CaSH

Catalytic Slurry Hydrotreatment

VTT: Tyko Viertiö | Juha Lehtonen |
Johanna Kihlman | Laura Sokka |
Alexander Reznichenko |
University of Oulu: Ville Tuppurainen |
Salla Ala-Kokko | Salla Seppä | Juha Tanskanen |
Juha Ahola |
Åbo Akademi University: Dmitry Murzin |
Zuzana Vajglova | Päivi Mäki-Arvela |
Narendra Kumar

VTT TECHNOLOGY 425

VTT TECHNOLOGY 425

CaSH - Catalytic Slurry Hydrotreatment

Final Project Report

Tyko Viertiö, Juha Lehtonen, Johanna Kihlman, Laura Sokka & Alexander Reznichenko

VTT Technical Research Centre of Finland

Ville Tuppurainen, Salla Ala-Kokko, Salla Seppä, Juha Tanskanen & Juha Ahola

University of Oulu

Dmitry Murzin, Zuzana Vajglova, Päivi Mäki-Arvela & Narendra Kumar

Åbo Akademi University

ISBN 978-951-38-8788-9

VTT Technology 425

ISSN-L 2242-1211
ISSN 2242-122X (Online)
DOI: 10.32040/2242-122X.2024.T425

JULKAISIJA – PUBLISHER

VTT
PL 1000
02044 VTT
Puh. 020 722 111
https://www.vtt.fi

VTT
P.O. Box 1000
FI-02044 VTT, Finland
Tel. +358 20 722 111
https://www.vttresearch.com

Preface

Efficient utilisation of biomass-based side streams as a low-carbon feedstock for fuel and chemical production is one of the important paths for decarbonisation of transport and chemical industry. Broad adoption of such approach is still hindered by substantial technical challenges. While existing refinery and petrochemical operations have been developed and optimised for fossil-based feedstocks, introduction of renewable, bio-based feeds cannot in most cases be a simple, drop-in solution, with both technical and economical bottlenecks hampering such transition.

Although lignocellulosic-based bio-oils produced by thermochemical liquefaction of biomass residues became increasingly available in last decades, their utilisation rate in modern refining and petrochemical processes remained negligible. This is largely due to chemically complex and unstable nature of lignocellulosic bio-oils, as their composition is drastically different to that of conventional fossil-based feedstocks. Several attempts to upgrade the physico-chemical properties of bio-oils to reach properties of hydrocarbon fuels and chemicals via catalytic hydrotreatment process have been made over last 30 years, however no standalone upgrading process has reached full commercial maturity, mainly due to technical challenges in designing efficient and stable catalytic process and catalyst for that process.

Development of scalable and economically robust upgrading path for lignocellulosic bio-oils required a holistic approach where catalyst, process and life cycle implications are all considered and developed cooperatively. We have selected a relatively less explored path of catalytic slurry hydrotreatment to be jointly developed, tested, and evaluated within this collaborative research project.

This publication outlines and summarises the outcome of the joint 2½-year co-research project Catalytic Slurry Hydrotreatment (CaSH) carried out by Åbo Akademi University, University of Oulu and VTT. The project was coordinated by VTT and was co-funded by Business Finland, Neste, Valmet, Fortum Waste Solutions, Meriaura, ESL Shipping, Savon Voima and BMH technology along with participating research institutes as part of the Neste Veturi ecosystem.

Table of Contents

List of abbreviations and symbols

CSTR	Continuously stirred tank reactor
EXAFS	Extended X-ray absorption fine structure
HDO	Hydrodeoxygenation
IEA	International Energy Agency
LCA	Life cycle assessment
TRL	Technology readiness level
WP	Work package

1 Introduction

Actions to mitigate the climate change require dramatic transformation of critical value chains in energy, transportation, and chemicals sectors. Development and implementation of fossil-free technologies is among main technical enablers for such mitigative actions. As direct electrification cannot fully replace fossil fuels in transportation sector, sustainable fuel options are especially needed for marine and aviation fuels. The share of advanced biofuels is expected to reach 15-20 % of the global transportation energy demand in 2035 (Figure 1).

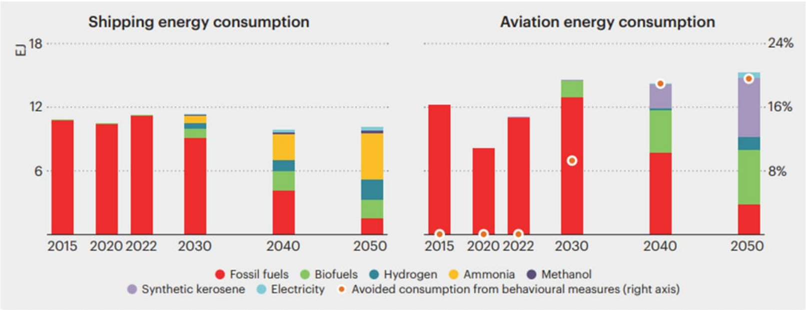


Figure 1. Projected energy consumption and energy carrier types in marine and aviation transport. Image and data from IEA report.[1]

Sustainable, low carbon paths to chemicals, polymers and transportation fuels are thereby critically needed to secure supply of crucial materials of high demand and societal value, and lignocellulosic biomass residues can play a major part in such transition.

Bio-oil production from pre-treated biomass side streams is a commercial technology deployed at small industrial scale. On the other hand, robust catalytic upgrading of the bio-oils into hydrocarbons which in turn can be processed to final transportation fuels or chemicals in existing refinery settings, has not been commercialized yet.

We have thus focused our efforts on addressing the disparity in technology readiness and pursuing an advanced concept for the catalytic upgrading via hydrotreatment in slurry reactors.

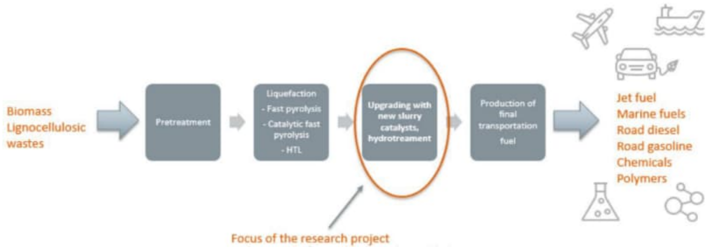


Figure 2 Schematic representation of the value chain relevant for CaSH project. Most technically challenging step in the value chain, being the focus of the project, is highlighted.

To summarise, the specific drivers and needs for the inception of CaSH project were well justified and are listed below:

- Low carbon chemicals and transportation fuels to combat climate change and improve sustainability of hydrocarbon value chain, addressing global challenges and national challenges and goals
- Increasing regulatory pressure on fossil fuels and growing customer demands in the areas of low carbon transportation, such as renewable jet fuels
- Need for new markets and application areas for Finnish companies in lignocellulosic value chain, by valorisation of forest residues from pretreatment and liquefaction to final higher value products such as chemicals and fuels.
- Need for new business opportunities for Finnish refineries and petrochemical companies.
- Need for new business opportunities in catalyst regeneration and metal recovery for the Finnish companies
- Need to develop capabilities, acquiring know-how and strengthening IPR portfolio around the catalytic bio-oil upgrading by Finnish research institutes and companies

1.1 State of the art, lignocellulosic bio-oils, upgrading and slurry hydrocracking

Thermochemical conversion of lignocellulosic biomass to bio-oils, via fast pyrolysis[2,3] and hydrothermal liquefaction[4] routes is a robust and scalable technology which has already reached industrial scale. The liquefaction process is feedstock-flexible, enabling the utilization of challenging secondary streams, such as agricultural and municipal solid waste.[5] It is also suitable for decentralized production, as the product, liquid bio-oil, can be transported to a central upgrading facility[6] The major challenges in the use of bio-oil are related to the high oxygen content, thermal instability and impurities originating from original biomass.[7] Therefore, the use of bio-oil is today limited to heating applications and co-feeding in small quantities at some few oil refineries.[8]

In order to incorporate lignocellulosic bio oils as feedstock to existing refinery operations, oxygen content has to be drastically reduced via catalytic hydrotreatment.[7] One of the main challenges is fast catalyst deactivation in bio-oils upgrading by hydrodeoxygenation due to high reactivity of bio-oil. The problem is especially severe for bio-oils with very high oxygen content such as fast pyrolysis bio-oil (~ 40 % oxygen). There have been efforts to solve this challenge e.g., by so called staged fixed bed reactor upgrading concept where the first bed is operating at lower temperatures (150 - 250 °C) to saturate the reactive oxygenates and to suppress catalyst coking. The main deoxygenation is then performed downstream at a higher temperature (Figure 3, left). However, this strategy has not fully solved the catalyst deactivation problem. The longest reported operation times with the staged hydrotreatment concepts are ca. 1000 h so far which is significantly below industrially accepted standard for a fixed bed unit operation.[9]

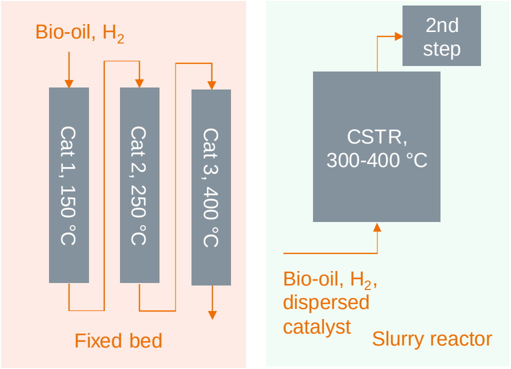


Figure 3. Schematic representation of bio-oil upgrading strategies. Left: staged fixed bed, right: slurry route.

A possible alternative approach to address catalyst deactivation and coke formation can be based on continuous feed of fresh or recycled dispersed catalyst to the slurry hydrotreatment unit (Figure 3, right). Though much less explored for the bio-oil upgrading, slurry phase hydrocracking of petroleum heavy residues has been developed to commercial scale by several refiners.[10] Following slurry-phase hydrocracking technologies have been commercialised for heavy fossil feeds should be mentioned, such as ENI's slurry technology, Honeywell UOP's Uniflex™ and KBR's Veba Combi Cracker (VCC™).

Modern technologies such as ENI slurry process allow for the full conversion of the challenging fossil feedstocks to the distillates and benefit from the use of the nanosized MoS_2 catalyst which is less prone to rapid deactivation.[11]

It must however be pointed out that despite of growing popularity of slurry hydrocracking processes, they have not been applied industrially for upgrading of bio-oils. Few literature examples of co-feeding bio-oils with e.g. vacuum residue or vacuum gas oil in slurry hydrocracking process were available as of 2020, such as recent report of Bergvall et. al from RISE.[12]

We have thus decided to pursue the development of slurry hydrotreatment process and catalysts in order to develop a robust and scalable upgrading platform for the lignocellulosic bio-oils in the frame of the CaSH research project.

2 Project structure and goals

The target of CaSH project was to secure Finland's leading position in developing and exploiting innovative technologies for the upgrading of abundant lignocellulosic biomass to low carbon chemicals, polymers and fuels.

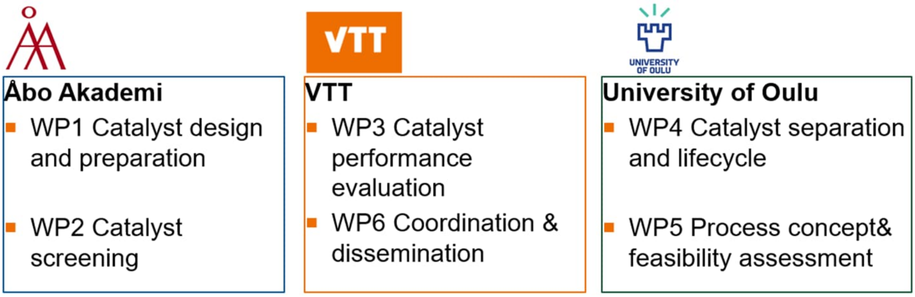
The main objective was set to develop a concept for slurry hydrotreatment of liquefied biomass including the reactor concept with a catalyst developed and selected in the project and catalyst/product recovery system. A proof-of-concept study was targeted to be performed on the laboratory scale for the developed concept, followed by analysis of economic potential and sustainability.

The specific objectives are:

- Development of a low-cost iron -based catalyst for slurry hydrotreatment of bio-oils
- Development of a robust sulfided catalyst for slurry hydrotreatment of bio-oils
- Selection of one catalyst fulfilling the required performance for the concept development
- Development of a slurry reactor and catalyst recovery/regeneration concept (process concept)
- Perform techno-economic assessment (TEA) for the selected process concept
- Perform life-cycle assessment (LCA) for the selected concept

The project was divided into six complementary work packages, with each research partners leading two WP's. (Table 1).

Table 1 Work package structure of CaSH project.



Åbo Akademi	VTT	University of Oulu
WP1 Catalyst design and preparation	WP3 Catalyst performance evaluation	WP4 Catalyst separation and lifecycle
WP2 Catalyst screening	WP6 Coordination & dissemination	WP5 Process concept& feasibility assessment

3 Summary of results

The following chapter will provide an overview of main scientific results achieved in CaSH project. We will highlight key findings related to catalyst development and scale-up, pilot scale upgrading operation in relevant process conditions, as well as development of process concept, followed by techno-economic and life cycle analyses. The intention of this publication is to provide major highlights, and the reader is addressed to the dedicated peer-reviewed publications by research partners to get additional insight and further details.

3.1 Catalyst development

Catalyst technology lies in a core of proposed CaSH concept. While no commercial catalysts for slurry bio-oil upgrading are available, the catalyst to be designed need to withstand challenging condition of slurry hydroprocessing while facilitating a sufficient degree of upgrading of the bio-oil feedstock. Furthermore, the development of bio-oil upgrading catalysts is a challenging task on its own, due to highly complex and unstable nature of the feedstock which makes analysis of the reaction outcome a time-consuming and demanding task.

Following features were incorporated in the catalyst development workflow of CaSH project in order to minimise the development risks and achieve meaningful results in short term:

- Two independent alternative platforms for catalyst formulation were explored: supported iron and iron-nickel catalysts as well as sulfided unsupported molybdenum catalysts
- Initial catalyst screenings were performed with representative model compounds, which simplified analytical workflow and results interpretation
- Selected promising catalysts were tested with real bio-oil in batch and semi-batch process conditions
- Most promising catalyst preparation were scaled up and tested in continuous slurry hydroprocessing of bio-oil at pilot scale, using slurry hydrocracking facilities at RISE research institute, Sweden

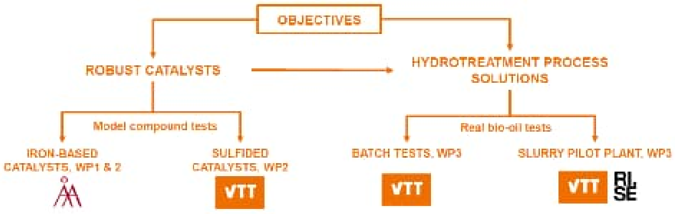


Figure 4. Main objectives and tasks in catalyst development workflow of CaSH project.

3.1.1 Supported Ni and Fe based catalysts

At Åbo Akademi, isoeugenol was used as a representative model compound for HDO (Figure 5)

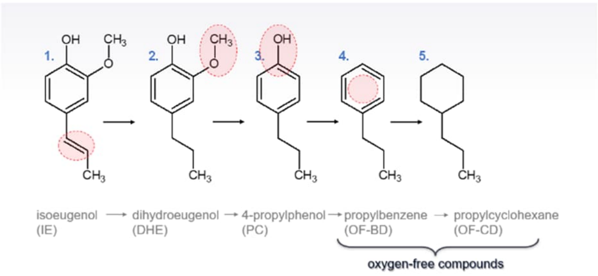


Figure 5 The reaction network in hydrodeoxygenation of isoeugenol.

Initially HDO of isoeugenol was performed in a batch mode in a co-processing with a solvent, hexadecane, which also underwent hydrocracking.

A series of iron- nickel catalysts supported on HY-5.1 zeolite has been tested. Different Fe-Ni metal ratios in the catalyst led to different reaction rates of processes and product distribution. The presence of just 0.26 wt.% isoeugenol in the mixture with n-hexadecane made hydroisomerization-hydrocracking of the latter two-fold less active. Catalysts with smaller metal particle sizes, lower than 6 nm were more efficient pointing out on structure sensitivity. Extremely high activity in co-processing was obtained over 2 wt% Fe – 8 wt% Ni/H-Y-5.1 catalysts with the median metal particle size of 4.6 nm and metals-to-acid site ratio of 8.6. Fe catalysts were much less active in isoeugenol hydrodeoxygenation, while high cracking activity of hexadecane was observed in the presence of Ni. Alkylation of n-hexadecane was a feature of 8 wt% Fe – 2 wt% Ni/H-Y-5.1, whereas, over the 5 wt% Fe – 5 wt% Ni/H-Y-5.1 bifunctional catalyst no undesired oxygen-containing cyclic products were detected. This catalyst exhibited the highest hydrogen consumption according to temperature programmed desorption, which can serve as a marker for efficient hydrodeoxygenation. The spent catalysts contained ca 40 wt% of coke with predominantly aliphatic species.

The catalysts were characterized in detail by N_2 physisorption, Fourier transform infrared spectroscopy with pyridine, inductively coupled plasma optical emission spectroscopy, X-ray diffraction (XRD), transmission and scanning electron microscopy (TEM–SEM), magic angle spinning nuclear magnetic resonance, X-ray photoelectron spectroscopy (XPS), Mössbauer spectroscopy, magnetic measurements, temperature-programmed reduction (TPR), and X-ray absorption spectroscopy (XAS). The results revealed that introduction of Fe led to a decrease of strong acid sites and an increase of medium Brønsted acid sites, while introduction of Ni increased the number of Lewis acid sites. The particle size of iron was approx. 5 nm, being ca. fourfold higher for nickel. XPS demonstrated higher iron content on the catalyst surface compared to nickel. Both Mössbauer spectroscopy and magnetic measurement confirmed the ferromagnetic behavior of all catalysts. In addition, the results from XRD, TEM, XPS, XAS, and magnetization suggested strong Fe–Ni nanoparticle interactions, which were supported by modelling of TPR profiles.

Key properties affected by the Fe–Ni metal ratio, which played a positive role in co-processing, were a smaller medial metal nanoparticle size (<6 nm), a lower metal–acid site ratio, as well as presence in the catalyst of fcc FeNi alloy structure and fcc Ni doped with Fe

Subsequently HDO of iso- and gihydroeugenol was performed in solventless conditions in continuous modes. To this end a low-cost bimetallic bifunctional 5–5 wt% FeNi/H-Beta-300 catalyst was investigated. The catalyst was characterized in detail by laser diffraction, scanning electron microscopy–energy-dispersive X-ray microanalysis, inductively coupled plasma–optical emission spectrometry, transmission electron microscopy, Fourier-transform infrared spectroscopy with pyridine, X-ray diffraction, Mössbauer spectroscopy, X-ray absorption spectroscopy, hydrogen temperature programmed reduction, nitrogen physisorption, thermogravimetric analysis, oxygen temperature-programmed oxidation, organic elemental analysis, soluble coke extraction with dichloromethane, and Raman spectroscopy. Selectivity of 80% to the desired oxygen-free compounds was obtained at *ca.* 80% of the initial dihydroeugenol conversion with 0.3 g of catalyst at 300 °C and 30 bar of hydrogen with a residence time of 12 min. Catalyst deactivation occurred *via* aliphatic coke formation which resulted not only in a decrease in conversion but also significant selectivity changes with increasing time-on-stream. The apparent activation energy of dihydroeugenol hydrodeoxygenation in solventless isoeugenol hydrodeoxygenation was calculated to be 6.3 kJ mol^{-1} ascribed to both external mass transfer limitations of hydrogen dissolved in dihydroeugenol and by rapid catalyst deactivation in the initial isoeugenol hydrogenation. The spent catalyst was successfully regenerated by coke oxidation and subsequently reused.

To analyze the role of the support 5-5 wt% Fe-Ni on different supports (USY-30, Y-5.1, Beta-38, Beta-300, ZSM-5, Al-MCM-48, SiO_2, Al_2O_3) have been investigated in HDO of dihydroeugenol. $FeNi/g\text{-}Al_2O_3$ exhibited the highest activity and selectivity to the desired products with a stable time-on-stream (TOS) behavior.

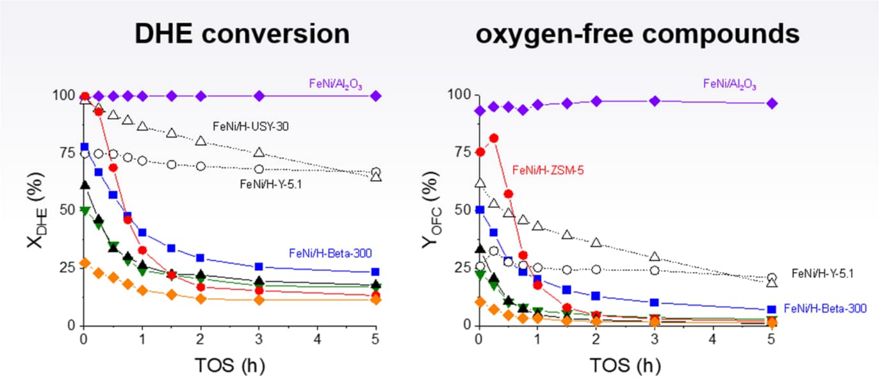


Figure 6. Dependence of conversion and the yield of oxygen free product as a function of time-on-stream.

3.1.2 Unsupported CoMo catalysts

To complement the catalyst development work at ÅA, VTT has chosen to focus on unsupported molybdenum sulfide-based catalysts for slurry bio oil upgrading. Following factors were considered when selecting catalyst route

- Well known and robust hydroprocessing catalyst chemistry of MoS with Co and Ni promotion[13]
- Hydrothermal and emulsion precipitation in order to access and control catalyst particle size for slurry upgrading process
- Low catalyst cost (compared to precious metal catalysts)

In an early screening phase, a representative set of hydrothermally precipitated Co-doped Molybdenum sulfided catalysts were prepared using screening Design of Experiment (DoE) approach, with synthesis stoichiometry and temperature as key variables. Resulting catalysts were evaluated in HDO reaction with isoeugenol as a model compound, showing broadly varying degrees of reactivity depending on the catalyst preparation conditions (Figure 6).Due to lower acidity of the catalysts compared to those described in chapter 3.1.1, no substantial cracking of dodecane which was used as a diluent was observed.
We were thus able to identify synthesis conditions allowing to prepare finely dispersed (average particle size below 50 micron), fully sulfided Co-doped molybdenum sulfide particulate unsupported catalysts with surface area below 200 m2/g. Catalyst formulations resulting in the highest activity with isoegenol, were subjected to further tests with real pyrolysis bio-oils. All prepared catalysts were

characterized for morphology (SEM), elemental composition (ICP), as well as for surface properties (Physisorption) and crystallographic properties (XRD)

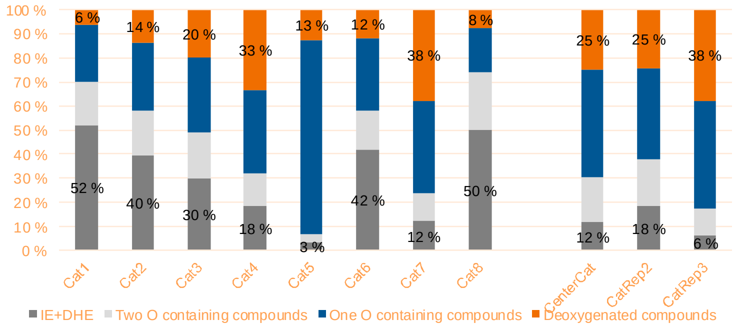


Figure 6. Catalyst screening results with selected hydrothermally precipitated CoMoS catalysts, only three types of products from isoegenol reaction network shown for clarity.

3.2 Catalyst scale-up

In order to run a successful pilot bio-oil upgrading campaign at RISE, catalyst amount necessary to upgrade at least 200 kg of pyrolysis oil needed to be secured. As commented in section 3.1, there is no commercial catalyst available for slurry phase upgrading of pyrolysis oils.

Due to availability of chemicals and synthesis reactors of needed scale as well as due to promising results with real bio-oil feeds, VTT has selected an unsupported CoMoS catalyst recipe, targeting to produce at least 500 g of catalyst. Synthesis recipe was modified in order to increase solid catalyst outtake, and bench scale synthesis autoclave has been fitted with Teflon lining to allow for low pH high temperature hydrothermal precipitation. In total, 600 g of precipitated catalyst was produced at VTT in several batches. Compared to lab scale catalyst, scaled-up batch showed lower surface area and somewhat lower activity in hydroprocessing model compound isoeugenol, but otherwise was found to be quite comparable to lab scale recipe.

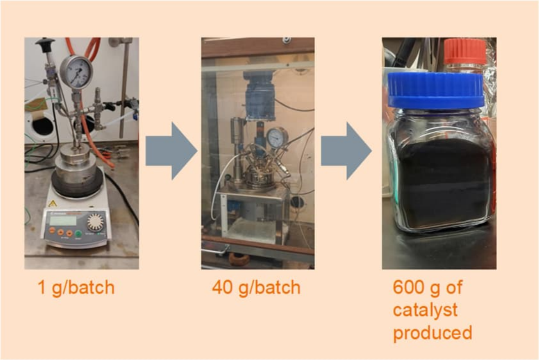


Figure 7. Reactors used to produce CoMoS precipitated catalysts during screening and scale-up phases at VTT.

3.3 Bio-oil upgrading – laboratory scale

Selected in-house produced catalysts were evaluated in semi-batch hydrotreatment of real pyrolysis oils (Figure 8). VTT-developed unsupported catalysts showed activity superior or comparable to that of traditional supported hydrotreatment catalyst obtained from commercial supplier-

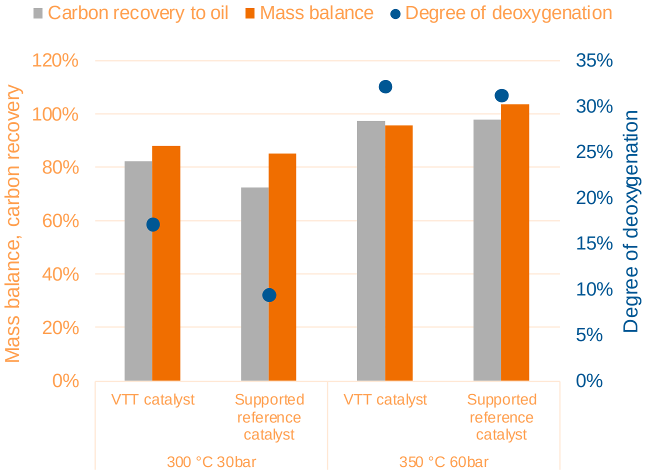


Figure 8. Laboratory scale evaluation of VTT unsupported catalyst Vs commercial reference, alumina-supported CoMoS hydrotreatment catalyst. Pyrolysis oil provided by Valmet, mass balance and deoxygenation degree as a function of severity of the reaction conditons.

3.4 Bio-oil upgrading – pilot scale tests at RISE

Performance of the scaled-up catalyst was verified during pilot campaign at RISE slurry hydrocracker plant in Piteå, Sweden. This unit allows to perform continuous operation in slurry hydroprocessing conditions, with feed rate between 0.5-2 kg bio-oil per hour. The campaign was caried out in April 2023. Large batch of fast pyrolysis oil was provided by Savon Voima.

In total, 70 hours of uninterrupted stable slurry hydrotreatment operation have been achieved with CaSH feedstock and catalyst after some initial struggles in determining suitable operation conditions (Table 2). The product was collected in separate fractions: heavy oil, light oil, product water and off-gas. Solids and cokes formed in the reactor were also collected and analysed.

Figure 9. Left: Slurry hydrocracker pilot plant of RISE, Piteå. Right: pyrolysis oil feed and products of slurry hydrotreatment campaign.

Table 2. Summary of test conditions in CaSH RISE campaign, bio-oil feed rate 1.5 kg/hour. Reference data is from previous RISE test runs with unsupported Mo ethylhexanoate sulfided *in situ*.

Catalyst	T,°C	p, bar	H2 consumption g/kg	Degree of deoxygenation	Oil (dry)
VTT	350	140	30.1	49%	59%
VTT	380	75	36.8	55%	55%
VTT	380	140	35.7	57%	55%
VTT	410	140	45.5	58%	44%
Reference	410	140	43.3	60%	44%

Elemental composition of major product fractions is shown in Figure 10. Oxygen present in bio oil organic fraction is largely converted into water. Van Krevelen diagram comparing the composition of CaSH product to that of typical bio feeds is depicted in Figure 11. It can be seen, that while additional upgrading via second HDO step is obviously necessary, CaSH process has managed to significantly close the gap in quality between pyrolysis and more conventional fatty oil feedstocks.

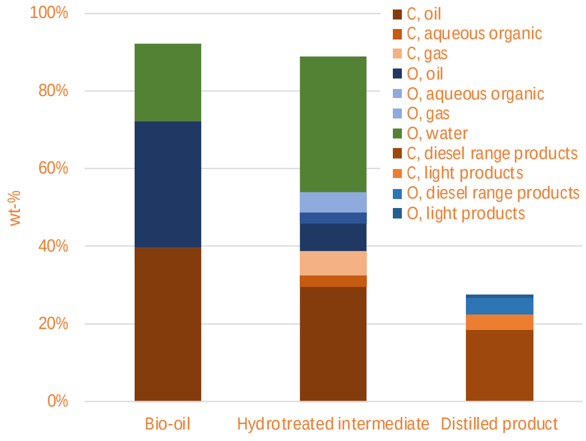


Figure 10. Elemental balance for oxygen and carbon, CaSH bio oil and main analysed slurry hydrotreatment products.

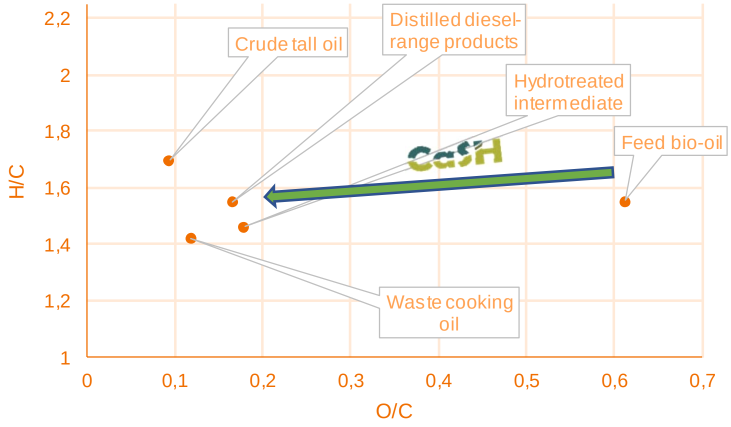


Figure 11. Van Krevelen diagram depicting typical bio feedstocks composition, starting material and upgraded products of CaSH are highlighted.

3.5 Catalyst reclamation and recycling

The focus was on the research of the used unsupported $CoMoS_2$ catalyst. In addition, fresh $CoMoS_2$ catalyst and supported catalyst were examined. Fresh catalysts were readily available and provided information on the behaviour of catalysts during general recovery processes. By studying the metal recovery with fresh catalysts, the impact of catalyst usage and deactivation on the efficiency of metal recovery could be evaluated. With the used catalyst, the focus of the research was on optimizing the efficiency of recovery once the behaviour of the catalyst had been studied using fresh catalysts.

Metal recovery was investigated using hydrometallurgical method. The catalysts were leached using both sulfuric acid and a sulfuric acid-hydrogen peroxide mixture. In addition, bioleaching was examined. Catalyst was analyzed with XRF before and after leaching. Furthermore, ICP-MS was used for analyzing the leaching solutions.

3.5.1 Results and discussion

In the study, high recovery rates were achieved despite the generally more challenging task of efficient recovery of metals using unsupported catalysts. Temperature varied between 25 and 70 °C. Reaction times were 15 minutes up to overnight experiments. Experiments were conducted in two different pulp density: 1 % and 10 % (S/L). Mixing was set at 500 rpm. Different leaching solutions were studied, and Figure 12 represents the difference in efficiency between sulfuric acid leaching and sulfuric acid-hydrogen peroxide leaching.

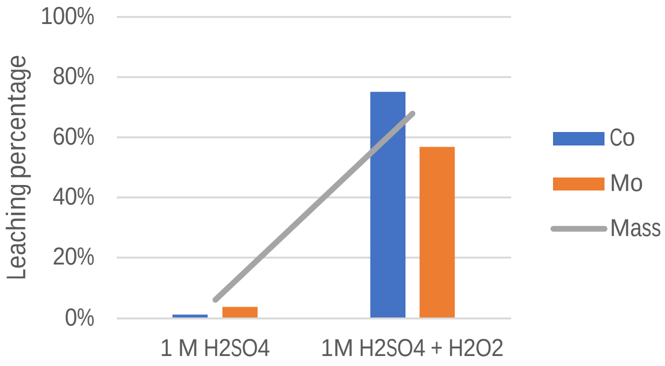


Figure 12**.** Leaching with sulfuric acid and sulfuric acid-hydrogen peroxide mixture (t= 30 min, T= 50 °C, Pulp density 10 % (S/L))

The growth medium used for cultivation of *At. thiooxidans* was utilized for bioleaching. *At. thiooxidans* oxidises sulfur to sulfuric acid in the presence of elemental sulfur, consequently decreasing the pH of the growth medium below two. Overnight experiments with bioleaching and sulfuric acid leaching had similar results and they are presented in Figure 13 It must be pointed out as significant finding, that the use of bioleaching allows to significantly reduce the usage of acid.

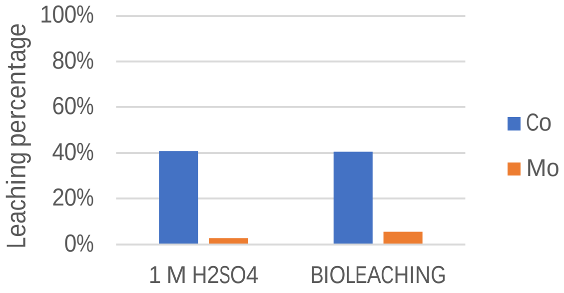


Figure 13. Sulfuric acid and bioleaching as leaching agents (overnight, T=50 °C, Pulp density 1 % (S/L)).

Two different methods were used to achieve high recovery of metals using unsupported $CoMoS_2$ catalyst. The recovery rates for cobalt and molybdenum were 90% and 87% respectively when a sulfuric acid-hydrogen peroxide solution was used for leaching (70 °C, 120 min, ρ=1% w/v). An even higher cobalt recovery was achieved by washing the catalyst with water after sulfuric acid-hydrogen peroxide leaching (70 °C, 30 min, ρ=10% w/v). In this case, the cobalt and molybdenum recovery rates were >99% and 68% respectively. Also, other washing agents were studied, and results are shown in Figure 14

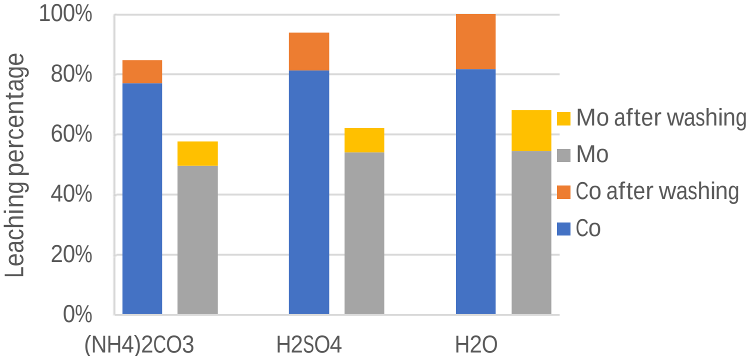


Figure 14. Washing agents and their effect in metal recovery (1 M H_2SO_4 + 15 m-% H_2O_2, T=70 °C, t=30 min, ρ=10 % w/v).

Additionally, it was observed in this work that the success of metal recovery is highly dependent on the catalyst, making it difficult to generalize the results. Thus, metal recovery shall be optimized based on catalyst type and operation conditions in recovery may be needed to tuned even when source of same type of catalyst will be changed.

Cobalt and molybdenum can be leached from unsupported sulfided catalyst by acid leaching. However, effective leaching demands oxidizing component usage. Hydrogen peroxide with reasonable loading is suitable oxidiser for this purpose.

3.6 Process concept development

The simplified conceptual process flowsheet forming the basis of process model development is shown in Figure 15.

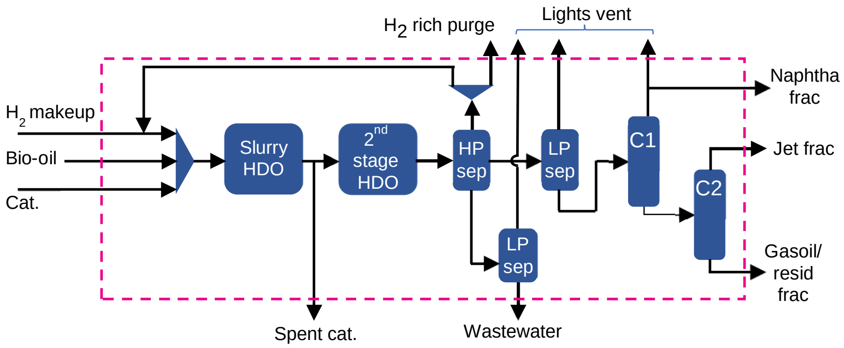


Figure 15. Conceptual process flowsheet of bio-oil hydrodeoxygenation (HDO).

Aspen Plus commercial simulation software (V12.1) was applied in forming the process simulation flowsheet model (Figure 16). Development of bio oil and HDO product model component ensemble and the description of bio-oil hydrogenation reaction stages relied on a composite set of bulk property data (particularly distillation curves of HDO oils) gathered from different literature sources. The slurry reactor stage performance was adjusted to reflect the experimental performance obtained in pilot stage studies described in section 3.3. The rest of the flowsheet was constructed from unit operation models capable of rigorous flash calculations and phase equilibria description derived from the underlying property method.

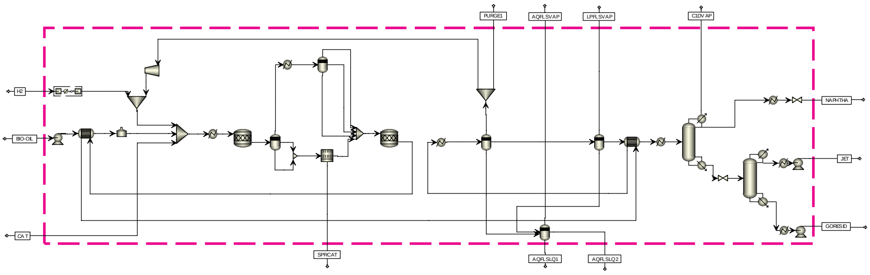


Figure 16. Aspen Plus simulation flowsheet of the bio-oil HDO process.

Some highlighted HDO final process performance metrics include 97.3 wt-%$_{dry}$ degree of deoxygenation with a final cumulative blendstock product oxygen content of 1.0 wt-%$_{dry}$ and 83.3 % carbon recovery from bio-oil to blendstock products.

In addition to the main HDO process (Figure 16), utilization of gaseous by-product streams by pressure-swing adsorption with combustion, steam and electricity generation was investigated (PSABLR process structure, not shown). 98 % of the electricity, 100 % of steam and 35 % of fresh H_2 required in the standalone HDO process could be offset by recovering H_2 and utilizing the energy content of gaseous by-product streams.

For capital cost estimation, the main process unit operations were mapped to actual process equipment (Figure 17). A draft tube slurry reactor configuration with custom sizing was suggested for the slurry reactor stage, while the second stage reactor was sized as a fixed bed reactor. Aspen Process Economic Analyzer was applied in sizing of equipment and final investment analysis.

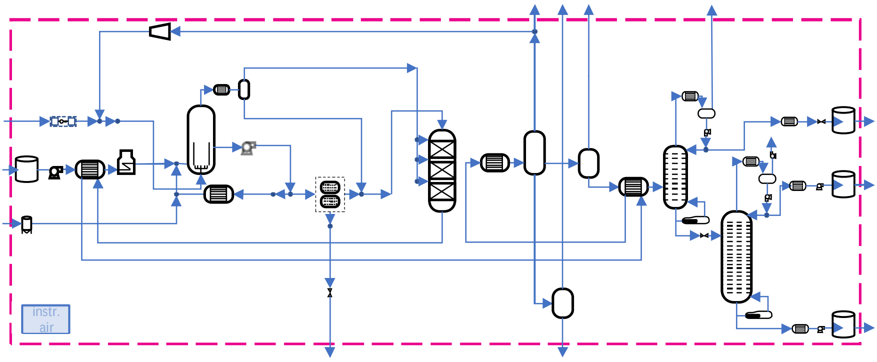


Figure 17. Mapped main process equipment of the bio-oil HDO process.

Estimated base case capital costs for HDO plant processing approximately 400 kt/operating year (330 days) of feed wet raw bio-oil and producing 150 kt/operating year of biobased blendstock products (naphtha, jet fuel and heavier gasoil/residue product fractions) were 153 million euros.

The final base case production cost metrics and cost element breakdown are highlighted in Figure 18.

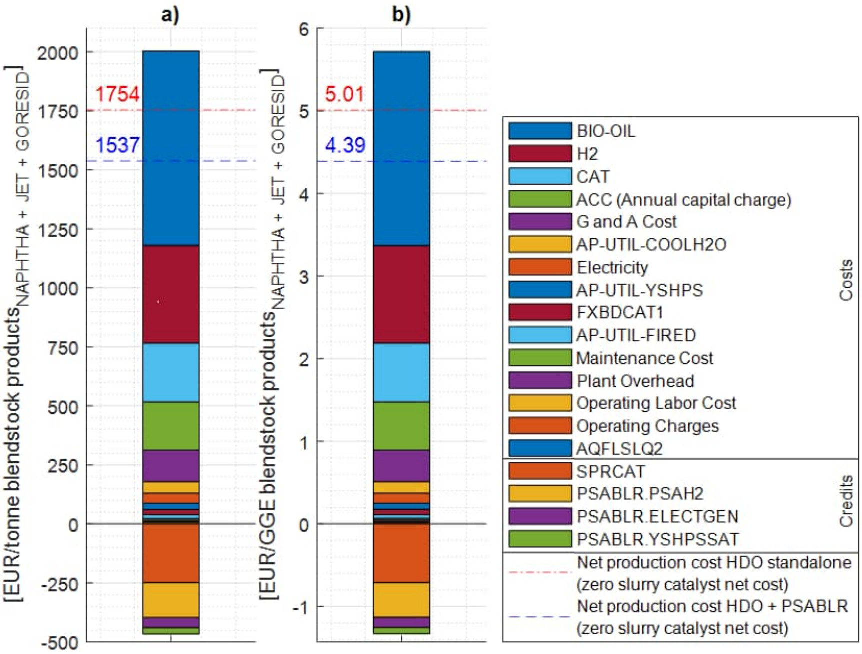


Figure 18. Base case production costs/credits breakdown allocated a) per sum of main blendstock products (NAPHTHA, JET & GORESID) mass and b) per main blendstock products gasoline gallon equivalent (GGE).

The estimated installed equipment costs for the first-stage slurry reactor configuration were on a similar level to the more conventional second stage fixed bed reactor configuration in the analysis. However, the analysis indicated that more significant differences in costing originate from the operating mode of the reactors (slurry vs. fixed bed) and that obtaining recovery value or increased reusable life is important for the slurry catalyst regardless for the relatively small loadings assumed.

Full investment and sensitivity analyses were conducted during the project, indicating that the process techno-economics are mostly hindered by raw material unit costs and product unit prices, which also have the highest sensitivity effect on economics.

3.7 Life cycle assessment

Life cycle assessment (LCA) is a tool for a quantitative and systematic evaluation of potential environmental impacts of a product or system throughout its whole life cycle. It can be used to support decision-making and to avoid a narrow view of environmental problems. Direct, indirect and embodied emissions, energy, wastes and materials are generally taken into account in the assessment.

The purpose of the assessment was to analyse the life cycle environmental impacts of the fuels produced in the process concept of the CaSH project. Data on most of the direct input and output flows was received from the University of Oulu's process concept simulation, which is described in section 6.1. LCA data was obtained mainly from the LCA database Ecoinvent, v. 3.8. Data on electricity and water consumption of the hydrogen electrolysis was taken from the literature[14], and data on biomass pyrolysis was based on VTT in-house database. Renewable electricity was assumed to be composed of 50% hydropower and 50% wind power.

Three different scenarios (cases) were calculated, with the source of electricity used in the electrolysis varied: renewable (Case 1); average Finnish (Case 2); average European (Case 3) electricity. As seen in Figure 19, Case 3 would result in highest greenhouse gas emissions (carbon footprint), also comparable or higher to those associated with fossil fuel production (Figure 20). Case 2 results also in quite high emissions, in about the same size as natural gas production and combustion.

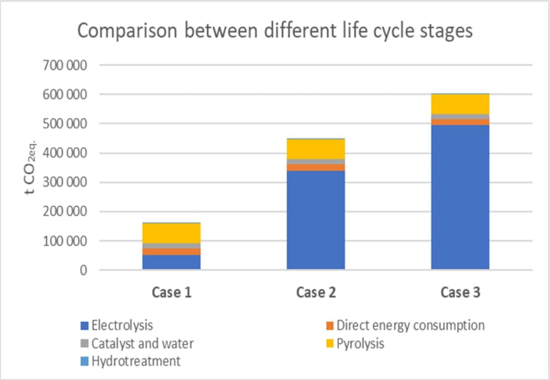


Figure 19. Calculated carbon footprints for three main cases.

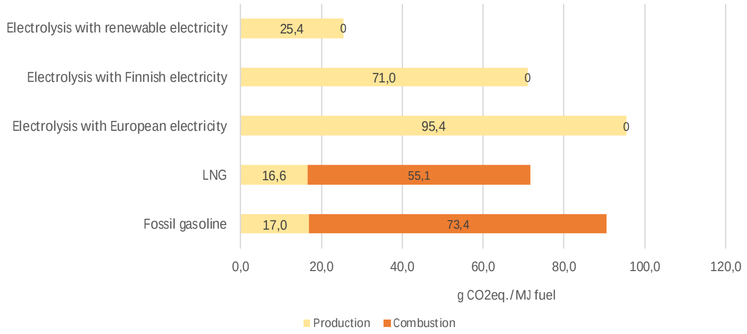


Figure 20. Greenhouse gas emissions associated with production and combustion of biofuel compared to the fossil gasoline benchmark (biogenic CO_2 emissions were not taken into account).

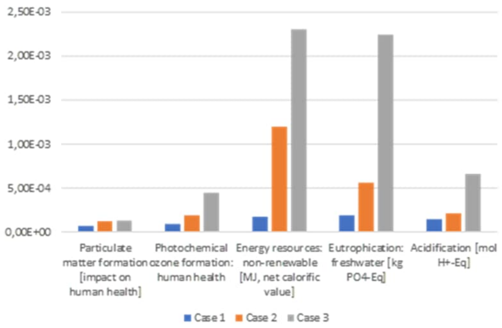


Figure 21 Other environmental impacts for all three cases.

In addition to the climate impacts, some other impacts were also analysed (Figure 21). In these impact categories, most impacts in the Cases 2 and 3 originate from electrolysis. Case 3 was found to have the highest impacts in all categories. High freshwater eutrophication impacts for Case 3 electricity production primarily originate from P emissions of hard coal production in the European electricity. The higher acidification and photochemical ozone formation impacts in Case 3 result from the high SO_2 and NO_X emissions of the European electricity production.

To conclude, LCA analysis confirms that overall substantial emission reduction Vs current fossil-based fuels can be realized in the case of CaSH production process but it is highly dependent on the source of electricity used in hydrogen production. Origin of electrical energy used to produce hydrogen is crucial forachieving footprint reduction.

4 Conclusions and outlook

In this report, we have presented the summary of major findings provided by all work packages of CaSH project. This summary fully indicates that all major scientific objectives have been reached in CaSH project:

- Novel catalyst systems for bio oil slurry hydrotreatment have been developed using two complementary catalyst design paths
- The catalysts have been tested in relevant operating environment with real bio oils and showed good performance
- Catalyst performance has been verified during a pilot campaign at RISE slurry hydrocracker plant, where significant amounts of pyrolysis oil have been processed to produced highly stabilized CaSH upgraded oil
- Concept for catalyst reclamation and metal recovery has been tested in laboratory scale
- Overall process concept for the slurry hydroprocessing plant has been developed along with a process model
- Life cycle assessment and techno-economic analysis of the process have been performed based on available data and process models

We can thus conclude that CaSH project has reached its target in developing the catalytic slurry hydrotreatment bio-oil upgrading process towards technology readiness level (TRL) 4. To bring the concept further to commercial exploitation, subsequent research and development activities will be needed. List of key research aspects to be considered includes, but is not limited to improvement of catalyst performance, demonstration of metal recovery, development and demonstration of the final hydroprocessing concept for the CaSH product. The authors are convinced that within several years of targeted research effort, all aspects mentioned above can be successfully tackled in subsequent projects.

Acknowledgements

Funding from Business Finland and CaSH consortium companies is gratefully acknowledged by the research partners. We would also like to appreciate the time and effort invested by the representatives of consortium partners to actively participate in the project work.

References

---

1 Net Zero Roadmap: A Global Pathway to Keep the 1.5 °C Goal in Reach, IEA, Paris, 2023. https://www.iea.org/reports/net-zero-roadmap-a-global-pathway-to-keep-the-15-0c-goal-in-reach, License: CC BY 4.0

2 Ringer M., Large-Scale Pyrolysis Oil Production: A Technology Assessment and Economic Analysis; National Renewable Energy Laboratory (NREL): Golden, CO, 2006; Technical Report NREL/TP-510-37779. https://www.nrel.gov/docs/fy07osti/37779.pdf.

3 Oasmaa, A. Historical Review on VTT Fast Pyrolysis Bio-oil Production and Upgrading. Energy & Fuels, 2021, 35, 5683-5695.

4 Mathanker, A. A Review of Hydrothermal Liquefaction of Biomass for Biofuels Production with a Special Focus on the Effect of Process Parameters, Co-Solvents, and Extraction Solvents. Energies, 2021, 14.

5 Pienihäkkinen, E., et al., Improving Fast Pyrolysis Bio-Oil Yield and Quality by Alkali Removal from Feedstock. Energy & Fuels, 2022. 36(7): p. 3654-3664

6 Patel, M. The development of a cost model for two supply chain network scenarios for decentralized pyrolysis system scenarios to produce bio-oil. Biomass and Bioenergy, 2019, 128.

7 Pinheiro P. Challenges and Opportunities for Bio-oil Refining: A Review. Energy & Fuels, 2019. 33, 4683-4720.

8 Inayat, A., Techno-Economical Evaluation of Bio-Oil Production via Biomass Fast Pyrolysis Process: A Review. Frontiers in Energy Research, 2022. 9.

9 Jones, Susanne B., Snowden-Swan, Lesley J., Meyer, Pimphan A., Zacher, Alan H., Olarte, Mariefel V., Wang, Huamin, and Drennan, Corinne. Fast Pyrolysis and Hydrotreating: 2015 State of Technology R&D and Projections to 2017. United States: N. p., 2016. Web. doi:10.2172/1247456.

10 Zhang, S. et al A Review of Slurry-Phase Hydrocracking Heavy Oil Technology, Energy & Fuels 2007 21 (6), 3057-3062 DOI: 10.1021/ef700253f

11 Bellussi, G. Hydroconversion of heavy residues in slurry reactors: Developmentsand perspectives, Journal of Catalysis 308 (2013) 189–200

12 Weiland, F. Corefining of Fast Pyrolysis Bio-Oil with Vacuum Residue and Vacuum Gas Oil in a Continuous Slurry Hydrocracking Energy & Fuels 2020 34 (7), 8452-8465 DOI: 10.1021/acs.energyfuels.0c01322

13 Horacek, J., Kubicka, D. 2017. Bio-oil hydrotreating over conventional CoMo & NiMo catalysts: The role of reaction conditions and additives. Fuel, 198, 49-57.

14 Jang, D. "Investigation of the operation characteristics and optimization of an alkaline water electrolysis system at high temperature and a high current density." Journal of Cleaner Production, 2023, 424.

Appendix A: Project publication, dissemination and international mobility activities

The project was executed during challenging times of COVID pandemics, therefore most steering group and research partners meetings had to held in an on-line format with a notable exception of a final research seminar held as face-toface meeting at VTT premises in August 2023.

Despite the travel challenges, project research partners managed to accomplish a set of international exchanges (total 12 weeks) in order to support project activities (Table A1).

Table A Error! Main Document Only.: Summary of international mobility.

Institute	**Partner**	**Scope**	**Outcome**
VTT	Outbound – RISE, SWE	Piloting trials at continuous Slurry Hydrocracker plant	Tyko Viertiö spent 1 month at Piteå, March 2023. Successful piloting trials with VTT catalyst and Savon Voima bio oil
UOULU	Outbound – TU Graz, AUT	Methods for cultivation and characterization of microbe strains	Juha Ahola spent about 1 week at Graz, January 2023. New options for bioleaching of spent catalysts
ÅA	Outbound –Charles University, Prague	HRTEM analysis of Fe-Ni catalysts	Dr. Zuzana Vajglova spent 1 week in Prague performing analyses
ÅA	Outbound BESSY, Hamburg	EXAFS analysis of Fe-Ni catalysts	Dr. Zuzana Vajglova spent 1 week in Hamburg, analyses performed
ÅA	Inbound - UCTP Prague	Catalyst preparation, exchange experience	Dr. David Kubicka visited ÅA in 2022
ÅA	Inbound – Orlen Uni CRE, CZ	Research internship	Complete, Pavla Vondrova, spent 1 month in ÅA

Work done in CaSH research project has resulted in four M.Sc theses completed at the premises of all research partners, and the results were used to support the workpackages of the project (Table A2).

Table A2: List of M.Sc theses produced within CaSH project

Institute	**WP's**	**Name**	**Title**
ÅA	1,2	Bibesh Gauli, 2021	Hydrodeoxygenation of lignin-derived model compound isoeugenol over Fe-, Ni-, and Fe-Ni-supported on zeolites[14]
VTT	1,2	Emil Högnabba, 2021	Catalysts for slurry-phase hydrotreating of bio-oil[14]
VTT (Aalto)	1,2	Aaro Tuisku, 2023	Emulsion-based synthesis and characterization of bio-oil upgrading catalyst CoMoS[14]
UO	5	Salla Ala-Kokko, 2023	Lignoselluloosapohjaisen bioöljyn hydrodeoksygenointiprosessin käsitteellinen suunnittelu[14]
UO	4	Salla Seppä, 2023	Metallien talteenotto käytetyistä katalyyteistä[14]

As of October 2023, multiple peer-reviewed publications summarizing key research results are still in active preparation by the research partners. Following publications have been already accepted and published:

1. Vajglová, Z, Yevdokimova, O, Medina, A, Eränen, K, Tirri, T, Hemming, J, Lindén, J, Angervo, I, Damlin, P, Doronkin, DE, Mäki-Arvela, P & Murzin, DY 2023, 'Solventless hydrodeoxygenation of isoeugenol and dihydroeugenol in batch and continuous modes over a zeolite-supported FeNi catalyst', Sustainable Energy and Fuels. https://doi.org/10.1039/D3SE00371J
2. Vajglová, Z., Gauli, B., Mäki-Arvela, P., Kumar, N., Eränen, K., Wärnå, J., Lassfolk, R., Simakova, I. L., Prosvirin, I. P., Peurla, M., Lindén, J. K. M., Huhtinen, H., Paturi, P., Doronkin, D. E., & Murzin, D. Y. (2023). Interactions between Iron and Nickel in Fe-Ni Nanoparticles on Y Zeolite for Co-Processing of Fossil Feedstock with Lignin-Derived Isoeugenol. ACS Applied Nano Materials, 6(12), 10064-10077. https://doi.org/10.1021/acsanm.3c00620
3. Vajglová, Z., Gauli, B., Mäki-Arvela, P., Simakova, I. L., KUMAR, N., Eränen, K., Tirri, T., Lassfolk, R., Peurla, M., Doronkin, D. E. & Murzin, D. Y. 2023. Co-processing of fossil feedstock with lignin-derived model compound isoeugenol over Fe-Ni/H-Y-5.1 catalysts. Journal of Catalysis, 421, 101-116. https://doi.org/10.1016/j.jcat.2023.03.016

Series title and number
VTT Technology 425

Title	**CaSH - Catalytic Slurry Hydrotreatment** Final Project report
Author(s)	Tyko Viertiö, Juha Lehtonen, Johanna Kihlman, Laura Sokka, Alexander Reznichenko, Ville Tuppurainen, Salla Ala-Kokko, Salla Seppä, Juha Tanskanen, Juha Ahola, Dmitry Murzin, Zuzana Vajglova, Päivi Mäki-Arvela & Narendra Kumar
Abstract	Catalytic Slurry Hydrotreatment (CaSH) was a public co-research project carried out by Åbo Akademi University, University of Oulu and VTT. The project was coordinated by VTT and was funded by Business Finland, Neste, Valmet, Fortum Waste Solutions, Meriaura, ESL Shipping, Savon Voima and BMH technology along with research institutes as part of the Neste Veturi ecosystem. The project was aiming at the development of a novel concept for the catalytic upgrading of lignocellulosic bio-oils for the production of renewable chemicals and fuels. This publication summarizes the results achieved in the project which was run between 01.01.2021-30.06.2023. The main outcome of CaSH project was development of robust and scalable catalyst systems for the upgrading of liognocellulosic bio-oils in slurry hydrotreatment conditions. Catalyst preparation and slurry hydroprocessing of fast pyrolysis bio-oil have been developed in the laboratory and have been later verified at pilot scale. Process concept for the slurry hydrotreatment plant has been developed and was supported with technoeconomic and LCA assessments. Main developmental needs for further technology maturation in the follow-up projects have been discussed and summarised by the CaSH team.
ISBN, ISSN, URN	ISBN 978-951-38-8788-9 ISSN-L 2242-1211 ISSN 2242-122X (Online) DOI: 10.32040/2242-122X.March 2024.T425
Date	March 2024
Language	English
Pages	30 p. + app. 0 p.
Name of the project	CaSH
Commissioned by	
Keywords	Bio-oil, biomass, renewables
Publisher	VTT Technical Research Centre of Finland Ltd P.O. Box 1000, FI-02044 VTT, Finland, Tel. 020 722 111, https://www.vttresearch.com

CaSH

Catalytic Slurry Hydrotreatment

Catalytic Slurry Hydrotreatment (CaSH) was a public co-research project carried out by Åbo Akademi University, University of Oulu and VTT. The project was coordinated by VTT and was funded by Business Finland, Neste, Valmet, Fortum Waste Solutions, Meriaura, ESL Shipping, Savon Voima and BMH technology along with research institutes as part of the Neste Veturi ecosystem.
The project was aiming at the development of a novel concept for the catalytic upgrading of lignocellulosic bio-oils for the production of renewable chemicals and fuels. This publication summarizes the results achieved in the project which was run between 01.01.2021-30.06.2023.
The main outcome of CaSH project was development of robust and scalable catalyst systems for the upgrading of liognocellulosic bio-oils in slurry hydrotreatment conditions. Catalyst preparation and slurry hydroprocessing of fast pyrolysis bio-oil have been developed in the laboratory and have been later verified at pilot scale. Process concept for the slurry hydrotreatment plant has been developed and was supported with technoeconomic and LCA assessments. Main developmental needs for further technology maturation in the follow-up projects have been discussed and summarised by the CaSH team.

ISBN 978-951-38-8788-9
ISSN-L 2242-1211
ISSN 2242-122X (Online)
DOI: 10.32040/2242-122X.2024.T425

beyond the obvious