPPING THE PROPERTIES AND PERFORMANCE OF NANOCELLULOSE- AND ALGINATE -BASED CELL FACTORY MATRICES

Ville Rissanen[1] • Tuukka Levä[1] • Lauri Nikkanen[2] • Vilja Siitonen[2] • Maria Heilala[3] • Josphat Phiri[3] • Thaddeus C. Maloney[3] • Sergey Kosourov[2] • Yagut Allahverdiyeva[2] • Mikko Mäkelä[1] • Tekla Tammelin[1]

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[2] Molecular Plant Biology, Department of Life Technologies, University of Turku
[3] Department of Bioproducts and Biosystems, Aalto University

BIOPROCESS TECHNOLOGY & MATERIALS ENGINEERING

WHY PHOTOSYNTHETIC CELL FACTORY?

- ✓ Sustainable alternatives for fossil-based chemicals and energy production
- ✓ CO_2 and sunlight as virtually unlimited sources
- ✓ Product range from biofuels and monomers to specialty chemicals and pharmaceutically active ingredients (APIs)

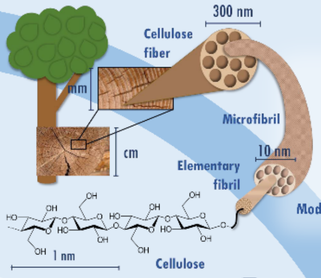
WHY IMMOBILIZE?

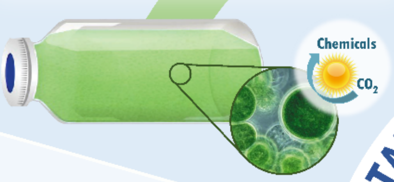
Bind cells within a carrier matrix to:

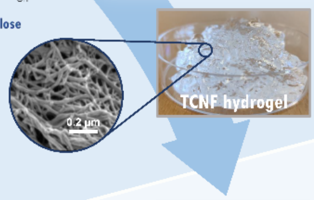
- ✓ Reduce water & energy use
- ✓ Increase cell density & viability
- ✓ Improve light-to-product ratio

WHY NANO-CELLULOSE?

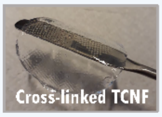
High mechanical strength
Porous hydrogel
Transparent
Non-toxic, biodegradable
Unique water interactions
Modifiable structure & properties

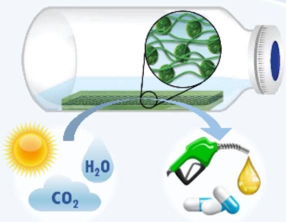






SUSTAINABLE CHEMICALS PRODUCTION WITH LEAF-INSPIRED CELL FACTORIES





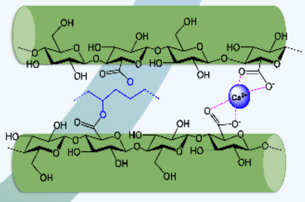
FINE-TUNING THE MATRIX COMPOSITION

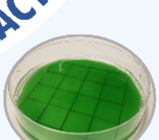
Combining nanocelluloses, e.g. TEMPO-oxidized cellulose nanofibers (TCNF) with chemical, ionic or polymeric cross-linkers to create self-standing hydrogel matrices for cell entrapment

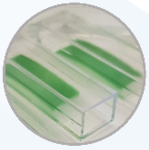
TAILORING MATERIALS FOR PRODUCTION SYSTEMS

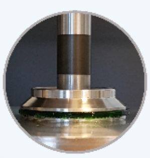
Assembling the 3D hierarchical matrix architectures based on the specific needs of the production host and operational conditions for:

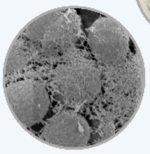
- ✓ Submerged and semi-wet production
- ✓ Gaseous and soluble products







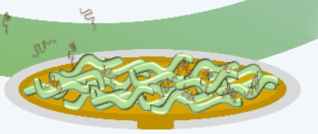




AIM TO OPTIMIZE MECHANICAL AND BIOLOGICAL PERFORMANCE

Interdisciplinary methodological toolbox combined with multivariate data analyses with aims to optimize:

- ✓ Mechanical performance via rheology (shear stress, wet conditions)
- ✓ Mass transfer via thermoporosimetry and SEM imaging (flow of nutrients, gases, water)
- ✓ Biological performance via MIMS and GC-MS (cell viability, productivity)



FROM FUNDAMENTALS TO FUNCTIONAL STRUCTURES

Using bulk and surface-sensitive analytics to reveal the structure-function-performance relationship of the matrix, as well as the interactions between the matrix components and the entrapped cells

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Solid-State Photosynthetic Cell Factories for Sustainable Chemicals Production Using Nanocellulose-Based Cross-Linked Functional Structures

Tuuli Virkkala[1] Ville Rissanen[1], Tuukka Levä[1], Sergey Kosourov[2], Suvi Arola[1],
Eero Kontturi[3], Yagut Allahverdiyeva[2], and Tekla Tammelin[1]

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Abstract

The poster presents functional structures for solid-state photosynthetic cell factories (SSPCFs) aiming at sustainable biocatalytic production of chemicals and fuels. As SSPFCs use carbon dioxide and sunlight as theoretically unlimited energy sources, they promote the transition from petroleum-based production towards circular carbon-neutral blue bioeconomy and contribute to mitigation of greenhouse gas emissions. These renewable platforms are constructed by immobilizing photosynthetic microalgal cells within nanocellulose-based matrices in a design that draws inspiration from nature and helps to overcome the challenges associated with traditional suspension cultures, such as water and energy consumption and light-to-product efficiency. However, the realization of this potential requires optimizing the SSPCF matrix in terms of its structure and properties. The matrix must be biologically compatible with the cells and mechanically robust in aqueous production conditions. In this sense, nanocelluloses are highly advantageous immobilization materials as their innate, remarkably hygroscopic nature and porous network structure sustain long-term cell viability, and different cross-linking strategies can be applied to provide mechanical stability for the colloidal fibril network even when submerged in growth medium. Moreover, the different cross-linkers allow structural control and tailoring of versatile matrix compositions for the specific requirements of various production systems.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 899576

BIOINSPIRED STRUCTURES BASED ON MIXED-LINKAGE GLUCAN AND NANOCELLULOSE INTERACTIONS

Tuuli Virkkala[1] • Ville Rissanen[1] • Suvi Arola[1] • Tekla Tammelin[1]
[1] VTT Technical Research Centre of Finland Ltd.

INTRODUCTION

Hemicelluloses called mixed-linkage glucans (MLGs) are found in grassy plants as structural components of the cell wall. Previously, MLGs have been shown to irreversibly adsorb onto cellulose fibrils[1], and due to these intrinsic interactions, MLGs efficiently gel nanocellulosic materials, such as TEMPO-oxidized cellulose nanofibers (TCNFs), even at ultra-low solids contents.[2] These features make MLGs an interesting bioinspired component for nanocellulose-based functional structures.

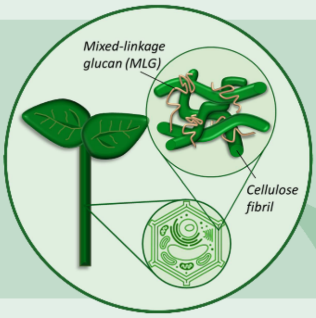


Figure 1. Schematic representation of the cellulose network (green) with interlaced MLGs (beige) in the plant cell wall.

OBJECTIVES

- ✓ Obtaining strong hydrogels from plant cell wall components i.e., nanocellulose and MLG
- ✓ Investigating interfacial interactions of the components
- ✓ Revealing strong bulk interactions in aqueous environment using rheological measurements
- ✓ Utilizing information in design of functional biomaterials

EXECUTION

- Adsorption of MLGs on TCNF surfaces via Quartz Crystal Microbalance with Dissipation monitoring (QCM-D)
- Viscoelastic properties:
  - Interfacial rheology of adsorbed layers by applying Voigt model[3]
  - Rheological measurements for wet strength of MLG-TCNF hydrogels at bulk level
- MLG charge and particle sizes with ζ-potential and Dynamic Light Scatterin (DLS) measurements
- AFM imaging for visual appearance

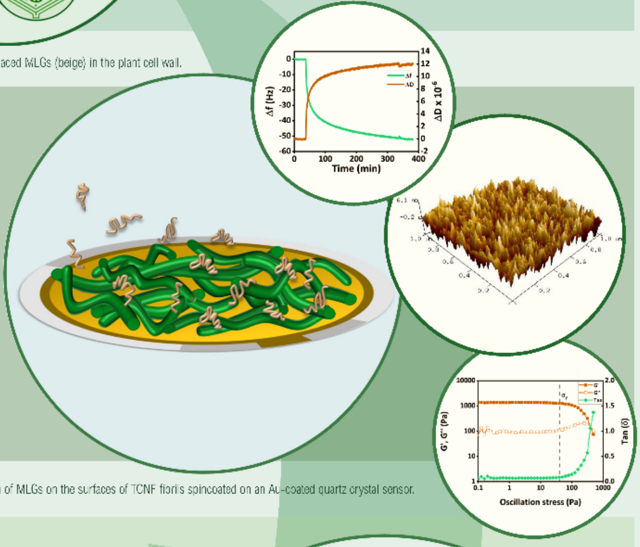
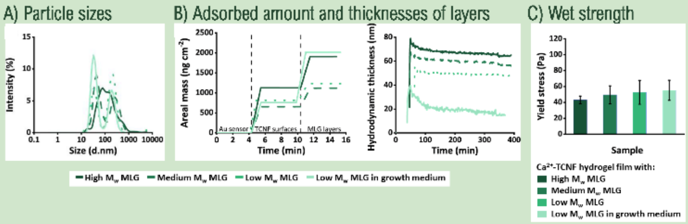


Figure 2. Adsorption of MLGs on the surfaces of TCNF fibrils spincoated on an Au-coated quartz crystal sensor.

RESULTS


A) Particle sizes

B) Adsorbed amount and thicknesses of layers

C) Wet strength

Figure 3. (A) Hydrodynamic particle sizes of MLG in solution at pH 7.4-7.6. (B) Areal masses and (C) hydrodynamic thicknesses of adsorbed MLG layers. 15 MHz, f_0 = 5 MHz, n = 3. Layer density assumed as 1.05 g cm^{-3}. (D) Yield stresses of MLG containing Ca^{2+}-TCNF hydrogel films in Pa. Standard deviations are given.

CONCLUSIONS

The surface sensitive measurements in conjunction with the rheological investigation enable understanding of both interfacial and bulk material interactions to reveal physical performance of hydrogels from plant-based components. Water stable structures from MLG and TCNF were obtained, and the data indicates a dependency of the viscoelastic properties of TCNF-MLG hydrogels on MLG molecular weight and medium composition. Altogether, these findings pave way towards a bioinspired functional material design with features such as high wet strength combined with biological compatibility with living cells.

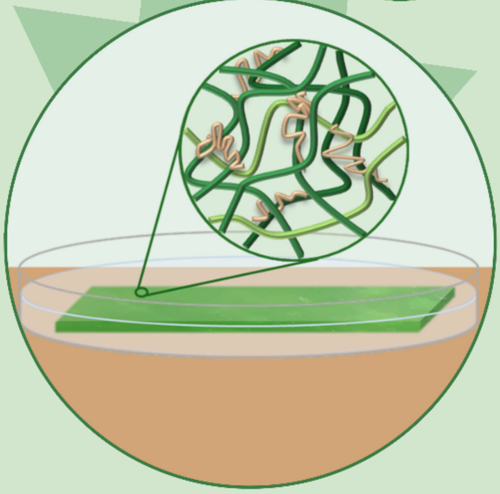


Figure 4. Conceptual view of a water-stable hydrogel consisting of TCNF and MLG.

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Structure – Function – Performance Interrelations in Materials Engineering

Nanocellulose as Bio-Template for Synthesis of Photo-catalytically Active Porous Silica

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Abstract

Sawdust is a waste of wood production and its available volume is large. Here we presents a new approach for more effective valorization of sawmill hardwood and softwood wastes (Beech and Cedar sawdusts). Firstly, the sawdust was used to extract lignin-containing and lignin-free cellulose nanocrystals (L-CNCs and CNCs). Both CNCs were applied as templates to prepare nanostructured porous silica for photocatalysis to degrade methylene blue dye. More specifically, both sawdusts were subjected to a partial delignification followed by a bleaching treatment to obtain pure cellulose fibers. Strong acid hydrolysis was used to isolate L-CNCs and CNCs from unbleached pulps and pure cellulose fibers, respectively. The obtained L-CNCs and CNCs were used without changing their surfaces as template cores for nanostructured silica free-surfactant synthesis. The synthesis was performed with a simple and efficient sol-gel method using tetraethyl orthosilicate as the silica precursor. The organic template cores were removed by calcination at 650 °C. L-CNCs and CNCs derived from Beech fibers were long and had a higher crystallinity, compared with those obtained from Cedar fibers. The nanostructured silica had similar morphology as the templates. Also, the pore sizes were closely related to the dimensions of L-CNCs and CNCs templates, with high specific surface areas. The photocatalytic degradation of methylene blue dye was studied and compared.

This study provided a simple route to extract L-CNCs and CNCs as organic templates to prepare nanostructured silica. The different silica structures showed excellent photodegradation of methylene blue.

Nanocellulose as Bio-Template for Synthesis of Photo-catalytically Active Porous Silica

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OBJECTIVES

I. The extraction of lignin-containing and lignin-free cellulose II nanocrystals (L-CNCs/CNCs) using sawmill wastes.

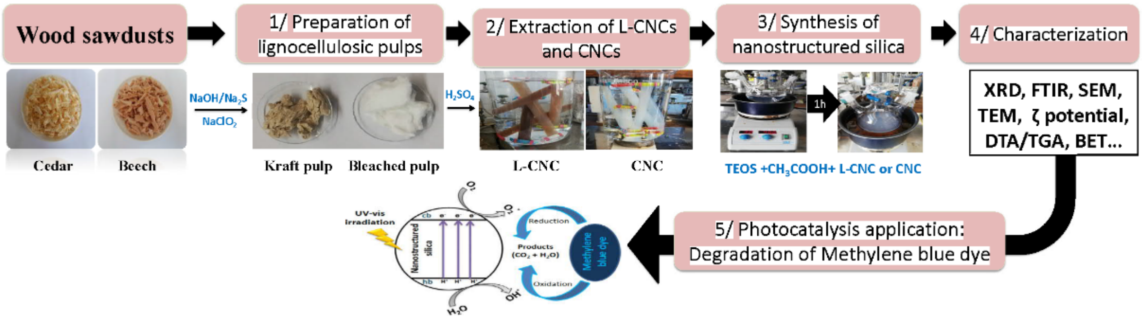
II. The use of L-CNCs and CNCs as bio-templates for free-surfactant synthesis of photocatalytically active porous silica.

III. The application of these active porous silica as photocatalysts in the water treatment.

INTRODUCTION

Sawmill industry produces a huge quantities of waste in the form of sawdust, these are sent directly to the areas for energy uses, which generates an environmental pollution due to the release of toxic gases. Nowadays, several studies have focused on the environmental and sustainable aspects of sawmill waste, through the valorization of all kinds of wastes from the wood processing industry.
In this study, both lignin-containing and lignin-free cellulose nanocrystals (L-CNCs and CNCs with allomorph of cellulose II) were extracted from Cedar (softwood) and Beech (hardwood) sawdusts. Both types of CNCs were investigated as templates for surfactant-free synthesis of nanoporous silica materials with a simple, efficient and low-cost sol-gel method where tetraethyl orthosilicate (TEOS) was used as a silica precursor of SiO_2 matrix. The morphology, geometric structure, pore size distribution, thermal stability, and specific surface area of the obtained nanoporous SiO_2 materials were comprehensively studied. The prepared hollow silica nanorods were further tested for photocatalysis degradation of methylene blue (MB) dye.

MATERIALS AND METHODS



Wood sawdusts → 1/ Preparation of lignocellulosic pulps → 2/ Extraction of L-CNCs and CNCs → 3/ Synthesis of nanostructured silica → 4/ Characterization

Cedar
Beech
$NaOH/Na_2S$
$NaClO_2$
Kraft pulp
Bleached pulp
H_2SO_4
L-CNC
CNC
1h
TEOS +CH_3COOH+ L-CNC or CNC

XRD, FTIR, SEM, TEM, ζ potential, DTA/TGA, BET...

5/ Photocatalysis application: Degradation of Methylene blue dye

RESULTS

A/ Preparation and Characteristics of L-CNCs and CNCs

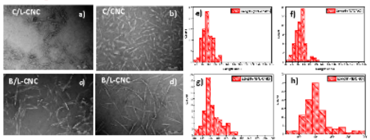


Fig. 1: TEM (a-d) and length (e-h) distribution of L-CNCs and CNCs

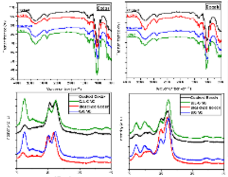


Fig. 2: FTIR spectra and XRD diffractograms of L-CNCs and CNCs extracted from Cedar and Beech sawdusts

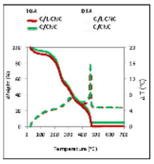


Fig. 3: TG and DTA curves of L-CNCs and CNCs extracted from Cedar sawdust

B/ Preparation and Characterization of Silica coated L-CNCs and CNCs and Hollow Silica

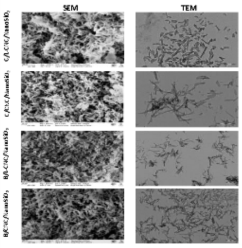


Fig. 4: SEM and TEM micrographs of the different silica nanocomposites

Table 1: Specific surface area and total pore volume of porous SiO_2 materials

Sample	Specific surface area (m^2/g)	Pore volume (cm^3/g)
C/L-CNC/NanoSiO$_2$	348 ± 3	1.98 ± 0.3
C/CNC/NanoSiO$_2$	392 ± 9	1.71 ± 0.03
B/L-CNC/NanoSiO$_2$	953 ± 20	1.17 ± 0.13
B/CNC/NanoSiO$_2$	1107 ± 24	1.15 ± 0.07

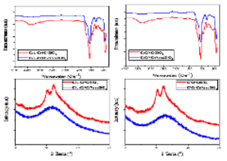


Fig. 5: FTIR spectra and x-ray diffractograms of L-CNCs and CNCs extracted from Cedar and Beech sawdusts as well as silica-coated L-CNCs and CNCs before and after calcination

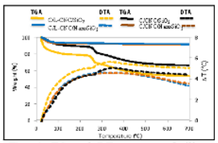


Fig. 6: TG and DTA curves of silica-coated L-CNCs and CNCs and hollow silica nanocomposites

C/ Evaluation of the Photocatalytic Performance

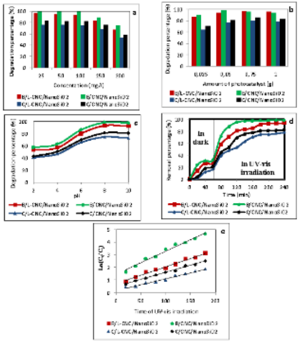


Fig. 7: Effect of key parameters on the degradation percentage of MB: (a) concentration of MB-mg/l, (b) amount of catalyst (g), (c) pH and (d) time (min) and (e) the kinetics of MB degradation

CONCLUSIONS

1) L-CNCs and CNCs extracted from purified Beech sawdust exhibit average lengths of about 150 nm and diameters less than 9 nm. However, in the case of Cedar source, the obtained L-CNCs and CNCs presented average lengths around 90-100 nm and diameters around 10 nm.
2) The prepared nanostructured silica materials were found to be quite uniform and coined the shape of L-CNCs and CNCs with high specific surface areas, which reached around 950-1100 m^2/g for B/L-CNC/NanoSiO$_2$ and B/CNC/NanoSiO$_2$. Correspondingly, the surface areas were less, around 350-400 m^2/g for C/L-CNC/NanoSiO$_2$ and C/CNC/NanoSiO$_2$, respectively.
3) Significant degradation rates of methylene blue dye were determined to reach higher than 90 % for B/CNC/NanoSiO$_2$ and B/L-CNC/NanoSiO$_2$ and around 70-8 % for C/CNC/NanoSiO$_2$ and C/L-CNC/NanoSiO$_2$, respectively

ACKNOWLEDGMENTS

We would like to thank Åbo Akademi University Research Mobility Programme for the fellowship.

Wood Based Textile Solutions

Organosolv Catalytic Fractionation of Nordic Forestry Wood Residues to Textile Fibers

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Abstract

Wood based cellulose fibers are an excellent alternative to cotton fibers due to the fact that cotton production requires huge resources like water, agriculture land and chemical pesticides which are highly energy demanding. The high value trunk part of the tree is mainly used for infrastructure, paper and pulp industry. The remaining low value part which are roots, tops & branches remains as a waste residue in the forest. People either burn them for the production of electricity which negatively impacts on environment due to CO_2 emission or they can slowly degrade into the soil. To valorize them in a more sustainable and environment-friendly way, here in we aimed to use the Swedish-forestry waste residues i.e. Poplar, Spruce tops & branches/ Beetle infested spruce as a main feedstock and performed an organosolv pulping on them under acidic conditions to obtain a high value dissolving grade wood pulp (DWP). The obtained DWP reaches the specifications of commercial dissolving grade pulps which are available in the market. We further taken a step ahead and transformed our dissolving wood pulp into textile fibers using wet-spinning process. Also, we were successful in regeneration of lyocell fibers upon blended a 20 % of our developed DWP with other commercial grade wood pulps. Thus, the properties of the obtained fibres are in the same range as standard lyocell fibre made from wood-based pulp in the market. Other waste streams like Poplar and Birch wood-based textile fibers as well as used synthetic-cotton blended textile recycling pulp fibers are under progress in our laboratory.

References

Di Francesco, D., Baddigam, K. R., Muangmeesri, S., & Samec, J. S. (2021). OrganoSoxhlet: circular fractionation to produce pulp for textiles using CO_2 as acid source. Green Chemistry, 23(23), 9401-9405.

Organosolv Catalytic Fractionation of Nordic Forestry Wood Residues to Textile Fibers

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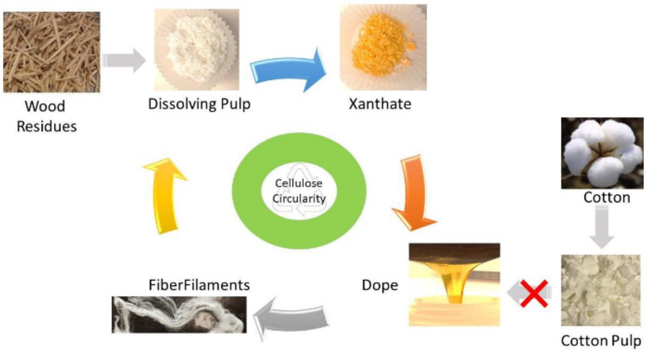
Introduction

Cotton farming causes depletion and eutrophication of water resources and brings other negative consequences on local environments through use of pesticides, herbicides, and harvest-aid chemicals. As an alternative to cotton fibers, we hypothesize that cotton fibers could be replaced with regenerated cellulose fibers from forestry waste wood residues.

- In Europe itself about ~100 million m^3 per year of damaged wood remained.
- According to Marklund, tops and branches of the whole spruce, about 33wt.%, was discarded during the milling process.

To address this, here in we showed the valorization of spruce wood waste by organosolv pulping to produce dissolving grade wood pulp and further regenerate it into viscose and lyocell fiber filaments for textile production.

Cellulose Circularity



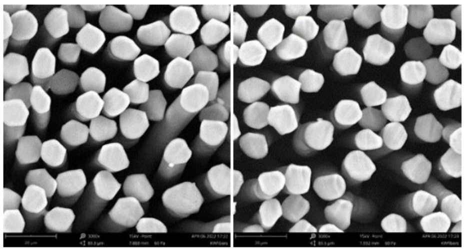
Properties of Dissolving Wood Pulp

Parameter	Unit	Spruce Pulp	Beetle infested Spruce	Poplar
Intrinsic Viscosity	mL/g	560	596	985
Cellulose	%	92	94	94
Brightness	% ISO	93	91	90
PDI	%	10	10	8.4
Fe	ppm	13	10	7.2
Mn	ppm	0.3	0.4	0.2
Cu	ppm	3.3	3.0	0.5

Regeneration of Fiber filaments obtained from Viscose process and Lyocell Process

Properties of Lyocell Fibers

SEM image of the lyocell fibres from organosolv Spruce pulp



Parameter	Unit	Organosolv Spruce Pulp Lyocell Fiber	Standard Lyocell Fiber
Titer	Denier	1.16	1.1 – 1.2
Tenacity	g/d	4.6	4.3- 4.7
Elongation	%	13.2	13-15
K/S	%	104	99

Conclusions

- Low value Poplar & Spruce forestry residues valorised into high value dissolving grade wood pulp
- The obtained DWP parameters compatible to both Viscose and Lyocell fiber regeneration.
- The fiber filaments were successfully regenerated through Viscose and Lyocell process without compromising the dope quality and smooth spinning.
- The mechanical properties of the our lyocell fibers are comparable to standard Lyocell fibers.
- Biorefining of Poplar & Spruce forestry residues could be an excellent substitute to cotton in production of dissolving grade cellulose that can produce textile fibers.
- Agricultural land dedicated to cotton could be reclaimed for food production by extending poplar plantations to produce textile fibers. This approach can fulfil the global food crises to some extent.

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- Davide Di Francesco, Kiran Reddy Baddigam, Suthawan Muangmeesria and Joseph S. M. Samec,* OrganoSoxhlet: circular fractionation to produce pulp for textiles using CO2 as acid source, *Green. Chem.* **2021**, *23*, 9401–9405.

Acknowledgements:
1. Department of Organic Chemistry & Department of Materials and Environmental Chemistry – Stockholm University, Sweden. 2. Municipal of Stockholm (Region Stockholm)
3. Mistra SafeChem

Wood based textile solutions

From Industry 4.0 to Research 4.0. a Modular Approach for the Development of Cellulosic Fibres

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Abstract

The research work in the field of high-performance cellulosic fibres is characterised by a high degree of adaptation needs. Research facilities must be able to be adapted after initial experiments and the knowledge gained thereby. The necessary adjustments are made under the conditions of a highly complex manufacturing process, which is determined by many influencing parameters. The development of high-performance cellulosic fibres demands an efficient systematic and, in part, self-optimising experimental working system, which must be intelligent in gathering data from the process and flexible in enabling the rearrangement of the process. Research 4.0 is a systematic approach aiming to support researchers working on the development of innovative yarns. Each module within the line represents a production step and is equipped with a PLC to control itself and to organise in association with other modules in the plant. The control hierarchy has an intelligent modular structure that configures itself according to the arrangement of each single module given by the hardware and the interfaces within the system. This paper will present the implementation of Research 4.0 as a tool for the development of a product from the idea to the practical implementation. Such a task needs a modular conceptual approach offering the required flexibility for the complete validation process: principle > process > product.

History of Digitisation

In the old, analogue world, there were things above all. Things were linked to names and pictures. Thus, the world of words and the world of images developed into the first stages of abstraction. The next level of abstraction was the mapping of things, words and pictures into numbers. That was the birth spark of the world of data.

The most common way to define the world of numbers is by using ten digits (0 to 9). However it was the invention of the binary number system by Gottfried Wilhelm Leibniz (1697) which allowed the representation of all numbers with only two digits (0 and 1). Thus, the world became mathematical and the fundament for digitisation was laid as it is the process of to putting information into the form of a series of the numbers 0 and 1, so that it can be understood and used by a computer or processed electronically. In 1788, Joseph-Louis de Lagrange represented in this work “Méchanique analitique” the thesis, that the world can only be completely described by means of algebraic operations, hence turning the mathematical description of the universe into a digital realm.

George Boole, proves in his work "An Investigation of the Laws of Thought" (1854), that logic and algebra are identical. Gottlob Frege followed with his "conceptual notation" of non-symbolic terms in "The Foundations of Arithmetic" (1884). This analysis of logical concepts and the machinery of formalisation was essential to Bertrand Russell's and Alfred North Whitehead's "Principia Mathematica" (3 vols., 1910–13), to Bertrand Russell's theory of descriptions, to Kurt Gödel's (1906–78) incompleteness theorems, and to Alfred Tarski's (1901–83) theory of truth. These theories paved the way mapping thinking to logic, and logic to math. Thus, the base of programming languages was created and algorithmic languages like ALGOL 60 were a first breakthrough in digitisation.

In parallel to the mathematisation of the world, a multitude of inventions were still necessary to link things, words and images as well as sounds to logical data. The development of telecommunications from Heinrich Hertz (1886-1888) to the transistors of John Bardeen, Walter Brattain and William Shockley (1946) gave birth to wireless radio technology, which has enabled the transmission of data through the space separating emitter from receptor. On this basis, the technical infrastructure of for a digitalised world emerged. The developments such as telegraph, telephone, television, radar, broadcasting, satellite and finally the Internet have been shaping the technical network that today enables global data exchange.

In the twentieth century, based on technical innovations combined with computer technology, a closely linked communication and information network of mobile media emerged, which forms the basis for today's visions of the future (Weibel et al., 2015). With the convergence of the various communication technologies on which the various digital control systems are based, the basis for the Internet of Things has been laid and thus for Industry 4.0 and Research 4.0.

Industry 4.0

In 2012, the German Federal Government set up a group of experts to analyse the opportunities and perspectives of information and communication technologies. As a future project of the high-tech strategy of the Federal Government, Industry 4.0 was born as a working concept. A group of experts was assigned the task of investigating the possibilities of information technology and digitisation in production research. The topic should be analysed across industries and disciplines for Germany as a business location. The inclusion of disciplines outside of the industry creates accents and emphases far beyond the core topic.

The core element of the "Industry 4.0" concept is the intelligent factory - the smart factory. The expert group appointed by the German Federal Government defines the concept of the intelligent factory as follows: "It is characterised by a new intensity of socio-technical interaction of all actors and resources involved in the production. The focus is on the networking of autonomous, self-controlling, self-configuring, knowledge-based, sensor-supported and spatially distributed production resources (production machines, robots, conveyor and storage systems, operating resources), including their planning and control systems. The smart factory is characterised by end-to-end engineering that includes both production and the product that seamlessly meshes the digital and physical worlds. The smart factory is also embedded in cross- company value networks" (Kagermann et al., 2012).

From the perspective of information technology, the eye-catching name "Industry 4.0" is used to: "propagate the widespread entry of information and communication technology and its networking into an Internet of Things, Services and Data that enable real-time production capability. Autonomous objects, mobile communication and real-time sensors allow new paradigms of decentralised control and ad-hoc design of processes. The ability to respond quickly and flexibly to customer requirements and to economically produce large numbers of variants at low batch sizes will increase and thus increase competitiveness once again. New forms of customer-integrated business processes become possible. The full-bodied promised "fourth industrial revolution" seems within reach" (Spath et al., 2013).

Therefore, the technology should be intelligent and able of organising itself. The production line divided in modules, which become cyber-physical systems that network with each other. Ahrens tries to get to the bottom of this terminology and delimited the artificial intelligence of technology from the human-centred concept of intelligence. He puts it: "Against such a background, it does not matter if technology is artificially intelligent or not, but on the fact that it supports people in bringing their intelligence and autonomy to full effect" (Ahrens, 2014a)

Transferring the principles of Industry 4.0 to Research 4.0

Adapting a definition of the main four goals in Industry 4.0 made by the German Federal Ministry of Education and Research (BMBF, 2017), a future project Research 4.0 shall aim to enable the development of innovative products (e.g. high performance fibres) by achieving the following goals:

- Delivering a high degree of flexibility in the spinning plants under the conditions of a high adaptability of the processes to new findings from the research work.
- Equipment supplier and researchers work in a close cooperation during the decision- making and development process.
- The development of the new products is accompanied by high quality services.
- Intelligent monitoring and decision-making processes are designed to enable researchers to control their experiments in real time and to easily make optimisation adjustments.

VDMA (the German Association of the Mechanical Engineering Industry) has developed a toolbox to support idea generation in the context of Industry 4.0. The stages of development represent the path to the realisation of the visionary final stage of Industry 4.0. We have tried to measure and evaluate our development according to this realisation concept (Stahl et al., 2016).

The toolbox allows the comparison of products with a benchmark of different goals that need to be met for a successful implementation of the vision Industry 4.0 (Stahl et al., 2016):

- Product related aspects
- Integration of sensors / actuators
- Communication and connectivity
- Functionalities for data storage and information exchange
- Monitoring
- Product-related IT services
- Business models around the product
- Production related aspects
- Data processing in production
- Machine-to-machine communication M2M
- Company-wide networking of production
- ICT infrastructure in production
- Man-machine interfaces
- Efficiency with small batches

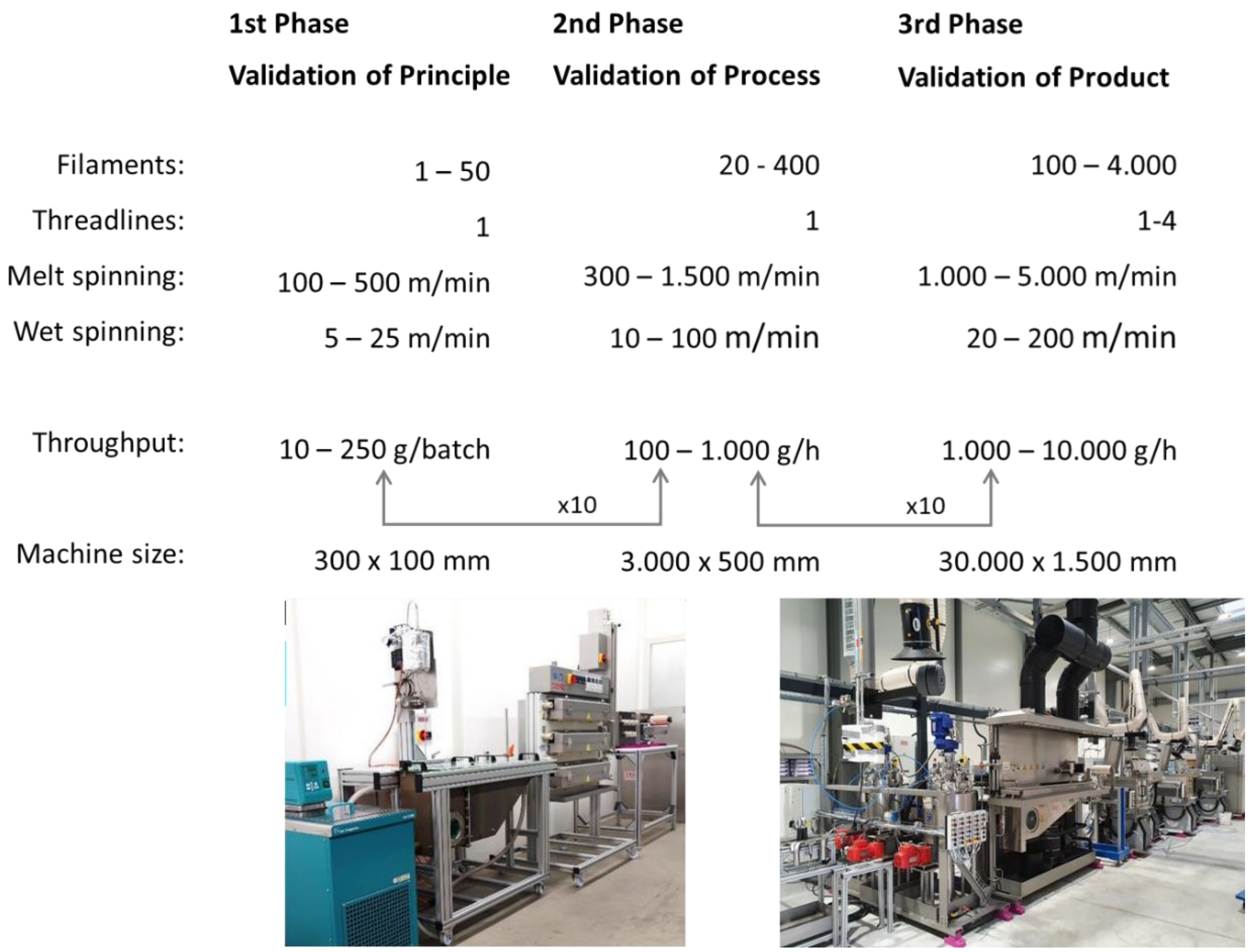
Implementation of Research 4.0 – MultiMode®

Research 4.0 at DIENES aims to enable researchers working on their development optimally supported by the system. The approach chosen has been a human-centred approach to create a system that can operate autonomously and with the capacity of organising itself. Either the starting point is technology which shall be equipped with social skills and characteristics such as in intelligence, autonomy and self-organisation, or the human being is the starting point and the technology the one to be reshaped to better support people in bringing their capabilities and qualities to full effect (Ahrens, 2014a).

The research work in the field of fibre development is characterised by a high degree of adaptation needs. The research facilities must be able to be adapted after initial experiments and the knowledge gained thereby. The necessary adjustments are made under the conditions of a highly complex manufacturing process, which is determined by many influencing parameters. This results in the following requirements for the flexibility of the electronics control of the research facilities:

- INTEGRATION: Easy integration of new production modules
- SCALABILITY: Easy replacement of production modules with modified specifications (e.g. throughput).
- FLEXIBILITY: Easy change of the order of production steps through configuration and integration of measurement and analysis sensors through multi-loop control
- HIGH PERFORMACE: Intelligent production modules for fast process interventions and synchronisation of the process control by a master control
- ANALYTICS: Convenient monitoring and evaluation options of the process parameters by a higher-level configurable PC-based process monitoring system.

The development of new innovative filaments demands an efficient systematic and, in part, self-optimising experimental working system, which must be intelligent in gathering data from the process and flexible in enabling the rearrangement of the process. DIENES' implementation of the Research 4.0 approach is called Multimode®. Due to the flexibility, Multimode® offers a tool for the development of a product from the idea to the practical implementation. Due to its modular conceptual approach, a MultiMode® pilot plant is suitable for the complete validation process: principle → process → product.



	1st Phase **Validation of Principle**	**2nd Phase** **Validation of Process**	**3rd Phase** **Validation of Product**
Filaments:	1 – 50	20 - 400	100 – 4.000
Threadlines:	1	1	1-4
Melt spinning:	100 – 500 m/min	300 – 1.500 m/min	1.000 – 5.000 m/min
Wet spinning:	5 – 25 m/min	10 – 100 m/min	20 – 200 m/min
Throughput:	10 – 250 g/batch	100 – 1.000 g/h	1.000 – 10.000 g/h
Machine size:	300 x 100 mm	3.000 x 500 mm	30.000 x 1.500 mm

Figure 82. MultiMode® – Validation process of principle, process and product (Source: DIENES)

The structure of the MultiMode® system

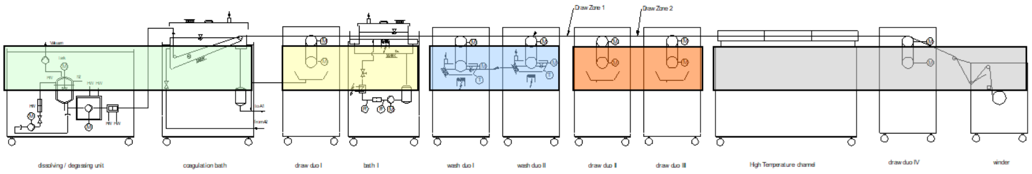
Under Multimode® every module represents a production step and can store knowledge at module level and act according to the function of the module in interaction with other modules. The Multimode® system runs on three levels:

- Slave (level 1 - MMS: MultiMode® Slave)
- Master (level 2 - MMM: MultiMode® Master)
- Upper control (level 3 - MME: MultiMode® Explorer)

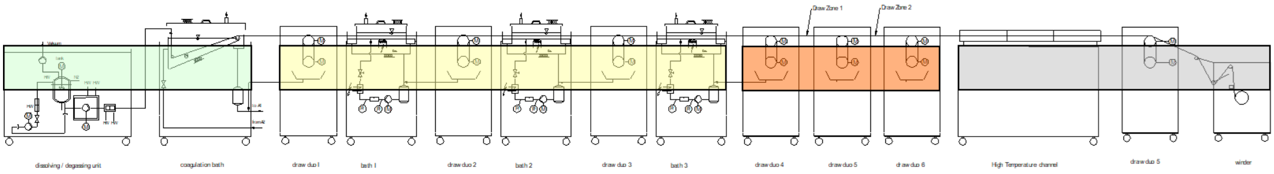
The requirements for a flexible control system have reached very high technical level alongside expectations from the user regarding ergonomic demands for the interaction with HMI (Human Machine Interface) and the equipment. The MultiMode® concept fulfils the following requirements:

- Easy extension or re-organisation of the modules in the system.
- Various process ideas can be tried out in one day by modifying the modules.
- Enables the operation of individual modules outside the plant.

The configuration of the system follows a hierarchical structure. The foundation is formed by the yarn treatment modules such as washing duo, washing bath or the spinning unit. Each of these MMS modules is equipped with a MultiMode® box, hence it is equipped with its own the intelligence based on a PLC to control itself and to organise the module in association with other modules in the plant. A single module can automatically take over a thread from a non- MultiMode® plant and process it, e.g. as an additional drafting stage or to eject a thread from a system and wind it up.



Option 1



Option 2

Figure 83. MultiMode® – Configuration change without programming (Source: DIENES)

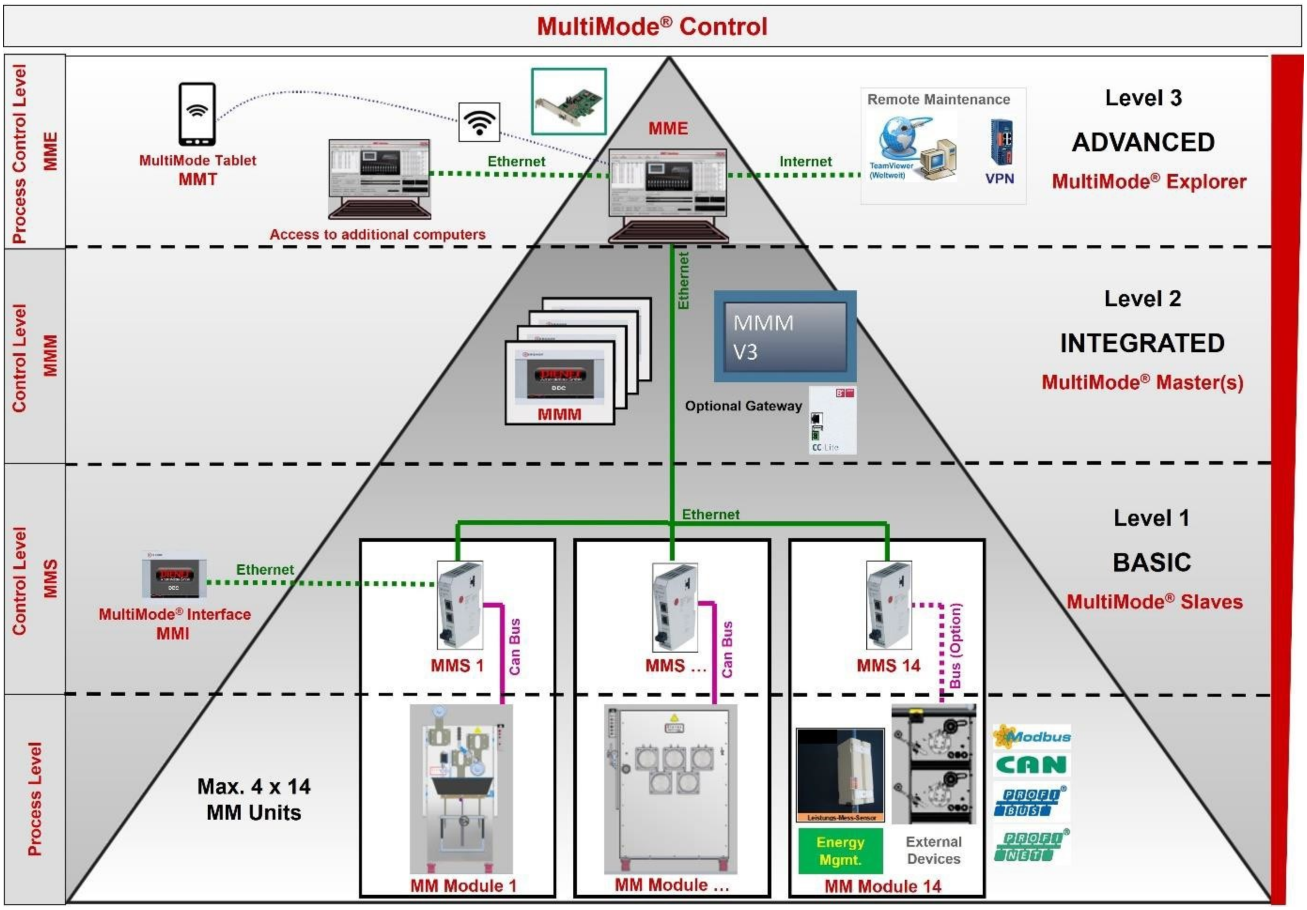


Figure 84. MultiMode® – Hierarchical structure (Source: DIENES)

Control hierarchy has an intelligent modular structure that configures itself according to the arrangement of modules given by the hardware and the interfaces within the system. Thus, a structure is realised that allows new arrangements by configuration and without any programming work required. From a control perspective, the process level with the MultiMode® boxes forms the control level "BASIC" with the MMS modules. Up to 14 of these basic modules can be switched to one MMM. This second control level "INTEGRATED" is organised by the MMM, which is also responsible for configuring and forwarding the information to the computer-based MME. The computer level control (MME) can be connected with 4 MMMs, that gives the possibility of 56 MMS modules connected to their corresponding MMM with their own local input displays or to an industrial PC via gateways allowing all visualisation and control options by means of a touch screen. The upper control level is the process control level "ADVANCED" and organises the elegance functions of the system.

The functions included at the MME include features like:

- Real-time evaluation of all sensors, which can be combined with each other in graph
- Data logging with a connection to an SQL database every second.
- Data management. The system has the possibility to transfer recorded data to EXCEL for further analyse.
- Access control with user administration (password protected) with different access levels to the operation system
- Tracking of all operator inputs (operator login required)
- Recipe management for saving current settings as a recipe under a freely assignable name to be used a later moment if necessary
- Alarm logging
- Mini-monitoring. Single parameters can be monitored in a small screen-in-screen application in real time. It is possible to add additional parameters to the “mini-monitor” and generate ad-hoc visualisations making it a quick and easy way for the user to analyse correlations between different production parameters.
- Long-term-monitoring of operation parameters.
- Printer function with no limitations allow printouts and screenshots of any view or diagram on the screen.
- Notepad function for making notes on the screen. When printing the full screen, these notepads are also printed.

If the MultiMode® line is connected to a wireless network of the Internet (e.g. via VPN), the MME offers additional functions: remote access to the plant for service and operation, operating the line via mobile phone or tablet (via DIENES app), etc.

Evaluation of the MultiMode® system with the Industry 4.0 benchmark

In section “Transferring the principles of Industry 4.0 to Research 4.0” a benchmark developed by VDMA was presented as a possible way to validate the adequacy of a concept or product to the principles of Industry 4.0 (Stahl et al., 2016). In this section VDMA’s guideline will be used to evaluate the MultiMode® approach as a Research 4.0 solution.

Product related aspects

Integration of sensors / actuators

Integration of sensors and actuators has been a standard in research facilities for a long time. As an example of further integration of sensors/actuators the speed control of godets is nowadays solved by thread tension control instead of fixed draw ratios. Thus, yarn tension sensors are used, which are analysed and interpreted to readjust the godets' drives accordingly.

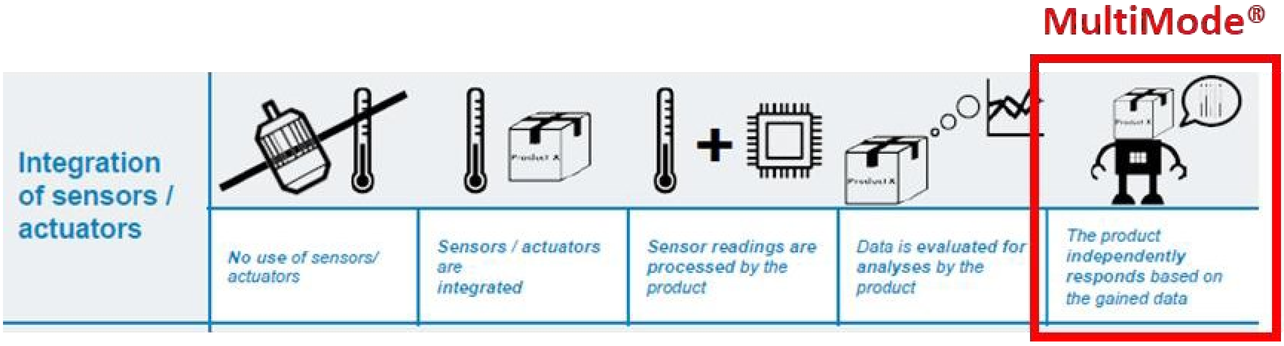


Figure 85. Integration of sensors / actuators (Source: VDMA)

Communication and connectivity

MultiMode® systems have open interfaces and are able to integrate various third-party products. It is compatible with today's common BUS systems. Access to the Internet allows a remote connection with the system. Remote service and support can be delivered this way.

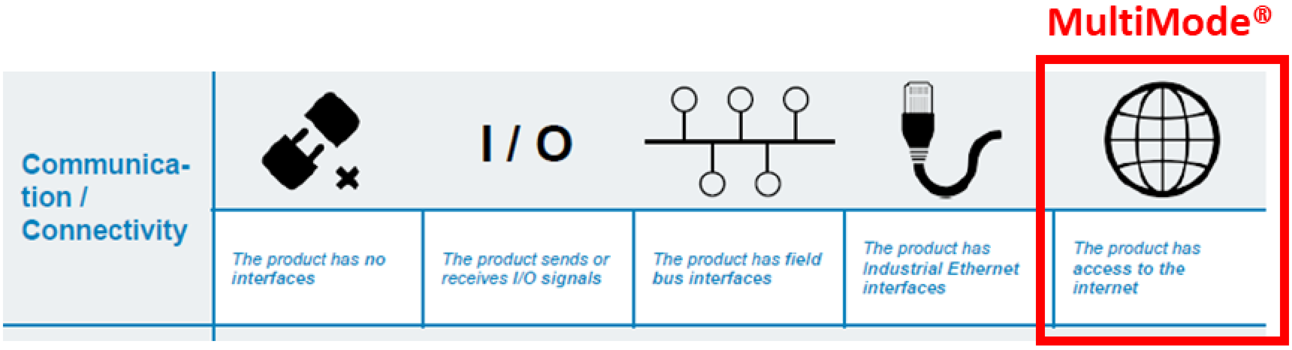


Figure 86. Communication and connectivity (Source: VDMA)

Functionalities for data storage and information exchange

The Multimode® System has an upper control system (MME) in which elegance functions are performed. This ranges from a single data monitoring that allows the researcher to explore system contexts and to analyse time series of data taken every second. To confirm correlations of a pair of data, the researcher can initiate long-term monitoring for confirmation and record the data every second within a defined time. Data can be graphically displayed. The selection of data to be recorded is arbitrary and freely selectable as every data is accessible. The system can transfer the data in a processable format (e.g. EXCEL file) for further analysis.

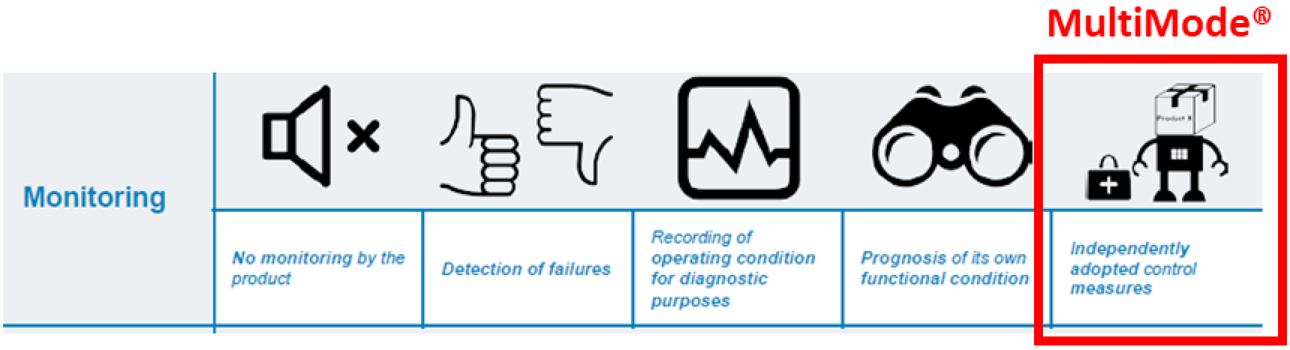
MultiMode®

Functionalities for data storage and information exchange	No functionalities	Possibility of individual identification	Product has a passive data store	Product with data storage for autonomous information exchange	Data and information exchange as integral part

Figure 87. Functionalities for data storage and information exchange (Source: VDMA)

Monitoring

A MultiMode® system is able to write down all production parameters defining the current state of the line to the second. This allows the researcher, in an attempt to produce a yarn in the event of success, to identify the adjustment parameters associated with that successful yarn section in the system and replicate the production conditions.



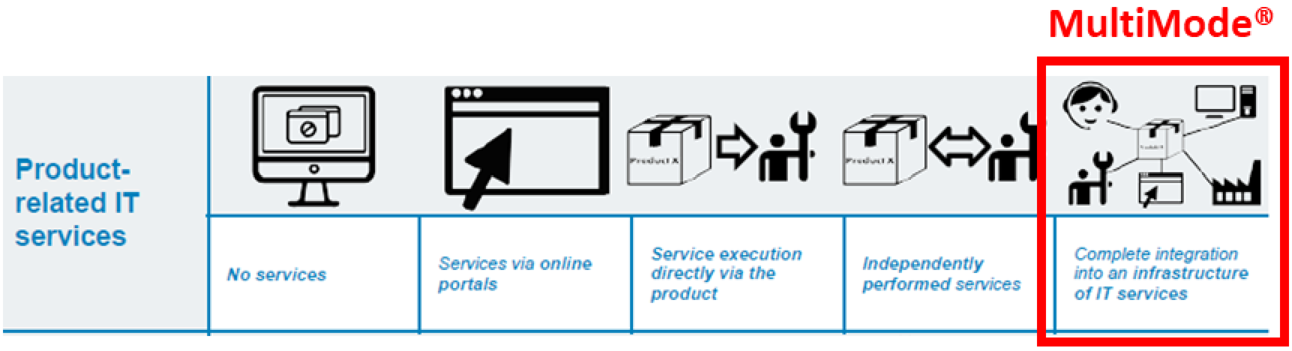
MultiMode®

Monitoring	No monitoring by the product	Detection of failures	Recording of operating condition for diagnostic purposes	Prognosis of its own functional condition	Independently adopted control measures

Figure 88. Monitoring (Source: VDMA)

Product-related IT services

If the access via VPN is granted, a full range of remote support and service is possible. Access to the line via mobile devices can be also organised this way.



MultiMode®

Product-related IT services	No services	Services via online portals	Service execution directly via the product	Independently performed services	Complete integration into an infrastructure of IT services

Figure 89. Product-related IT services (Source: VDMA)

Business models around the product

The remote connection and the possibility to store and monitor big amounts of production data makes a complete integration of services possible.

Figure 90. Business models around the product (Source: VDMA)

Production related aspects

Data processing in production

Data are collected and the process is monitored automatically while the evaluation of the running conditions of the plant is still done manually. The evaluation of the dependency on various parameters is supported by analysis tools and allow systematic correlations to be identified in prototype plants in order to automate processes in subsequent production on large-scale plants.

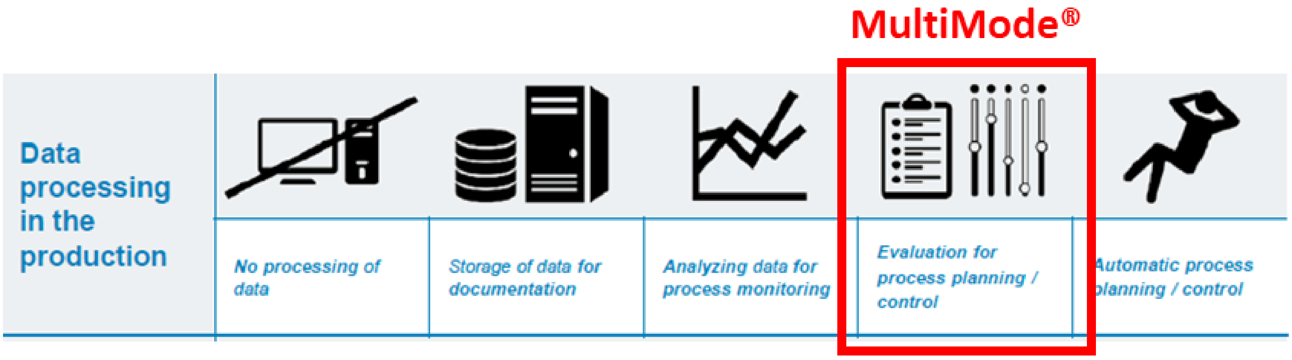


Figure 91. Data processing in production (Source: VDMA)

Machine-to-machine communication M2M

MultiMode® provides the necessary interfaces for intelligent communication between the modules. A special feature is the self- organisation of the MMM after a rearrangement of the MMS modules at machine level. Communication with external units, i.e. access to the system from the outside via mobile devices or Internet or even reporting an alarm of the system to external devices is possible.

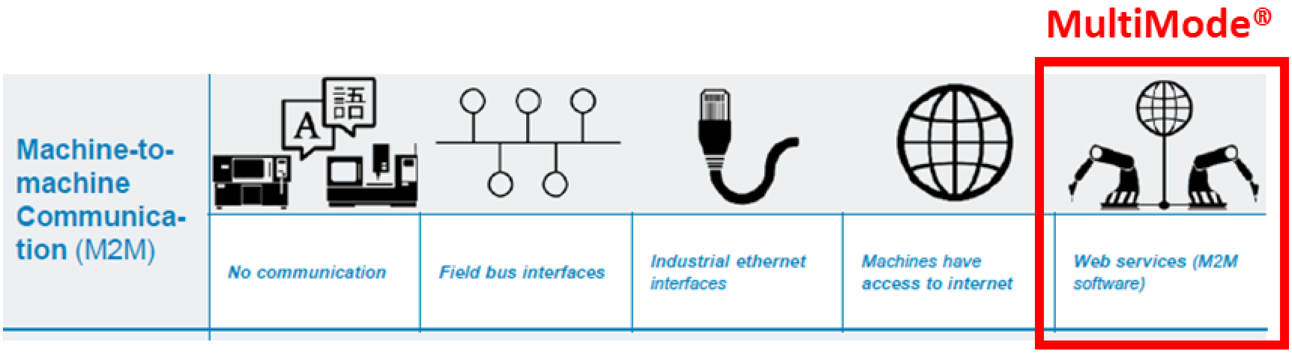


Figure 92. Machine-to-machine communication M2M (Source: VDMA)

Company-wide networking of production

An enterprise-wide communication of the individual research results, which are obtained by pilot lines in the research departments, does not seem as a main goal. Within the research plant environment, it is possible to allocate the respective running conditions to the second of the produced yarn quantity and to communicate them within the researchers' network. This information is available in a processed format. If the research team wants it, the results from their work can be stored into a data server (SQL) which can be used as a knowledge database.

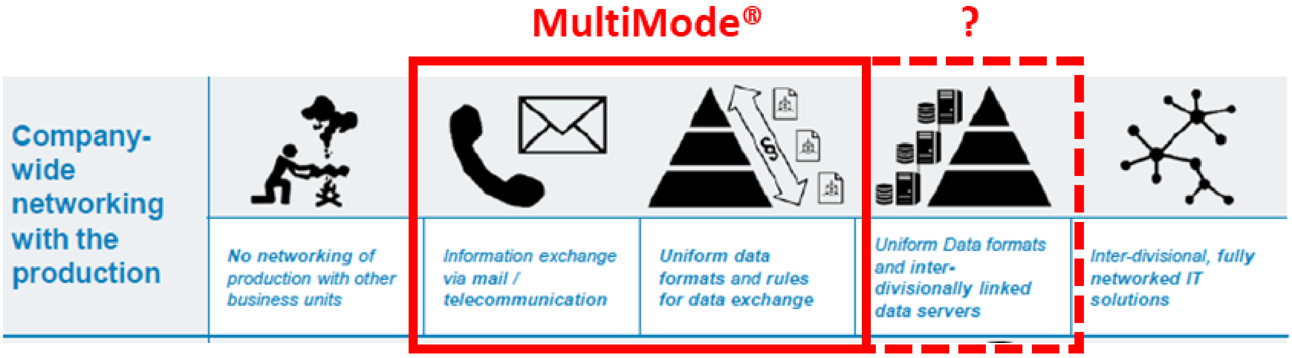


Figure 93. Company-wide networking of production (Source: VDMA)

ICT infrastructure in production

The infrastructure of Information and Communications Technology (ICT infrastructure) has different priorities in research than in production. The network does not have to go beyond the normal connection to the intranet and the normal connection within the company. Connecting a MultiMode® system to research partners is possible. Partners can access the system remotely via software (TeamViewer) and also call technical support via remote access service. Experimental design and statistical trial optimisation are still outside the MultiMode® system. Integrating these tasks and developing concepts for automation here are further development stages for the future.

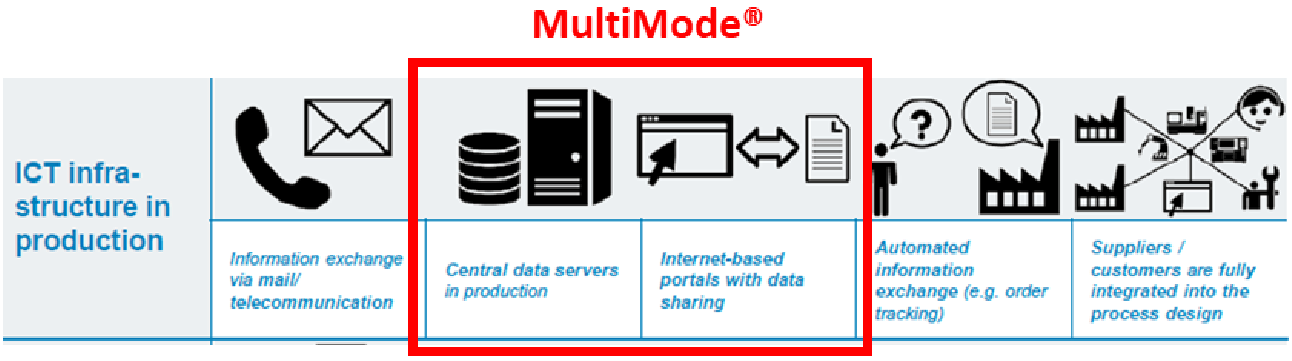


Figure 94. ICT infrastructure in production (Source: VDMA)

Man-machine interfaces

The use of mobile devices allows watching and controlling functions. Apps have been currently developed that use a mobile device to exchange data with the MultiMode® control system via a WLAN limited to the system. The setting of on-site parameters exactly at the point where the yarn forms or the yarn runs over a pair of godets allows the researcher to observe the change in the process in real time. Operators don't have to walk all the way down to MMM or MME.

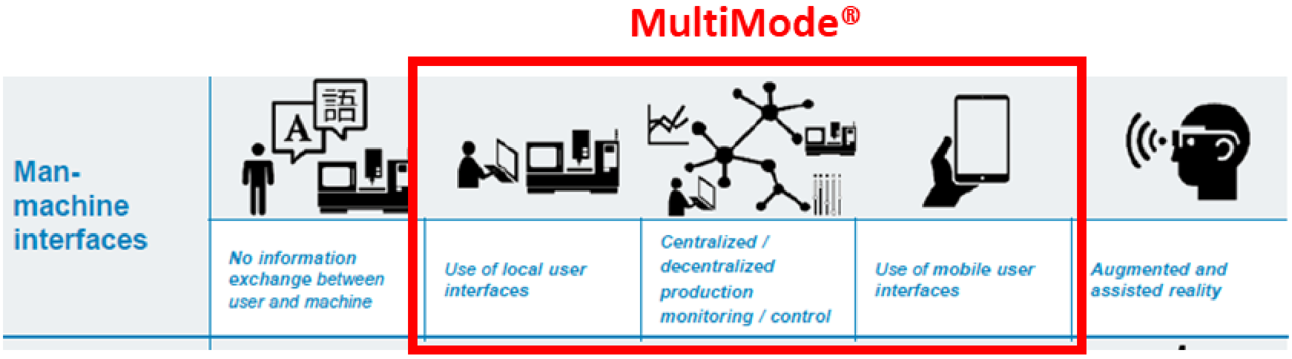


Figure 95. Man-machine interfaces (Source: VDMA)

Data processing in production

In terms of a high degree of flexibility, which makes it possible to carry out experiments efficiently and goal-oriented, two tools have to be mentioned: a very detailed recipe management allows the storage and use of operational parameters from already performed experiments and the continuous tracking and monitoring of operational parameters.

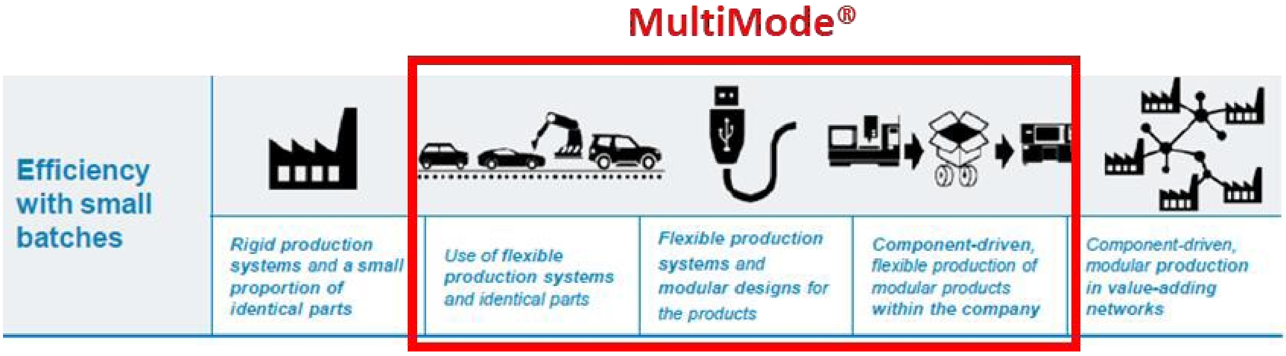


Figure 96. Data processing in production (Source: VDMA)

Conclusion

Many aspects of the Industry 4.0 approach, which have been developed for industrial production, are transferable to research production facilities resulting in a Research 4.0 approach. A full integration into the logistics chain of production is less important in this case. However, the researcher needs to be enabled to managing digitally the entire process flow of his research work. Research 4.0 offers transparency within the working process and a traceability of the results supporting the research team ins its creative work and keeping open all paths to innovative developments.

MultiMode® has been presented as a Research 4.0 solution developed by DIENES. The approach chosen has been a human-centered approach to create a system that can operate autonomously and with the capacity of organising itself. A benchmark developed by German experts has been used to evaluate how MultiMode® meets most of the requirement drawn for Industry 4.0. All product-related aspects are met to their full extent while some production-related need some improvement: e.g. integration of big data analysis to recognise patterns and apply them to an automatic process planning and control, implementation of augmented reality solutions to enhance the man-to-machine interaction (e.g. VR googles), etc.

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Your Experts in Fiber Processing

DIENES

From Industry 4.0 to Research 4.0.
A modular approach for the development of cellulosic fibres

RESEARCH 4.0 as adaptation of INDUSTRY 4.0

Human-centered approach to create a system that can operate autonomously and with the capacity of organising itself.

- Delivering a high degree of flexibility in the spinning plants under the conditions of a high adaptability of the processes to new findings from the research work.
- Equipment supplier and researchers working in a close cooperation during the decision-making and development process.
- Intelligent monitoring and decision-making processes are designed to enable researchers to control their experiments in real time and to easily make optimisation adjustments.

Research work in the field of fibre development is characterised by a high degree of adaptation needs. Necessary adjustments are made under the conditions of a highly complex manufacturing process. This results in the following requirements :

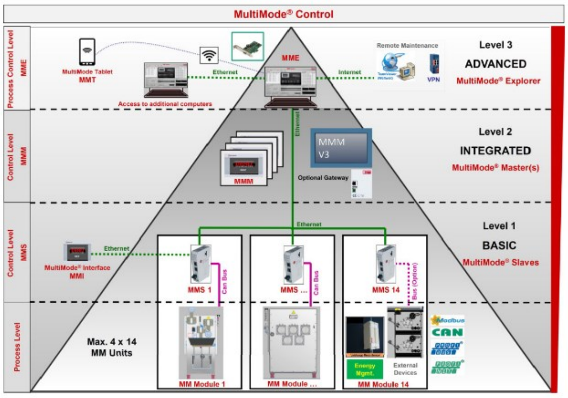
INTEGRATION	Easy integration of new production modules
SCALABILITY	Easy replacement of production modules with modified specifications
FLEXIBILITY	Easy modification of production steps' positioning within the production line
HIGH PERFORMANCE	Intelligent production modules synchronized by a master process control level
ANALYTICS	Continuous monitoring and evaluation of process parameters

The Multimode® system runs on three levels: Slave, Master and Explorer

Each Multimode® module represents a production step and can store knowledge at module level and act according to the function of the module in interaction with other modules.

MultiMode® fulfils the following requirements:

- Easy extension or reorganisation of the modules in the system.
- Various process ideas can be tried out in one day by modifying the modules.
- Enables the operation of individual modules outside the plant.



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Spindyeing Man-Made Cellulose Fibres with Vat Dyes

Nicole Nygren, Marike Langhans, Marja Rissanen, and Michael Hummel

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Abstract

Textiles are an important part of our everyday life, and the pace of production has increased worldwide, especially in the past few decades. The textile industry is one of the most polluting industries, with the dyeing process being the step with the highest environmental impact. There has been a rise of awareness among consumers of the issues related to fast fashion and the environmental impact that it has. This has led to a demand for bio-based and biodegradable fibres as the consumers behaviour has started to be affected.

The impact of the dyeing process could be lowered through spindyeing, which is already used for colours in synthetic fibres that are produced in big quantities. In our research we have applied this method to dry-jet wet spinning of man-made cellulose fibres using different Vat dyes (i.e. Indigo, Indanthren BrGreen FFB Coll, Indanthren Red FFB Coll, Cibanon Olive BMD & B2G MD, Cibanon Brilliant Orange 3R MD, and Cibanon Marineblau).

The dyed fibres showed high fibres properties comparable to undyed fibres with tenacities up to 53,91 cN/tex and elongation up to 11,6 %. The wash and rubbing fastness of the knitted fabrics were studied and compared to conventionally dyed fabrics.

**Aalto University
School of Chemical
Engineering**

Spin-dyeing man-made cellulose fibres with Vat dyes

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Department of Bioproducts and Biosystems Aalto University, FI-00076 Aalto, Finland

NWBC 25-27.10.22

Introduction

The textile industry is one of the most polluting industries

The dyeing process is the step with the highest environmental impact

The need for bio-based and biodegradable fibres is rising quickly

Spin-dyeing is proposed as a more environmentally friendly solution to traditional dyeing.

Saves water

Saves energy

Reduces the need for harmful chemicals

Reduces the CO_2 footprint

Reduces the amount of effluents and wastewater

Conclusions

- It is possible to spin-dye Ioncell fibres with Vat dyes
  - ➢ No significant changes in the fibres' tensile properties
  - ➢ The trend is that the addition of dye slightly lowers the tenacity of the fibres
- Reactive dyes washes out during the spinning process
- Pigments gave very good dyeing results, with lower amounts of dye
- The dyed fabrics have excellent wash fastness and rubbing fastness
- The produced yarn (20 tex) has an elongation up to 7 % and a tenacity up to 31 cN/tex.
- There is potential to recycle both the fabrics [1] produced as well as the ionic liquid from the spin bath [2].

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BUSINESS FINLAND

EXPANDFIBRE

Results

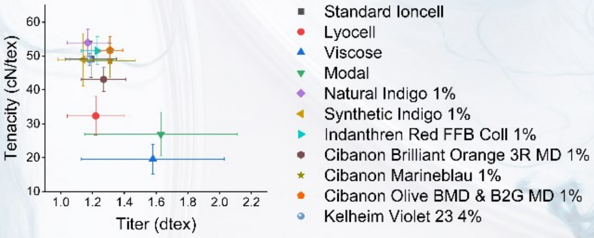


Figure 1. The effect of the different dyes compared to commercial staple fibres and standard Ioncell

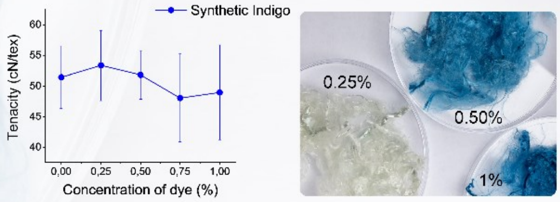


Figure 2. The effect of the dye concentration on the tenacity of the fibre.

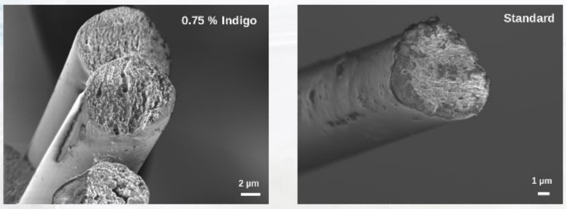
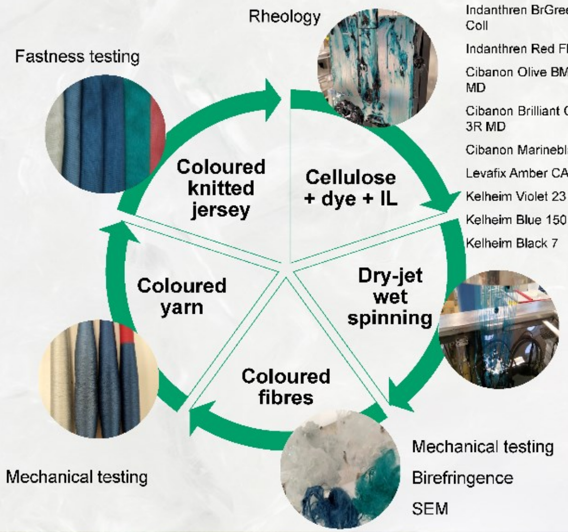


Figure 3. SEM pictures of the cross-section of spin-dyed fibre (0,75% Indigo) and standard Ioncell fibre

Materials & Methods



Rheology

Fastness testing

Coloured knitted jersey

Cellulose + dye + IL

Coloured yarn

Dry-jet wet spinning

Coloured fibres

Mechanical testing

Mechanical testing

Birefringence

SEM

Dyes:

Natural Indigo

Synthetic Indigo

Indanthren BrGreen FFB Coll

Indanthren Red FFB Coll

Cibanon Olive BMD & B2G MD

Cibanon Brilliant Orange 3R MD

Cibanon Marineblau

Levafix Amber CA-N

Kelheim Violet 23

Kelheim Blue 150

Kelheim Black 7

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Functionalized Biocelsol - Regenerated Cellulosic Fibres with Improved Dyeability with Anionic Reactive Dyes

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Abstract

Majority of current textile fibres are produced from oil-based raw materials and thus have a role in global warming and micro plastic issue. This has created an opportunity to increase the production of man-made cellulosic fibres (MMCFs), and consequently boosted the development of novel technologies in the field of cellulose dissolution and regeneration. Special properties of MMCFs will reassert the fibres as replacement for the existing oil-based fibres and thus fill the gap in demand.

The functionalized Biocelsol fibres used in this work were produced by wet spinning technique from the cellulose dope containing low amounts of 3-allyloxy-2-hydroxypropyl substituents. These substituents provided reactive double bonds in the structure of regenerated fibres. The functionalization was done by attaching amine groups in the fibres. The formed functionality is permanent and proofed to enhance the dyeability of fibres significantly.

The efficient dyeability was seen as darker shade of textile made from functionalized fibres compared to the textile made of reference fibres when using the same amount of dye. This property enables to decrease the dye and electrolyte concentrations in the dye liquor or use totally salt-free dyeing approach. All the options will reduce the environmental impact of textile dyeing by decreasing the formation of toxic filtrates and spent liquors.

In this work the improved dyeability was used as a design effect (tone-on-tone) in knitted textile by altering the yarns made of reference and functionalized Biocelsol fibres according to designed pattern. The textile was dyed after knitting in one dyeing bath providing different shades for parts prepared from reference and functionalized yarns.

Functionalized Biocelsol - regenerated cellulosic fibres with improved dyeability with anionic reactive dyes

Marianna Vehviläinen[1], Marjo Määttänen[1], Harri Setälä[1,2] and Marja Rissanen[3,4]

[1]VTT, [2]current Spinnova Ltd, [3]Aalto University, [4]current Tampere University of Applied Sciences

Why functionalization?

- Chemical functionalization of man-made cellulosic fibres (MMCFs) reasserts the fibres as replacement for oil-based fibres
- Functionalization of fibres increases the usability of the fibres and provide textile fibres for special products with functional properties such as hydrophobic, hydrophilic, fire-retardant, antimicrobial properties or improved dyeability
- Functionalization is more permanent and requires lower chemical dosages than conventional finishing

Functionalized Biocelsol fibres for enhanced dyeability

The functionalized Biocelsol fibres were produced by wet spinning technique from the cellulose dope containing low amounts of 3-allyloxy-2-hydroxypropyl substituents (Allyl). These substituents provided reactive double bonds in the structure of regenerated fibres. The functionalization was done by attaching amine groups in the fibres. Four types of fibres were spun to yarns: Biocelsol reference without modification, Allyl-substituted Biocelsol, Amino-functionalized Biocelsol and Viscose fibres. The yarns were knitted into a textile structure, that was dyed with reactive dyes in a salt-free dyebath. The efficient dyeability of yarns made from functionalized and other Biocelsol fibres compared to the viscose fibres is visualized by darker stripes in designed textile (Figure 3)

Fig.1. Process for producing functionalized Biocelsol textiles

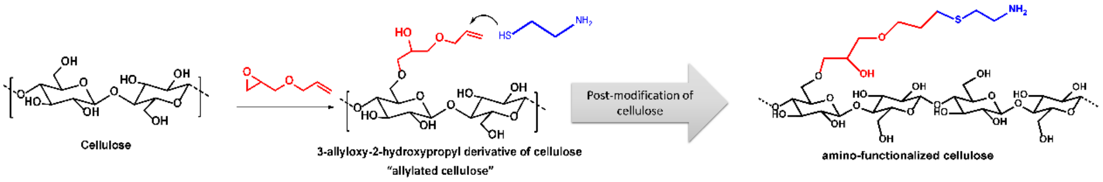

Figure 2. Chemical modification by allylation and then functionalization with thiol reagents such as cysteamine.

Figure 3. FuncBiocelsol dress.

Yarns used in the dress (from the lightest to the darkest green shade): Viscose, Biocelsol, Allyl-substituted Biocelsol and Amino-functionalized Biocelsol.
The prototype outfit is designed by Susanna Raiskio, Aalto University
Photo: Mikko Raskinen/Aalto University

Conclusion

- Chemical modification and functionalization of Biocelsol fibres improved dyeability (absorption and fixation) of reactive dyes
- Possibility to decrease dye or salt amount in dyeing ➡ reduction in water effluents
- Treatment can create interesting visual effects and patterns
- Dyeing is one example for chemical functionalization of man-made cellulosic fibres

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beyond the obvious

Wood Based Textile Solutions

Enzymatic High-Consistency Processing of Softwood and Eucalyptus Kraft Pulps for Textile Fibres

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Abstract

The use of paper grade pulp is an intriguing possibility for broadening the raw material base for regenerated textile fibres. However, the use of kraft pulp requires modification of the molecular weight distribution of cellulose prior to dissolution to ensure good dope quality. Enzymes offer a possibility for selective modification of cellulose and hemicellulose Mw of kraft pulps. Previously, the combined mechano-enzymatic treatment has been shown to allow decreasing enzyme dose and time required for the treatment. Thus, combined mechano-enzymatic pulp processing done at high pulp consistency could be an industrially feasible and environmentally benign way to adjust the molecular weight of kraft pulp prior to dissolution. In this work, the possibilities to adjust the molecular weight of softwood and eucalyptus kraft pulp fibres at high consistency were studied using enzymes capable of hydrolysing cellulose and hemicellulose polymers. Interestingly, with sole endoglucanase, the dose needed for the treatment of eucalyptus kraft pulp treatment was found to be nearly 30-fold higher than for softwood kraft pulp. However, modification of xylan allowed decreasing endoglucanase dose for eucalyptus kraft pulp drastically. Reasons for the different processabilities of softwood and eucalyptus kraft pulps are suggested.

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Enzymatic high-consistency processing of softwood and eucalyptus kraft pulps for textile fibres

Elisa Spönla • Jenni Rahikainen • Stina Grönqvist
VTT Technical Research Centre of Finland, Espoo, Finland

Introduction

The use of paper grade pulp in the production of regenerated textile fibres is an intriguing possibility enabled by novel technologies that dissolve and regenerate hemicelluloses together with cellulose. The use of paper grade pulp calls for adjustment of the viscosity of cellulose prior to dissolution to obtain good solubility and spinnability. Endoglucanases could be an industrially feasible and environmentally benign alternative to modify molar mass distribution of kraft pulp prior to dissolution. High-consistency conditions are shown to enhance endoglucanase action.[1,2]

The aim of this work was to compare enzymatic treatment of softwood and eucalyptus kraft fibres at high consistency.

Materials and methods

Softwood kraft pulp (Metsä) and eucalyptus kraft pulp (Celbi) were treated at high consistency (20-24%) using a commercial endoglucanase-rich enzyme (FiberCare R) and pure *T. reesei* mannanase Man5A and xylanase Xyn11A in a farinograph mixer (Brabender, Germany) at 50 °C for 2 h using 25-30 rpm mixing.

Results

- Considerably higher endoglucanase dose was needed with euca kraft pulp to adjust pulp viscosity compared to softwood pulp (Fig. 1)
- The use of xylanase or removal of xylan with cold caustic extraction enhanced euca kraft processing with endoglucanase considerably, hemicellulases were not enhancing the action of endoglucanase on softwood kraft pulp (Fig. 1)
- Endoglucanase treatment at high consistency was found to heavily cut the softwood fibres whereas the effect on euca fibres was less pronounced on fibre length

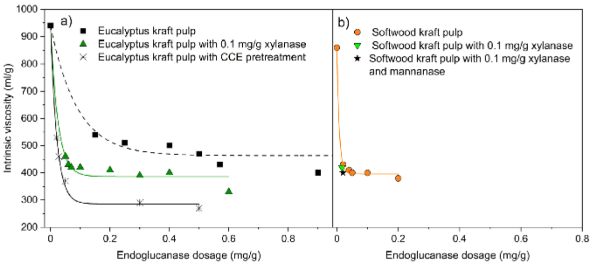

Figure 1. Intrinsic viscosity of eucalyptus (a) and softwood (b) kraft pulps as a function of endoglucanase dose in high consistency treatments (20-24% consistency, 2h, 50°C, pH 6). Xylanase and mannanase were used in some treatments together with endoglucanase and a cold caustic extraction (CCE) pretreatment was done before enzymatic treatment for some eucalyptus kraft pulp samples.

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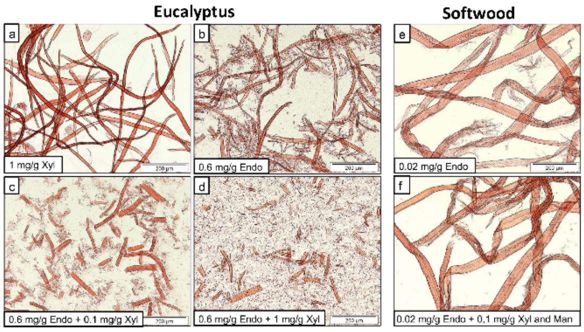

Figure 2. Optical microscopy images of eucalyptus (a-d) and softwood (e-f) kraft pulps after high consistency enzymatic treatment (20-24% consistency, 2h, 50°C, pH 6). The abbreviations endo, xyl and man correspond to endoglucanase, xylanase and mannanase respectively.

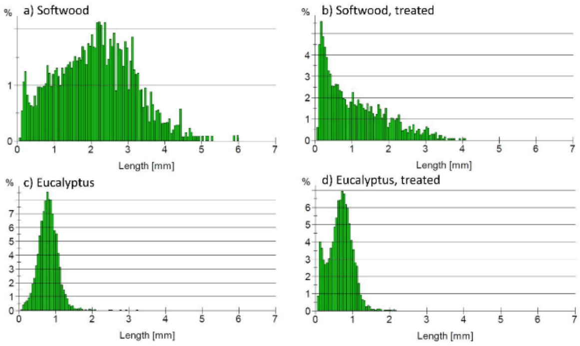

Figure 3. Weighted distributions of fibre lengths of untreated softwood (a) and eucalyptus (c) kraft pulps and endoglucanase treated softwood (b) and eucalyptus (d) kraft pulps (20% consistency, 50 °C, 2h, 0.04 mg/g and 0.9 mg/g of endoglucanase for softwood and eucalyptus pulps respectively). The treated pulp samples had similar intrinsic viscosity levels.

Conclusions

- The viscosity of softwood and euca kraft pulps can be adjusted to the desired level for dissolution using high consistency enzyme treatments
- Eucalyptus kraft pulp is more resistant to enzymatic processing with endoglucanase compared to softwood kraft pulp
- Xylan prevents endoglucanase action in eucalyptus kraft fibres by acting as a barrier for enzyme accessibility
- The shorter fibres that are less likely to be cut in high consistency processing and the barrier caused by xylan are most likely to explain the challenge of adjusting viscosity of euca kraft with endoglucanase
- In general – the cellulose polymers in euca kraft fibers are less accessible for endoglucanase enzymes compared to cellulose in softwood kraft fibres

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Author Index,
List of Tables and
Table of Figures

Author Index

Abdelaziz, Omar 217
Allahverdiyeva, Yagut 237, 239
Almhofer, Lukas 215
Alomari, Bana 88
Antonietti, Markus 211
Arkell, Anders 29, 177, 217
Arola, Suvi 111, 239
Arora, Prakhar 209
Asikainen, Jaakko 77
Bachér, John 195
Badara, Olamide 98
Balakshin, Mikhail 36, 187, 201
Bammer, Daniela 215
Battestini Vives, Mariona 217
Beaumont, Marco 104
Behfar, Mohammad 112
Berg, Mats 158
Bernardes Figueiredo, Monique 176
Bertella, Stefania 162
Bhattacharyya, Shubhankar 118
Bischof, Robert 215, 231
Bogren, Johannes 12
Borisova, Anna S. 60, 199
Borrega, Marc 18, 60, 199
Bourgeois, Antoine 176
Brännvall, Elisabet 193
Buser, Remy 176
Canga Rodríguez, José 245
Capanema, Ewellyn 29, 36
Cazeils, Emmanuel 117
Charmillot, Justine 176
Cho, MiJung 201
Dahiya, Deepika 219
Davin, Julien 124
Deshpande, Raghu 134
Dias, Ananda 11
Diment, Daryna 201
Dobele, Galina 233
Drobne, Damjana 93
Ek, Åsa 12
Ek, Monica 130
El Hajam, Maryam 241
Engstrand, Jonas 130
Esteves, Cláudia 193
Etzold, Hendrik 68
Fant, Thomas 117
Fearon, Olesya 43, 166, 195, 197
Felby, Claus 199
Filonenko, Svitlana 211
Gatt, Etienne 176
Gonzáles, Eva 107
Gröngröft, Arne 68
Grönqvist, Stina 25, 147, 182, 213, 263
Guizani, Chamseddine 197
Gunde-Cimerman, Nina 93
Gupta, Deepika 243
Gustafsson, Birgitta 243
Gustafsson, Jan 241
Håkansson, Helena 243
Hakovirta, Marko 77
Hanhikoski, Saara 158
Hannula, Simo 147
Hannus, Mikael 11
Häntzschel, Julian 88
Härkönen, Mika 10, 17, 24
Harlin, Ali 10, 77, 147, 213
Hassinen, Jukka 25
Heilala, Maria 237
Henriksson, Gunnar 134
Henschen, Jonatan 130
Héroguel, Florent 176
Hietala, Sami 98
Holopainen-Mantila, Ulla 199
Hörhammer, Hanna 221
Hosseinaei, Omid 29
Hulteberg, Christian 217
Hummel, Michael 107, 259
Hupa, Leena 241
Hyppönen, Felix 229
Idrissi Kandri, Noureddine 241
Jääskeläinen, Anna-Stiina 158
Johansson, Ann-Christine 209
Johnson, Karin 10, 17, 24
Jonkergouw, Christopher 111

Jurkjane, Vilhelmine 233
Kalliola, Anna 43, 60, 124, 166, 195, 197
Källman, Björn 118
Kamppuri, Taina 147
Kane, Anuja 243
Känsäkoski, Silja 144
Karami, Peyman 162
Karisalmi, Kaisa 158
Kasipandi, Saravanan 144
Kellock, Miriam 199
Kemppainen, Katariina 124
Keränen, Janne 77
Khakalo, Alexey 112
Kilpeläinen, Ilkka 9, 148
Kilpi, Jorma 221
Kilpinen, Antti Topias 223
King, Alistair 104, 152
Klüh, Daniel 139
Köchermann, Jakob 68
Koiranen, Tuomas 139
Kokol, Vanja 93
Kononenko, Veno 93
Kontturi, Eero 98, 223, 239
Kos, Monika 93
Koso, Tetyana 104
Kosonen, Harri 152
Kosourov, Sergey 237, 239
Kröger, Marcel 98
Kruus, Kristiina 12, 199
Kukula, Pavel 229
Kumar, Vinay 112
Kuusela, Pirkko 221
Laari, Arto 139
Lahtinen, Panu 60
Langhans, Marike 259
Lappalainen, Timo 111
Lehtonen, Juha 144, 229
Leppänen, Ilona 111, 112
Levä, Tuukka 237, 239
Li, Jiebing 18, 62
Liitiä, Tiina 43, 124
Lindström, Mikael E. 134
Lipnizki, Frank 217
Lohtander-Piispa, Tia 111, 112
Luterbacher, Jeremy S. 162
Maaheimo, Hannu 199
Määttänen, Marjo 60, 213, 261
Mackintosh, William 24
Mäkelä, Mikko 197, 221, 237
Mäkelä, Tuomo 195
Mäkilä, Ermei 241
Maloney, Thaddeus 237
Marjamaa, Kaisa 199
Mathew, Aji 243
Mazar, Adil 30
Meca, Luděk 229
Meinander, Kristoffer 182
Meisel, Kathleen 68
Melin, Kristian 139
Mikkelson, Atte 60
Morina, Donika 182
Morits, Maria 182
Müller-Probandt, Steffen 245
Muratova, Madina 201
Myöhänen, Mari 158
Neethi Rajagopalan 43
Nieminen, Harri 139
Nieminen, Kaarlo 107
Nikkanen, Lauri 237
Nilsson, Pia 13
Nitzsche, Roy 18, 68, 75
Nordin, Tommy 118
Novak, Sara 93
Nygren, Nicole 259
Ohra-aho, Taina 144, 197
Öhrman, Olov G.W. 209
Ölmhult, Maria 177
Österberg,.Monika 11, 25, 105, 182
Östlund, Sören 193
Pääkkönen, Timo 98
Paleologou, Michael 18, 30
Pasanen, Antti 197
Paulik, Christian 215, 231
Peebo, Karl 48
Pehu-Lehtonen, Lauri 124
Phiri, Josphat 237
Pioletti, Dominique 162
Plavniece, Ance 233
Polizzi, Viviana 166
Potthas, Antje 147
Poukka, Outi 124
Preegel,Gert 48, 235
Questell-Santiago, Ydna 176
Rahikainen, Jenni 147, 199, 263

Rajagopalan, Neethi 43
Ralph, John 199
Rana, Vijay Kumar 162
Rautiainen, Sari 144, 229
Reddy Baddigam, Kiran 243
Reyes, Guillermo 152
Richter, Łukasz 162
Rigo, Davide 187, 201
Ringman, Jori 9, 17
Rissanen, Marja 259, 261
Rissanen, Ville 237, 239
Rojas, Orlando 25, 152
Rummukainen, Hannu 221
Ruwoldt, Jost 171, 207
Salo, Satu 182
Samec, Joseph S. M. 243
Schaper, Gerrit 88
Schlackl, Klaus 215
Schmitz, Marc 43
Scholten, Philip 176
Schöner, Jörg 158
Setälä, Harri 261
Sevastyanova, Olena 134, 193
Shafaghat, Hoda 209
Shaikh, Manzoorahmed 243
Siipola, Virpi 197
Siitonen, Vilja 237
Sipponen, Mika 11
Sirviö, Jari 221
Sixta, Herbert 9
Sjögård, Pauliina 124
Sjöstrand, Björn 243
Sjöström, Jenny 134
Slabon, Adam 231
Sorsa, Olli 197
Spönla, Elisa 60, 147, 263
Stellacci, Francesco 162
Sulaeva, Irina 147
Sundvall, Öjvind 118
Tammelin, Tekla 10, 17, 25, 111, 112, 237, 239
Tamminen, Tarja 199
Tanase-Opedal, Mihaela 171, 207
Tarasov, Dmitry 201
Teixeira Polez, Roberta 182
Theliander, Hans 134
Thuvander, Johan 217
Tomani, Per 12, 18, 29
Torvinen, Katariina 112, 197
Tropp, Uku Erik 18, 48
Tukiainen, Pauliina 24
Uhlir, Liselotte 118
van Zessen, Erik 18, 53
Vandezande, Pieter 124, 166
Vehviläinen, Marianna 213, 261
Viertiö, Tyko 229
Vikman, Minna 43
Vikström, Tomas 134
Vilkman, Marja 197
Virkkala, Tuuli 239
Virtanen, Tommi 197
Vivod, Vera 93
Volperts, Aleksandrs 233
von Weymarn, Niklas 13
Vyörykkä, Jouko 18, 43
Wadsborn, Rickard 18, 53
Wang, Luyao 241
Wng, Xiaoju 241
Wegmann, Chloé 176
Widsten, Petri 112, 182, 197
Wikberg, Hanne 124
Winberg, Iris 124
Witthayolankowit, Kuntawit 243
Wolfsgruber, Maria 231
Xu, Chunlin 241
Yamamoto, Akio 112
Yuliya, Popova 201
Zahel, Martin 88
Zerouale, Abdelaziz 241
Zhurinsh, Aivars 233

List of Tables

Table 1. Characteristics of the obtained LignoForceTM lignin. 32
Table 2. Lignin hydroxyl functional groups 32
Table 3. Plasticizer materials used in the mortar and gypsum experiments. 44
Table 4. Biodegradation and relative biodegradation of oxidized Lignins in soil and aquatic environments. 46
Table 5. Comparison of C5 and C6 sugars. 50
Table 6. Comparison of LIGNOVA Crude and Pure. 50
Table 7. LIGNOVA in the composite and PF resin industries 51
Table 8. Crude, blonde and white microcrystalline cellulose. 51
Table 9. Microcrystalline cellulose applications. 52
Table 10. Sodium and sulfur content in recovered pilot sulfur cake, washed and unwashed compared to sodium sulfate. 58
Table 11. Comparisons of different films prepared 65
Table 12. Main assumptions for costing 71
Table 13. LCB products, reference products with emission factor and substitution ratio 71
Table 14. Investment and annual costs of the lignocellulose biorefinery concept 73
Table 15. The changes in production of graphic papers, packaging paper and paperboard, paper and paperboard, excluding newsprint, pulp for paper, pulpwood, round and split, all species (production), total fibre furnish, wood pellets and other agglomerates, wood pulp and newsprint between 2000-2020, 2010-2020 and compound annual growth rate (CAGR) between 2010-2020. 79
Table 16. The average content of surface groups and hydrodynamic-size for different forms of CNF/CNC with their minimum inhibitory (MIC) and bactericidal (MBC) concentrations against (G-) E. coli and (G+) S. aureus after 24 h of exposure 95
Table 17. Zeta potential, surface charge and phosphate content reported for phosphorylated CNC and CNF compared to this work. 101
Table 18. Geometric features of the spinnerets 108
Table 19. Diameters of distribution plate holes 108
Table 20. Characteristics of kraft vs organosolv pulping regarding the LigniOx integration. 128
Table 21. Inputs and outputs of the fossil and biobased process (t/a) 142
Table 22. Pre-treatments of kraft pulps and characteristics after pre-treatment 149
Table 23. LNPs' surface density and antimicrobial properties of LNPs-coated samples 185
Table 24. Samples selected for application as a replacement of PF wood adhesives. 204

Table of Figures

Figure 1. Mechanical and physical properties of the PU foams produced in this study. 34
Figure 2. ABES bonding strength (at 90 s press time) of plywood PF blended with lignins 38
Figure 3. The effect of the L/S ratio (P-factor = 500) and P-factor (L/S=1) on the carbohydrate contents in acetone-extracted LCCs (AELs) 38
Figure 4. (a) Schematic diagram of the use of LCCNPs as surfactants in Pickering emulsion polymerization process. (b) Digital images of THFMA-Pickering emulsions stabilized with LCCNPs from AEL-500 and PLCC at different time. (c) Time evolution of mean droplet size of THFMA-Pickering emulsions stabilized with PLCC NPs and AEL-500 NPs. (d) Optical microscopic and (e) Digital images of latex dispersion after polymerization process. (f) A SEM image of the P-LCC NPs-coated poly(THFMA) microbeads after free radical polymerization at 65 ºC. 39
Figure 5. Examples of different scenarios for AqSO process as an advanced integrated biorefinery.. 40
Figure 6. Initial slump values for different plasticizer chemistries commonly used in concrete production.. 45
Figure 7. Slump values for polynaphthalenesulfonate and LigniOx K1 and LigniOx K2 in gypsum.... 45
Figure 8. Comparison of oxidized kraft lignin (LigniOx lignin) with fossil-based dispersant (left) and fossil- based superplasticizer admixture (right). 47
Figure 9. Fibenol's main process route: pre-treated biomass separation to cellulosic sugars and LIGNOVA Crude. 49
Figure 10. Fibenol's advanced process route: pre-treated biomass separation to C5 sugars, microcrystalline cellulose and LIGNOVA Pure.. 49
Figure 11. Ultilization of the Thiopaq techniqe to produce elemental sulfur from the green liquor. .. 54
Figure 12. Activity of bacteria as a function of the salt concentration and pH is 10 55
Figure 13. Sulfur produced and the bacteria in the laboratory trials (left) and crystals of sodium bicarbonate formed during the initial trials (right). 55
Figure 14. Picture of the demonstration/pilot plant used in the mill environment. 56
Figure 15. Temperature and pH profile of the reactor liquor in the demonstration plant over two years of operation.. 56
Figure 16. Flow of green liquor to the reactor over two years of operation. 57
Figure 17. Size-dependent sawdust biorefinery processes 64
Figure 18. Maximum heat release rate comparison.. 66
Figure 19. Simplified scheme of the lignocellulose biorefinery for the production of dissolving pulp, malic acid and BCD-oligomers from beechwood 69
Figure 20. Sankey diagram of the biomass and energy flow through the studied lignocellulose biorefinery 73
Figure 21. Greenhouse gas (GHG) emissions of a) the lignocellulose biorefinery products, b) of the reference products, and c) savings (PUR: polyurethane, CO_2-eq: CO_2 equivalent) 74
Figure 22. CO_2 emissions of EU-28 PPI between 2000-2015 (includes also UK)................ 80
Figure 23. Emission reduction potential form pulp industry from lignin and hemicelluloses.................... 81
Figure 24. Formation of DAC via periodate oxidation of cellulose and application as a wet strength agent by binding to cellulose fibres. 88

Figure 25. Preparation of cationic DAC using Girard's reagent T. 89
Figure 26. a) DO of produced DAC dependent on reaction time, b) IR spectra of DAC and cationic DAC (with increasing DS). c) charge of cationic DAC dependent on DS. 90
Figure 27. Relative wet strength of produced handsheets with varying amount of added DAC. 91
Figure 28. SEM images of native (CNF/CNC), oxidized (CNF/CNC-ox) and HMDA-functionalized 96
Figure 29. Reaction scheme 99
Figure 30. AFM image of the produced pCNC 102
Figure 31. AFM height image of wax particles on cellulosic thin film (upper image) and water droplets on a wax particle treated cotton fabric illustrating the waer repellance achieved by combining roughness and low surface energy. 106
Figure 32. Locations of distribution plate holes 108
Figure 33. Simulated flow magnitude in spinneret 1 having distribution plate 1 109
Figure 34. Smoothed simulated velocities at spinneret exit for different spinneret geometries and plate distributions 110
Figure 35. A. The effect of CNF to HEC medium viscosity on mechanical properties, B. the effect of HEC and HPMC at low, medium, and high viscosities with the ratio of 60:40 (CNF:additive) on the mechanical properties, and C. Images of films with poor tear resistance (left panel) and improved tear resistance (right panel). 114
Figure 36. A. Mechanical properties of films with fiber additives B. Pictures of native CNF film in comparison to films with lyocell, pulp, and MFC as additives. 115
Figure 37. A. The effect of film thickness to mechanical properties of films prepared from CNF:HEC with a ratio of 60:40 using low and high viscosity HEC. B. The tear difference between easily tearing film (left panel) and film with improved tearing resistance (right panel). 115
Figure 38. Comparison of mechanical properties of CNF films containing chestnut tannin and unbleached CNF in different ratios. B. Antimicrobial effect of the CNF films containing chestnut tannin and unbleached CNF against S. aureus. 116
Figure 39. The CrillEye module 120
Figure 40. Principle of Crill measurement 120
Figure 41. Refined fibres (left) and fibres with thin fibrils (crill) (right) 120
Figure 42. Bleached pulp 121
Figure 43. Fibre reject 121
Figure 44. Plot of Crill value of (6a) bleached pulp and (6b) rejected fibers vs hydrolysis reaction time 122
Figure 45. Solubility vs pH: Kraft and organosolv lignin before and after LigniOx oxidation. 125
Figure 46. Simplification of reactions during alkali-O_2 oxidation of lignin 126
Figure 47. A concept for combined lignin recovery, alkali-O_2 oxidation (LigniOx) and membrane filtration of oxidised lignin for the production of dispersants in a kraft pulp mill 127
Figure 48. Sodium (Na) and sulphur (S) balances of reference kraft pulp mill and different oxidation options. Grey refers to Na balance and black refers to S balance, unit of Na/S being kg/adt pulp. 127
Figure 49. Esterification of cellulose to form cellulose oxalate. 131
Figure 50. Lignin solubilizing reaction in oxygen delignification 135
Figure 51. Oxygen species present during oxygen delignification 135
Figure 52. Kappa number (a) and intrinsic viscosity (b) of reaction filtrate from kraft pulp delignified in the presence of oxygen, air or nitrogen. 136
Figure 53. pH of reaction filtrate (a) and relationship between pH and kappa number (b) from kraft pulp delignified in the presence of oxygen, air or nitrogen. 137

Figure 54. Brightness of reaction filtrate from kraft pulp delignified in the presence of oxygen, air or nitrogen. 137
Figure 55. Acetic anhydride production process (The red colored boxes belong to the coal based upstream process and the yellow colored boxes belong to the biobased process 141
Figure 56. Additional annual difference in Million €/a of biobased and fossil case 143
Figure 57. a) Stress-strain values of regenerated fibres from differently pre-treated pulps, amount of total hemicelluloses left in fibres indicated; and b) effect of hemicellulose left in regenerated fibres on elongation. 150
Figure 58. Molecular weight curves regenerated fibre (from ST-EX pulp). 150
Figure 59. Elastic moduli and effect of atmosphere condition (air-tight and in contact with open air at room 155
Figure 60. Man-made cellulosic fibers a) after spinning and bleaching with distilled peracetic acid, 160
Figure 61. Chemical structure of maleated sunflower oil high oleic (MSOHO) and impact of hydrophobation treatment on cellulosic fibres. 160
Figure 62. Overview of traditional extraction method side reactions (top) and the extraction and simultaneous functionalization of lignin with TALD and GA via AAF (bottom). 164
Figure 63. Concept for production of lignin polyacids. 168
Figure 64. Molecular weight and yield of oxidized ligninswith varying oxidation parameters. 168
Figure 65. Lignin polyacids production concept with fractionation step 169
Figure 66. SEM images of lignin coated-cellulose fibers (left) and kraft fibers (right) 173
Figure 67. Density and basis weight (left) and mechanical testing results (right) of handsheets 174
Figure 68. Water-uptake (left) and contact angle (right) 174
Figure 69. Photograph of LNPs-coated samples. 184
Figure 70. SEM image of LNPs-coated filter papers. 185
Figure 71. Outlook of reactive extraction (REx) integrated biorefinery. 188
Figure 72. Left: modification of lignin during reactive extraction (ethoxylation and esterification). Right: an HSQC spectrum of REL produced at reaction time (reflux) of 1h, [EtOH] = 70 % and [H_2SO_4] = 0.15 M. 189
Figure 73. The effect of time 190
Figure 74. LCC region of HSQC spectrum of RELs. 191
Figure 75. Experimental approach. 203
Figure 76. The effect of the enzyme load on the lignin content in enzymatic solids. 203
Figure 77. The effect of the enzyme load (10, 20, 40 and 100 mg/g) on the total glucan yield in enzymatic solids ES500, ES1000 and ES2000 204
Figure 78. The effect of temperature on the bond strength of ES- PF blends. 204
Figure 79. Visual abstract 224
Figure 80. Yields of glucose and xylose (water-soluble carbohydrates) from aspen wood flour in hydrolysis with liquid hydrochloric acid at different acid concentrations over time in 21 °C. 225
Figure 81. Yields of glucose and xylose from aspen wood flour in gas hydrolysis. 226
Figure 82. MultiMode® – Validation process of principle, process and product 249
Figure 83. MultiMode® – Configuration change without programming 250
Figure 84. MultiMode® – Hierarchical structure 250
Figure 85. Integration of sensors / actuators 252
Figure 86. Communication and connectivity 252
Figure 87. Functionalities for data storage and information exchange 253
Figure 88. Monitoring 253

Figure 89. Product-related IT services 253
Figure 90. Business models around the product 254
Figure 91. Data processing in production 254
Figure 92. Machine-to-machine communication M2M 255
Figure 93. Company-wide networking of production 255
Figure 94. ICT infrastructure in production 256
Figure 95. Man-machine interfaces 256
Figure 96. Data processing in production 257

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Title	**NWBC 2022** The 10th Nordic Wood Biorefinery Conference
Author(s)	Atte Virtanen, Katariina Torvinen & Jessica Vepsäläinen (Eds.)
Abstract	Nordic Wood Biorefinery Conference (NWBC) will present the latest discoveries and innovations in bio-based materials, chemicals, and products from wood biorefineries. Research themes of NWBC 2022 are: • Low emission biorefineries and side-stream valorization • Engineered lignin products • Novel cellulose modifications • High performing wood-based products for industrial scale • Structure – function – performance interrelations in materials engineering (including modeling) • Wood-based textile solutions • Circularity of wood-sourced carbon and emerging policies • Assessing environmental aspect The NWBC 2022 conference book will consist of 40 oral contributions including several key note speeches and 26 poster presentation. They will cover extensively many aspects of conference themes and show a way of future developments in area of wood biorefineries. The conference organizing committee wish you insightful and fruitful readings!
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