Bio-Based Carbon Materials Road-Map

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Summary

In this study we surveyed technological possibilities to obtain bio-based carbon business in Finland applying biomass derived polymers and precursor structuring prior to carbonization. We reviewed application requirements for carbon materials of several applications including high performance engineering materials as well as materials for high efficient separation and applied energy technologies. We made designs for novel carbon materials to meet these requirements based on our background knowledge of possibilities of wood based polymeric materials, precursor production and carbonization processes. Most promising carbon designs were selected for material demonstrations, and then further for product demonstration. Main outcome of the project was road-map for bio-based carbon materials. Case examples for the roadmap were selected based on our follow-up of industrial needs for tailored carbon materials as well as information obtained from material and products demonstrations done within the project. This report is a public summary of the work done concentrating on the road-map.

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Contents

Abbreviations

AC	Activated carbon
ANG	Absorbed natural gas
AW	Anti wear
CAGR	Compound annual growth rate
CB	Carbon black
CF	Carbon fibre
CMC	Cellulose micro crystals
CMF	Cellulose micro fibrils
CNC	Cellulose nano crystals
CNF	Cellulose nanofibrils
CNT	Carbon nanotube
COF	Coefficient of friction
DES	Deep eutectic solvent
DLC	Diamond like carbon
DP	Degree of polymerization
EP	Extreme pressure
GAC	Granular activated carbon
GDP	Gross domestic product
HM	High modulus
HT	High tenacity
HTC	Hydrothermal carbonization
IAB	Industrial advisory board
IM	Intermediate modulus
LNG	Liquid natural gas
MWL	Milled wood lignin
NBC	Nuclear biological chemical
P&P	Pulp and paper
PAC	Powdered active carbon
PAN	Polyacrylonitrile
PF	Phenol formaldehyde
PLA	Polylacticacid
PTFE	Polytetrafluoroethylene
RMD	Reactive molecular dynamics
RO	Reverse osmosis
SC	Supercapacitor
SDS	Sodium dodecyl sulphate
SM	Standard modulus
TEMPO	(2,2,6,6-tetramethylpiperidin-1-yl) oxidanyl/oxyl
TUT	Tampere University of Technology
TWC	Tampere Wear Center (at TUT)
UHM	Ultra high modulus

1 Introduction

Carbon materials have many general properties which makes them attractive in various applications. Carbon is a traditional material meaning that it has been utilized by people for a long. These long used conventional carbon materials include graphite, carbon black (CB) and activated carbon (AC) materials. In last century new carbon materials with tailored properties has been developed. These included carbon fibres, highly oriented graphite and many others. In recent decade's even more sophisticated nano-sized or nano-structured carbon materials have been produced. Carbon materials, especially newest nano-carbons, but also macroscopic carbons such as carbon fibres are intensively studied at the moment. Division of carbons into conventional, new and nano-carbons is presented in Table 1; this division mainly adopted from Inagaki & Radovic (2002). Nanocarbon can further be divided into 1) single nanostructured materials, 2) films and nanostructured coatings and 3) nanostructured bulk materials (Frost&Sullivan, 2009).

Table 1   Division of carbons into conventional, new and nanocarbons (Inagaki & Radovic, 2002)

Conventional carbons	New carbons – many are nano-structured	Nano-carbons (including nano-structured and -sized

• Graphite electrodes
• Carbon black
• Activated carbons (AC)
	• Carbon fibres (vapour grown and from precursors)
	• Highly oriented graphite
	• Porous carbons (AC fibres, molecular sieves)
	• Glassy carbons
	• High-density isotropic carbons
	• Intercalated compounds
	• Diamond like carbons
	• Graphite foil
		• Many materials from *New carbons* –group are nano-structured
		• Nano-sized carbons
		  • Carbynes
		  • Fullerenes
		  • Carbon nanotubes (CNT)
		  • Graphene

While nano-carbon materials are typically prepared via gas synthesis methods, macroscopic carbon materials are usually prepared by carbonization of suitable solid precursors. These precursors can have various shapes and dimensions depending on the application field. Shapes include everything from particles to fibres and wires, and to sheets and fabrics as well as spatial objects such as 3-D fabrics and foams; and dimensions from nearly nano to microscopic and macroscopic sized. Precursors have originally been and still can be produced from bio-based polymers. As an example first carbon fibres were produced from cotton fibres by Thomas Edison for his electric light bulb experiments; and viscose was used in production of carbon fibres since 1920's. Also paper, starch, and textiles have been carbonized and shaped to be used in composites e.g. in nose-cones for rocketry (Marchessault, 2011).

Nowadays bio-based precursor materials have been in many applications replaced by synthetic polymers, but interest for returning to renewable raw materials has been increased lately. One reason for this interest is high and/or fluctuating prices of synthetic precursors e.g. polyacrylonitrile (PAN) for carbon fibres. Another incentive towards bio-based raw materials, especially in case of lignin, is availability of lignin as side-stream from pulp and paper industry; utilization of lignin as raw material would be more beneficial than burning it to energy, which is currently a common practice. Sustainability of renewable precursors can be also considered as an advantage, even though economics usually determine the industrial interest.

Bio-based tailored precursors for advanced carbons and applications (BioPreCarb) -project was *Small strategic research opening* -type project funded by Tekes. This kind of projects focus on new high-level competences in areas expected to be important for businesses in the future. In BioPreCarb

project we surveyed technological possibilities to obtain lignocellulose based high performance structured carbon business in Finland. This could lead to new possibilities for Finnish forest industry to renew offering from raw materials towards value chain of high performance carbon products, or new possibilities for processing and end-user industry to participate in multi-national carbon production value chains.

The focus of this project was to use bio based renewable polymers as raw materials for solid pre-structured precursors which were then carbonized into novel structural carbon materials for various applications. Our approach was to design novel structural carbon materials to meet requirements of selected added value performance applications. These structural carbons made of bio-based precursors were of different shapes and sizes. We were aiming for advanced properties and functionality obtained with different precursor processing and carbonization methods. We also tried to find new process paths in carbon production, more economic and ecological processes for current carbon materials and completely new application fields for carbons to replace other materials. Project partners were VTT technical Research Centre of Finland Ltd (VTT) and Tampere University of Technology (TUT) and work was carried out with guidance of Industrial Advisory Board (IAB) representing industrial view.

This reports reviews application fields and summarises shortly experimental work done, but main focus is on road-map work which was the main outcome of the project.

2 Scope of Bio-Based Carbon Materials Project

The scope of project is presented in Figure 1, application fields discussed in chapter 2.1 and raw materials, precursor types and carbonization in
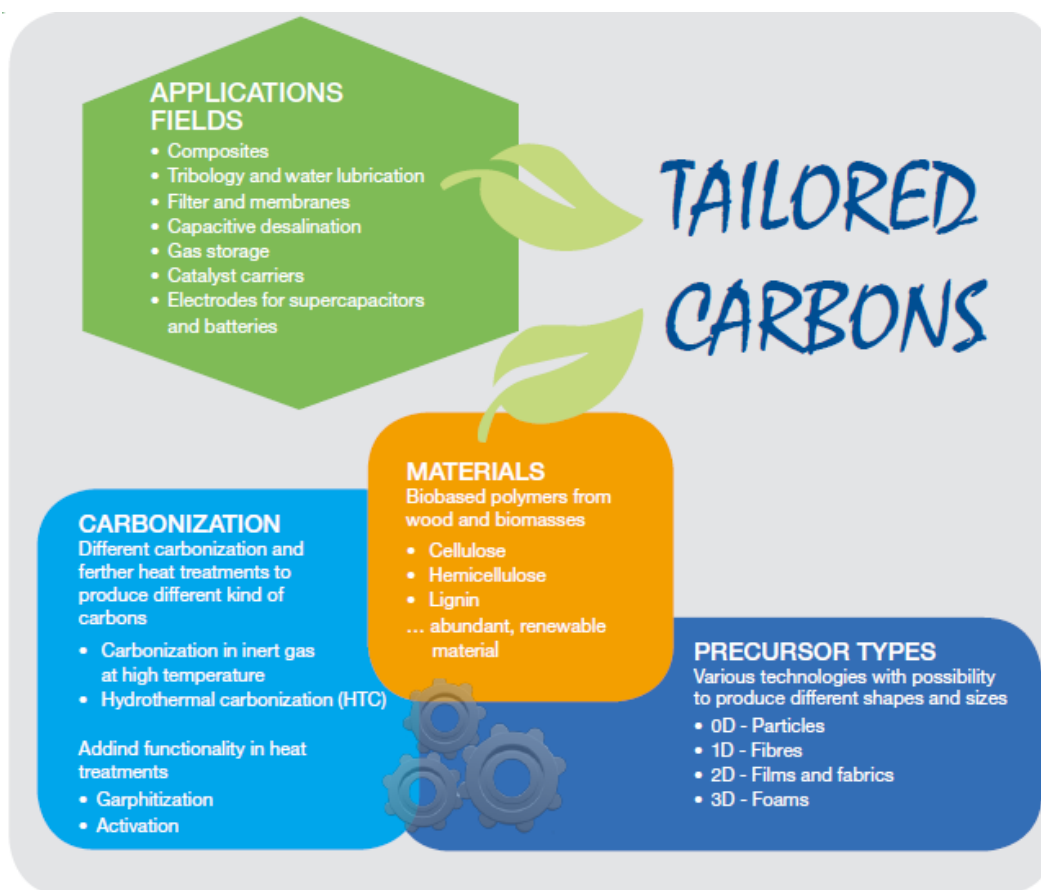

Figure 1   Scope of the bio-based carbon materials project

2.1 Application Fields for Tailored Carbon Materials

Carbon is an attractive material for various applications due to its properties, such as low density, inert nature, stability in wide temperature range, and resistance to several corrosive gases. The crystalline structures of carbon range from amorphous to highly ordered graphite. Advances in material sciences during the last decades have enabled the preparation of various structures, such as fibres and foams, and the adjustment of their electrical, thermal, and other properties. Brittleness and susceptibility to chipping are drawbacks of carbon materials for some otherwise interesting application areas (Wang *et al.*, 2012).

There are several potential application areas for bio-based carbons (Ioannidou & Zabaniotou, 2007). We saw the most promising ones being in high-performance engineering materials, in separation processes as well as in various energy applications. Other possible application areas suitable for bio-based carbons include, e.g., heat exchangers and heat sinks especially in high-temperature and corrosive environments (Wang *et al.*, 2012). Three-dimensional carbon foam structures can be used in thermal insulation, impact absorption and related applications.

The material requirements of carbon, such as mechanical properties and porosity, widely vary between applications, which allows for the utilization of different qualities of raw materials,

geometries and shapes of carbon precursors, and types of carbonization processes. It is also possible to find production routes for bio-based carbon that fulfil the requirements of more than one end-use.

Selected applications, listed below, are discussed in the following chapters.

1) Light weight composites

2) Low friction and tribology materials, including wear of components

High performance engineering materials

3) Filters and membranes

4) Capacitive desalination

Separation processes

5) Support materials for catalysts

6) Gas storage

7) Electrodes

Energy applications

Light Weight Composites

Carbon-based reinforcements and additives can be used in various types of composites as particles, nanotubes, fibres, foams, and weaves. Carbon particles, the simplest of the shapes, can be utilized in elastomers and thermoplastics as reinforcement. They are the most widely used filler type e.g. for enhancing the conductivity properties of composites.

Carbon fibres are widely utilized in composites in the areas of transportation, gas storage, wind energy and construction, due to their light weight combined with good strength properties. In passenger vehicles, composites of carbon fibres and resin are used for structural, semi-structural, as well as non-structural purposes. The market of carbon fibre composites for the automotive industry is driven by the increasing global demand for light weight composites due to regulations for CO_2 emission reductions, while restraining factors include recyclability issues, lack of engineering experience, low production volumes, and high costs. Carbon fibres account for from 13% to 20% of total costs for carbon fibre composites. (Frost&Sullivan, 2011)

The composite market is expanding rapidly. In 2011, the total demand for carbon fibre was 46,000 mega tons, and it is expected to expand by 235 % from 2011 to 2020. In the 2010s, the average annual growth was 10 %, and the pace has been increasing since. Aerospace industries represent 20 % of the consumption, sports and other consumer products 15 %, and other industrial applications such as vehicles 65 %. (Roberts *et al.*, 2011). The rising consumption of carbon fibre is driven by car and aerospace industries.

The advantages of carbon compared to other materials include high elastic modulus and tensile strength, low density, and good adhesion with resins (Frost&Sullivan, 2011). The requirements for mechanical strength and other properties of carbon fibres in various components vary; different grades from standard (SM) to high modulus (HM). Typical ranges of parameter values area given in Table 2. Carbon fibres are attractive materials both in a form of chopped fibres as well as fabrics. In addition to carbon-polymer composites, carbon fibres can also be combined with metals, ceramics, carbon and hybrid matrices to form composites (Frost&Sullivan, 2008).

Carbon fibre composites are also discussed in Road-map (see Chapter 4.5).

Table 2   Summary of carbon fibres in composites

Application	Properties of carbon in current applications	Motivation for replacement with bio-based carbon	Experience of project partners
Carbon fibres as reinforcement in composites	Tensile strength: 2.5 GPa to 6 GPa Young's modulus: 220 GPa to 750 GPa Density: 1.80 g/cm^3 to 2.15 g/cm^3 Elongation at break: 0.4% to 2.1% Thermal conductivity in 0°C: SM: 7 W/mK to 17 W/mK, HM: 20 W/mK to 50 W/mK Thermal expansion ratio in 0°C: SM:-0.1·10^{-6} 1/K to 0.5·10^{-6} 1/K HM:-0.5·10^{-6} 1/K to 0 .1·10^{-6} 1/K Specific resistance: 14 μΩm to 16 μΩm Ohmic resistance: 30 Ω/m	- Cheaper raw material than PAN. - High carbon content of natural polymers. - Availability of raw material - Moving to a natural, non-oil based materials. - Large difference in electrical conductivity between the polymer matrix and carbon fibre. - The increasing market size of composites.	TUT - Equipment and know-how to manufacture composite structures. - Filament winding machine. - Test equipment for measuring mechanical and chemical properties.

Lubrication and Wearing of Components

The major source of energy losses in mechanical systems is caused by friction; It has been estimated that about 30 % to 50 % of all energy in industrialized countries goes to overcome it. Not only energy savings are achieved by lowering friction, but also durability of the systems is improved, which leads to more cost-efficient and sustainable solutions. Companies operating in the field of tribology applications include Shell, Exxon Mobile, British Petroleum, Castrol, Chevron, and Neste Oil. Producers of tall oil for lubrication include Eastman, Arizona Chemical, Forchem Oy, Oy Pinifer Ltd, and coating manufacturers Morgan Advanced Materials (Diamonex-coatings) and Millidyne Oy. In the bio-based lubricant market, Royal Dutch Shell, Exxon Mobile, British Petroleum, Chevron, Castrol, and Total are among the leaders.

Wearing of components and machineries causes considerable costs in societies. In industrial countries, the estimated annual costs due to friction and wear are approximately 5 % of GDP. Wearing of a material is a complex phenomenon involving several contributing factors such as particle dimension, bulk mechanical properties, debris morphology, and transfer films. Tribology is the science and engineering of interacting surfaces in relative motion.

Lubrication is one of the major means to decrease friction. Lubricating oils consist of 93 % base-oil and 7 % additives, and they represent 90 % of the total lubricant consumption. At present, lubrication formulations are mainly based on mineral oil. In 2011, the share of mineral oil-based lubricants was 97 %, while the share of bio-based lubricants was 1 %. In 2011, approximately 37 Mtons of lubricants were consumed worldwide, and the consumption is expected to reach 42 Mtons by 2018. (Transparency Market Research, 2013). The average price of a conventional lubricant is approximately 2 €/l (Johnson, 2010). Another possibility to decrease friction is low friction surfaces. Table 3 summarises properties of carbon materials in selected tribology applications: as lubrication additive and as filler in low friction coatings.

Table 3   Summary of the carbon in lubrication applications

Application	Important parameters in current applications	Motivation for replacement by bio-based carbon	Experience of project partners
Various carbon materials in lubricants	Carbon allotropes and forms used - Graphene, graphite, activated carbon, carbon blacks, mesoporous carbons, and carbon nanotubes, diamond-like carbons (DLC) Parameters of carbon additives - Effect on friction and wear properties of lubricant - Size of particles, and uniformity of size distribution - Concentration of the additive - Surface chemistry of particles - Interactions with the base oil	- Need for green, environmentally friendly lubrication, e.g., water-based lubricants. - Need to reduce not only the friction coefficient of a lubricant, but also wear of material surfaces. - Need for novel technologies in general. The quality of the present additives could be improved to prevent surface abrasion.	VTT - Water-lubricated DLC coatings. - Characterization an tribological performance of DLC films. - Environmental effects of DLC coatings. - Bio-based lubricants.
Carbon fillers in polymer matrix	Types of carbons used - Carbon fibre - Vapor-grown carbon fibre - Carbon nanotubes (CNTs) - Layered graphene	- Search for cheaper materials than current carbon fibres and nanofillers. - More efficient self-lubricating effect would be created with layered carbons.	TUT - Tampere Wear Center (TWC) - Various polymer processing facilities

Carbon materials as lubrication additives. Various solid lubricant materials, micro- and nanoparticles, and surface patterns have been developed for tribological purposes. Carbon can be used in the form of graphene or graphite as dry lubricant or as an additive in oil. Activated carbon, carbon blacks, mesoporous carbons, and carbon nanotubes have also been used as additives in lubricants (Baik *et al*., 2008).

Graphene, the atomically thin and strong carbon material with low surface energy, is a good candidate for some applications. Oleic acid–modified graphene has been studied as an additive in oil lubrication showing good anti-wear performance and a reduction of up to 17 % in friction coefficient with an optimized graphene concentration from 0.02 wt% to 0.06 wt% (Zhang *et al*., 2011). In addition, it has been found that when carbon nanomaterials such as CNTs and graphene nanosheets are added to base lubricants, the friction coefficients were considerably reduced (Senatore *et al*., 2013). The optimal concentration of graphite nanosheet additives in paraffin oil was 0.01 wt% (Huang *et al*., 2006). Furthermore, when multi-walled carbon nanotubes (MWCNTs) functionalized with sodium dodecyl sulphate (SDS) have been used as an additive in water-based lubricants, good anti-wear and friction reduction properties as well as enhanced load-carrying capacity have been achieved (Peng *et al*., 2007).

There is a clear need for novel lubrication solutions. Commercial graphite additives exist, but they are designed to be easily dispersed within polymer matrices. In lubrication applications, the lubricants need to perform in various, sometimes extreme conditions. Thus, the stability of the formulations is essential. In addition, the emphasis of development efforts should be put on, not only enhancing lubrication performance by lowering the friction coefficient, but also on the reduction of wear of material surfaces.

Green lubrication brings about benefits in decreasing the environmental impact of today's lubrication solutions by replacing the harmful additives and mineral oils by stable vegetable or plant-based oils, e.g. tall and canola oil, or water-based lubricants. At VTT, water lubrication (Ahlroos *et al*., 2011) has been one of the key topics in the tribology research area.

Carbon Fillers in Polymer. A good lubrication effect is achieved by low-friction coatings that include diamond-like carbon (DLC), molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) dry coatings. Figure 2 shows the potential of DLC materials in reduction of friction and wear. Different physical and chemical processes that are taking place during the motion of rubbing or sliding surfaces are denominated as wear.
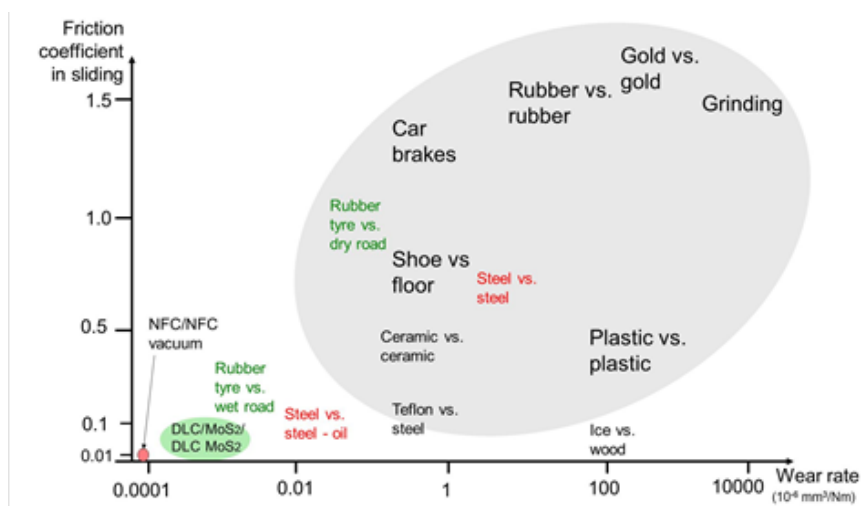

Figure 2   Friction and wear reduction by DLC coatings (Holmberg, 2009)

Wear resistance of polymer materials can be affected by adding fillers or reinforcing fibres to the polymer matrix. Fibres enhance mechanical properties, impact resistance, thermal conductivity and creep resistance of polymer systems. The improved mechanical properties typically yield enhanced wear characteristics, and resist wear, such as plowing or tearing, of non-adhesive components. Fillers can act as solid lubricants for self-lubricating materials such as polytetrafluoroethylene (PTFE), MoS_2, or graphite, especially when the use of liquid lubricants is undesirable. Fillers form a beneficial third-body transfer film between the surfaces and thus decrease the wear rate of the surfaces. Also nanofillers improve mechanical properties and create a beneficial transfer film.

The average prices of various carbon filler materials are as follows[1]: for carbon fibres over 15 €/kg, CNTs from 300 $ up to 100 000 $/kg, and carbon nanofibres starting from 200 $/kg. Graphite is relatively cheap. These prices are relatively expensive, and cheaper materials are constantly sought, which suggests that the market prospects for bio-based carbon are good.

Filters and Membranes

Activated carbon has been used as an air and water filtration medium for a long period of time. In filter applications porous solids or fibrous materials remove particles from air flow. In water filtering applications, porous or nonporous materials or membranes act as sieves and deep filters. Typically carbon used in air and liquid filtration applications are activated carbon particles embedded into actual filter structure, and they are used for removal of trace substances and gaseous species e.g. odours, but is some special cases carbon can also be used as filter structure. Carbon is used e.g. in molecular sieve membranes, which are typically used in the petroleum industry for purifying gas streams from water. Such carbon molecular sieves can be produced by carbonization of polymeric membranes.

The total market volume of filters was 46 billion € globally in 2010 (Freedonia, 2012). Internal combustion engines and related filter products represent 45 % of the market, while other air and

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[1] www.cheaptubesinc.com, www.nanotubes.cn, 26.9.2013

fluid filtration products share the rest of the market (26 % and 29 %, respectively). MANN+HUMMEL, Donaldson, MAHLE International, DENSO, and Parker Hannifin are global market leaders in filtration materials.

Table 4   Summary of carbon in filtration applications.

Application	Important parameters in current applications	Motivation for replacement by bio-based carbon	Experience of project partners
Activated carbon in filters	- Large surface area of the material and a high flow-through. - Sufficient elasticity and deformation during carbonization. - Sufficient mechanical strength. - Efficient removal of particles.	- Filtration is a growing market. - The use of nanotechnology increases the performance requirements of filtration.	VTT - Aerosol filtration and water membrane research and measurement facilities
Carbon membranes	- Pores of porous carbon separates gas molecules based on sieve effect	- Permselectivity by functionalization	

Activated carbon in filters. Activated carbon materials are used in various filtration applications. AC materials can be used in air filtration applications as adsorbents in granule or powder form (loose, bonded, embedded), or fibres (loose, felted, woven, embedded). Adsorbents such as AC are typically impregnated into fibrous filter media such as nonwoven forming media generically known as combi-filter (BCC Research, 2014a); while fibrous structure removes particulates from air flow, AC is capable of removing foul odours and gases from air streams in applications ranging from HVAC (heating, ventilating, and air conditioning) systems to gas masks and respirators. Also fully AC materials such as charcoal cloths have been manufactured e.g. by carbonizing woven cellulose fabrics (Sutherland, 2008) and various woven and nonwoven materials (VTT research carried out in 1990's). AC combi-filters are also used for liquid filtration e.g. for industrial removal of odours from oil, removal of odours and tastes from foods and beverages. Larger AC blocks can be used in applications, such as adsorbent filters in small-scale water purification systems, e.g. purification of potable water in caravans and boats.

Carbon membranes. From the 1970s, carbon membranes have been used in gas separation. Membranes can be made of porous solids with a controlled pore size approaching dimensions of gas molecules. A membrane can be used in the form of a flat sheet, or it can be supported on a tube, capillary, or hollow fibre. Carbon membranes are more selective and thermally and chemically stable than polymeric membranes. However, brittleness of carbon membranes are is a disadvantage (Ismail & David, 2001). In the future, higher permselectivity with acceptable productivity is required, even with complex and aggressive feeds.

Cellulose and its derivatives have been mentioned as possible raw material sources for carbon membranes in a review written by Ismail and David (2001), but the number of studies concerning cellulose is still small based on the fact that the writers do not site any such study.

Capacitive Desalination

Desalination of brackish water, seawater, and industrial and municipal wastewaters for reuse and irrigation is a promising application field which could benefit from high-performance carbon materials. The research company ASD Reports (2012) estimated the global desalination market at $18.37 billion in 2012. The recent market review by TechNavio (2014) has put the compound annual growth rate (CAGR) in this market at 8.9 % for the period from 2013 to 2018.

The desalination market is dominated by reverse osmosis (RO) desalination plants (Shannon *et al.*, 2008). The capacitive desalination process is a promising desalination technique compared to RO process because it can operate at low pressure and does not require a membrane. Lower energy

consumption can be achieved and the problem with membrane fouling is avoided. The cost of desalination is less than that of RO process.

Capacitive desalination is a technique where saline water flows through or by porous electrode pairs. Ions in the water are attracted to the electrode by a static electric field, and separated from the bulk. The process is reversible and the ions can be released into the concentrate when electric field is switched off or reversed. Capacitive desalination technique utilizes porous electrode made from high surface area and conductive carbon materials (Suss *et al.*, 2012).

There are 16,000 desalination plants operating worldwide producing about 66.5 million m^3 of water per day. The companies using capacitive desalination technique include Voltea (NL), Reticle Inc. (US). ESTPURE (CN) has the largest production capacity, 1000 units/systems per year.

The types of carbon available for capacitive desalination applications are given below. Their pore characteristics are given in parentheses.

- AC/carbon cloth (random micropores with diameters less than 2 nm and mesopores with diameters ranging from 2 nm to 50 nm).
- Carbon aerogel monolith (meso pores).
- Ordered mesoporous carbon (ordered uniform meso pores).
- Activated carbon with added ion exchange membrane coating to enhance ion selectivity.
- Electrospun ultrafine carbon fibre webs (micro, meso and interfibre macro pores).

Summary including drawbacks of current carbon solutions as well as motivation for bio-based materials is given in Table 5.

Table 5   Summary of capacitive desalination applications

Application	Drawbacks of current carbon solutions	Motivation for replacement by bio-based carbon	Experience of project partners
Water desalination by capacitive deionization (capacitive desalination)	- Many mesoporous carbons are based on phenol formaldehyde resin, which is highly toxic. - Production of uniform mesoporous carbon based on templating is nontrivial and costly. - For many precursors, stabilization is required before carbonization. - High temperature is needed for carbonization and activation. - Carbon yield is low. - Porous electrodes have relatively low mechanical strength and conductivity. - Coal-based carbon often contains sulphur.	- Cellulose is an abundant carbon source from the Finnish pulp & paper industry - There is a huge market for desalination applications.	VTT - Electrical double layer supercapacitor printing on paper which is related to capacitive desalination (Keskinen *et al.*, 2012) TUT - Printed supercapacitor on plastic substrate (Lupo, 2013)

Carbon monoliths can be produced from carbonization of phenol formaldehyde (PF) resin, partially carbonized PF resin that is extruded and sintered later, by conversion of AC by hot isostatic pressing, or by carbonization under compaction. Carbon monoliths are promising electrode materials due to their high specific surface area, mechanical strength and high electrical conductivity. Activated carbon is produced by carbonization and subsequent chemical or physical activation of various materials such as nutshells, coconut husk, peat, wood, lignite, coal, and petroleum pitch. Preformed precursors such as fibres and textiles can be carbonized. (Kim *et al.*, 2004; Zou *et al.*, 2008)

Support Materials for Catalysts

Catalysts increase the rate of chemical reactions by providing an alternative reaction mechanism that involves a lower activation energy and different transition state. They can enable reactions that

would otherwise be blocked or slowed by a kinetic barrier. Catalyst may increase the reaction rate or selectivity, or enable the reaction at lower temperatures.

There is a general need for cheaper and more durable catalyst-support structures. There are several challenges in production and use of catalysts. CO formation for example, often occurs in fuel cells during catalysis, conductivity is poor, there are dispersion problems in catalyst ink preparation, and availability of carbons pose problems in current solutions. Thus, good electrical conductivity, high oxidation resistance and application specific morphology are needed for good catalyst supports for fuel cells, as well as in electrolytic processes and metal-air batteries. Graphitized polymer webs, polymer templated mesoporous carbons and combinations thereof can provide the required properties. Bio-based carbon has wide possibilities in catalyst structures in the form of carbonized wovens, sheets and papers.

The global demand of catalysts was estimated at approximately 29.5 billion $ in 2010, and is expected to experience fast growth in the next years (Acmite, 2011). The companies representing chemicals, pharmaceuticals, polymers, oil refinery operations, food industry and such, include BASF, Akzo Nobel, Johnson Matthey, 3M, Kemira, Bayer, Solvay, to name a few.

Catalyst is supported on a material, usually activated carbon, carbon black, or alumina that enables a higher specific activity and thus effectiveness of the catalyst. The support can be a porous film or agglomerate consisting of particles. Carbon alternatives have typically much larger specific surface area than aluminas. In current fuel cell solutions the catalyst is first bound on either carbon black powder or carbon nanotubes that are in single- or multiwall-tube or fibre format. This catalyst layer is applied on a gas diffusion layer, or backing layer, made of carbon fibre woven or carbon fibre paper or sheet. Aspects of using carbon in these applications are summarized in Table 6.

Table 6   Summary of carbon in catalyst carrier application.

Application	Important parameters for carbon in present applications	Motivation for replacement by biobased carbon	Experience of project partners
Catalyst support for fuel cells	- Present carbon solutions: carbon fibres as woven, and paper/sheet materials, CB and CNTs - Durability, high conductivity - Surface area, purity, surface chemistry - Recycling capability, price - Catalyst activity, selectivity, price	- Pollution free driving (automotive industry) - Metal-free carbon-based catalysts - Reduced price of fuel cells - Cheaper and more durable structures of catalyst layer and its support	- VTT has wide experience in catalysts. - Carbon nanofibre supports has been produced from PAN

VTT has experience in manufacturing carbon nanofibre webs in 2D for fuel cell catalyst supports (e.g. Heikkilä, 2012a; 2015a; 2015b), applying catalyst nanoparticles onto various carbon supports, development of carboneous catalyst carriers for fuel cells and electrolyzers, durability research of carbon supports, catalysis in practice, and co-operation with universities and other research institutes.

Gas Storage

There are several ways to store gases under normal or high pressure. Gas can be compressed into liquid at cold temperatures, compounded with a substance, or absorbed in a medium. Typical absorption mediums include graphite nanofibres, activated carbon, or zeolite. The most common gases that are transported and stored are natural gas (methane) and increasingly hydrogen. Liquid natural gas (LNG) storage markets are developing due to the increasing interest in vehicles fuelled by gas. Microporous carbon can be used as an absorbent material for absorbed natural gas (ANG) technology (see Table 7).

Table 7   Summary of carbon in gas storage application

Application	Requirements for carbon	Motivation for replacement by bio-based carbon	Experience of project partners
Microporous carbon as an absorbent material for absorbed natural gas (ANG) technology	Selective optimization of porosity. High adsorption capacity.	Alternative raw material source	ANG technology has been developed at VTT in the 90s. Activated carbon fibre structures with high adsorption capacity were developed

Adsorbed gas has a higher density compared gas without an adsorbent at same conditions. The adsorption phenomenon can be used either to reduce the filling pressure of a gas tank or to increase the storage capacity. Lower filling pressure enables a lighter structure of the pressure vessel, which is essential in vehicle applications. Low pressure and low weight are both factors that are important for the competitiveness and safety of natural gas fuelled vehicles.

A gas storage container can be filled with a special adsorbent with a high adsorption capacity. Activated carbon fibres are known to have a high adsorption capacity especially for methane, and a significantly lower capacity for hydrogen. The absorption of gas occurs under pressure into the pores of the absorbent material during the filling of container. Gas is released from the container by decreasing the pressure, but heating is required in order to compensate the heat of adsorption.

The most important property of carbon is high micro-porosity, since it enables the highest adsorption capacity per volume of gas. The properties of microporous carbon adsorbents can be adjusted and selectivity optimized further to meet the particular needs. Advanced carbon materials have also an ability to both selectively store targeted gas and filter undesirable contaminants from the mixture (Frost&Sullivan, 2012b).

Several different activated carbon qualities prepared from different raw materials can be used. Alternative adsorption materials include porous organic compounds such as amberlite (e.g. produced by Rohm & Haas) or Dow resins, zeolites such as Davidson molecular sieves, and silica based compounds such as xerogels, aerogels and mesoporous material configurations (e.g. MCM41, Mobil Composition of Matter No. 41, produced by Mobil). 3D structures such as foams of bio-based carbon are suitable for gas storage applications (Frost&Sullivan, 2009).

ANG storage market has not yet achieved full commercialization, and is still in research, demonstration or early commercialization phase. The benefits are known, but wide market penetration has not yet occurred. Development of an ANG storage system includes not only the adsorbent, but also development of filling and release station technology and demonstration of overall technical and economic feasibility to allow for a successful commercialization.

Electrodes for Energy Storage

Graphite is the state-of-the-art anode material for Li-ion batteries, and activated carbon powder (PAC) for supercapacitors (SC). There is a huge development potential for novel carbon materials including high-surface nonwovens, and templates for 3D-carbon nanostructures in all these electrochemical applications. The need for capacity improvement and less expensive components drives the development of both supercapacitors and Li-ion batteries, the former progressing at a faster pace. Requirements for carbon properties are summarized in Table 8.

Table 8   Summary of carbon electrode applications for energy storage.

Application	Properties of carbon in present applications	Motivation for replacement by bio-based carbon	Experience of project partners
Activated carbon for supercapacitor (SC) electrodes	- High specific surface area 1000-2000 m^2/g - Surface wettability - Controllable pore size and its distribution - Stability inside the required potential window - Lack of functional groups to avoid irreversible redox processes during operation - Precursors coconuts, seaweed, titanium carbide	The increasing demand will increase also the need for anode materials; WBC will offer a new raw material source. Potentially cheap and abundant raw material source.	VTT - Conventional and printed SCs 2005-2013. - Wide range of materials applied and developed.
Graphite for Li-ion battery electrodes	- Li intercalation between crystal planes - High degree of lithiation, good reversibility - High-temperature graphitization process	The increasing demand will increase also the need for anode materials; WBC will offer a new raw material source.	- Composite materials for Li-ion batteries. Printing of batteries.

Activated carbon for supercapacitor electrodes. The total market size of supercapacitor products was about 470 million $ in 2010 (BCC Research, 2011), forecasted to reach 1200 million $ in 2015. The average price for a standard activated carbon is 30 €/kg. There are about 70 companies in the market including Maxwell (US), Nesscap, Batscap, Panasonic, APowerCap, Tecate, Asahi Glass, LS Cable, Rubycon, and Skeleton Technologies.

Artificial graphite is produced from various precursor materials such as coke, pitch, wood, coconuts, and titanium carbide. The development is aiming at improving capacitance and power characteristics of supercapacitors. The recent work and publications show excellent results for various bio-based precursors produced with the hydrothermal carbonization technique available at VTT.

Graphite for battery electrodes. The market size of Li-ion batteries was about 15 billion $ and the annual growth 8 % in 2011 (Yano Research Institute Ltd). The graphite material accounts for a very small share of these figures. The global demand for graphite was 2.5 megatons and production 2.3 Mtons in 2012, of which batteries accounted for 95 ktons (68 % natural and 32 % synthetic graphite). Companies operating in this field include Altairnano, Axeon, Concorde Battery, Panasonic, Boston Power, E-One Moli Energy, Electrovaya, EnerDel, Johnson Controls (SAFT), Li-Tec Battery GmbH, NEC, Primearth EV Energy Co, Sanyo, Thunder Sky, Valence Technology, LG Chem, SB LiMotive, and GS Yuasa.

There is a trend to create smaller, lighter, and less expensive batteries. Bio-based carbon can be used in the place of the graphite anode. The future requirements will probably be fulfilled with non-carbon materials, and as a consequence the prospects for bio-based carbon in this application are relatively small. However, the overall consumption of anode materials will increase due to the steadily increasing market.

2.2 Materials, Precursor Processing and Carbonization

As plants absorb carbon from atmosphere during their growth, biomass is in general rich in carbon. Lignocellulosic biomass or its fractions are industrially processed into materials with different properties. These materials can be used as raw materials for precursors that are further carbonized into carbon products, as shown in Figure 3.
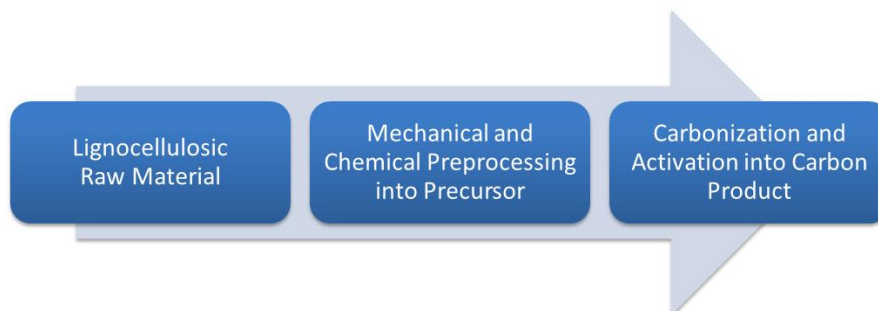

Figure 3   Processing steps of carbon products.

Main components of all lignocelluloses are cellulose, hemicellulose and lignin. These all are suitable raw materials for carbon due to their relatively high carbon contents. They are polymers and can be processed various ways to form solid precursor structures. They can be modified, e.g. chemically or using additives, in order to obtain desirable functionality and change processability properties, provided that the added-value of the selected application(s) covers the increased costs. The current uses of wood-based polymers in carbon materials are summarized in Table 9. Also other side streams from bio-refineries, or other sources of biomass can be used as carbon precursors.

Table 9   Current uses of lignocelluloses in carbon applications.

Material	Description	Typical carbon applications, examples and state-of-the-art
Cellulose	Celluloses utilized in this project include: pulp and cellulose fibres; modified cellulose including dissolved pulp, cellulose carbamate, and Biocelsol; and cellulose derivatives.	Viscose has been used in carbon fibre production, but it has been overcome by PAN and pitch [i] due to its lower tensile modulus [ii]. Viscose is still used in low-end applications. Foam like carbons made by, e.g., pyrolysis of aerogels, based on supercritical drying of cellulose acetate gels [iii]
Hemi-celluloses	Xylan, galactoglucomannans and their derivatives.	Carbon materials for catalyst carriers by hydrothermal carbonization (HTC) [iv], usually carbonization of lignocelluloses, not pure hemicellulose.
Lignin	The properties of lignin depend on the extraction method, e.g., sulphur-free types of lignin are of interest. Lignin can be modified to obtain better processability and specific properties.	Acid precipitated lignin has been carbonized and chemically activated to produce microporous carbon for rechargeable hydride battery [v]. Carbon fibre (30 µm) has been produced from melt-spun kraft lignin [vi], and open cell carbon foam by carbonizing calcium lignosulfonate in an inert environment [vii]. Simultaneously carbonized and sulfonated lignin has been used as a solid acid catalyst in biodiesel production and sugar dehydration [viii].

Refs. [i] (Frank, 2012); [ii] (Frost & Sullivan, 2008); [iii] (Guilminot, 2007); [iv] (Falco, 2013); [v] (Babel & Jurewicz, 2008); [vi] (Kadla, 2002); [vii] (Spradling & Amie, 2011); [viii] (Guo, 2012a & 2012b)

Carbon structures and shapes can be created by carbonizing preformed polymeric precursors in the form of from small particles (0D), fibres (1D), sheets (2D), and 3D structures. There are several polymer processing techniques than can be used. A summary of selected methods is given in Table 10 and a brief introduction to the technique; requirements posed on the material are presented in

following chapters in alphabetical order. Precursor geometries that are possible to be produced with the technique mentioned, and suitability for processing carbon precursors is briefly discussed.

Table 10   Methods for producing carbon precursors.

Methods	Precursor geometry	Works related to lignocelluloses done at VTT, TUT, and externally
3D printing	2D or 3D, applied on 2D or 3D surfaces	At VTT, tracks, and scaffolds with customized porosity has been printed on flat or curved surfaces. Materials used in these trials include biodegradable polymers (polycaprolactone, polylactic acid (PLA) and hybride) and pure/modified cellulose nanofibrils (CNF). Other groups have produced similar structures for medical applications, but not used CNF.
Electro-spinning	0D, 1D, 2D	Electrospinning of nanofibres from e.g. cellulose acetate [i], organosolv lignin [ii], and cationized cellulose. Electrospun PAN sheets have been carbonized at VTT.
Extrusion spinning	1D	Traditional spinning technologies, also studied at VTT and TUT, are used for bio-based polymers, e.g. wet spinning of cellulosics from NaOH such as Biocelsol [iii] and cellulose carbamate processes [iv], newer methods include use on dry-jet-wet spinning, ionic liquids as well as Lyocell [v]. Fibres has been made by melt-spinning of lignin [vi].
Film forming	2D	All methods for producing dense films and most methods for porous films for have been applied for bio-based polymers at VTT.
Foam forming	2D (<0.1mm) - 3D (>100mm)	VTT has studied several bio-based raw materials including wood fibres (paper making pulp), regenerated cellulose, peat, and agro fibres. The potential of the methods is high also for production of carbon precursor.
Freeze-drying	0D, 1D, 2D, 3D	At VTT, drying methods of CMF and CNF and their blends with polymers have been developed. In the literature, results on freeze-drying of, e.g. cellulose nano-crystals (CNC), CNF, xylan-cellulose composites have been reported. The typical intended use is high-porosity aerogels.
Non-solvent precipitation	1D	VTT has published results on precipitation of cellulose ester and aromatic polysaccharide derivatives to be used in fillers and pigments. Preparation techniques of nano- and microparticles from cellulose acetate presented in literature.
Polymer foams	3D	VTT has studied extrusion foaming of PLA in the PROFOAM project. There is a large amount of publications and patents on foams of PLA, viscose, cellulose derivatives, and cellulose acetate, and foams reinforced with nanocelluloses. Stabilized hydrogels: Foamed cross-linked hydroxypropyl cellulose [vii]. VTT has patented a process for preparing cross-linked cellulose ether foam particles [viii].
Spray drying	0D, 1D	Spray drying in nanocelluloses (CMC, CNF), and carboxymethyl cellulose has been done at VTT. Spray drying is a common last step in recovering various biopolymers, such as hemicellulose or lignin.
Supercritical drying	0D, 3D	The method has been applied on drying nanocelluloses and lignocelluloses to extract aerogels and particles.
Textile processes	1D, 2D	Several nonwoven techniques are very suitable for producing 2D precursor webs due to their porosity: The maturity of processes allows for production in industrial scale. The carbonized product can be used as a crushed material or as platelets. AC nonwovens have prepared from regenerated cellulose [ix].

Refs: [i] (Heikkilä *et al.*, 2013); [ii] (Heikkilä *et al.*, 2012a&b); [iii] (Nousiainen & Vehviläinen, 2009; Vehviläinen *et al.*, 2008); [iv] (Valta *et al.*,, 2010 & 2011); [v] (Jiang, 2012); [vi] (Awal &Sain, 2013; Wikström *et al.*, 2013); [vii] (Kabra *et al.*, 1998); [viii] (Turunen *et al.*, 2009); [ix] (Cislo, 2004)

The final steps in preparing carbon products are carbonization with thermal gas phase or liquid phase hydrothermal processes, and depending on the application, functionalization with graphitization or activation. Thermal processes are summarized in Table 11 and thermal and hydrothermal carbonization (HTC) processes compared in Table 12.

Table 11   Carbonization and activation processes.

Process	Description	Materials and processing method examples
High-temperature carbonization	Carbonization of raw materials in water-free inert (or reactive) atmosphere in temperature typically from 600 °C to 1400°C producing typically amorphous or disordered structure.	Common process for producing carbon materials from natural and synthetic precursors. Has been used in preparation of carbon nanofibres using electrospun cellulose [i] and freeze dried CNF aerogel [ii] as precursors.
Graphitization	Organized planar layered, highly oriented and well-crystallized graphite, planar structure of carbon above 2000°C	Graphite formation requires highly organized precursor structure. Thin graphite layers observed in surface of carbonized cellulose fibres [iii].
Activation	Porous carbon with high degree of microporosity and high specific surface area (>500 m^2/g). Typical activation treatments are by water vapor or CO_2.	Traditionally in powdered or granular forms, but we aim to activate 1D-3D structures. AC fibres & membranes [iv] and fabrics [v].
Hydrothermal carbonization (HTC)	HTC process converts wet input material into carbonaceous solids, suitable for materials with low dry content (5-10wt%).	Has found to be '*an effective way to increase the turnover time of the carbon contained in the biomass*' [vi]. VTT has patent application concerning HTC [vii]
Refs: [i] (Kuzmenko, 2012); [ii] (Jazaeri, 2011); [iii] (Kaburagi, 2005); [iv] (Ioannidou & Zabaniotou, 2007); [v] (Babel, 2003); [vi] (Sevilla & Fuertes, 2009); [vii] (Grönberg *et al.*, 2014)		

Table 12   Characteristics of high temperature carbonization and HTC processes

	High temperature carbonization	HTC (Wikberg *et al.*, 2015)
Processing conditions	Gas phase, inert atmosphere, temperatures typically 1500-1800, also above 2000°C	Aqueous phase, mild temperatures, typically 180-250°C, exothermal process, self-generated pressures
Precursors	Solid objects from particles (0D) to fibres (1D), sheets and fabrics (2D) and 3D objects	No restrictions, aqueous streams and wet biomass/sludge possible
Precursor processing prior to carbonization	If thermoplastic like lignin: stabilization. Impregnation to increase carbon yield e.g. for cellulose	Often not necessary, grinding or other pre-treatment can be beneficial in some cases.
Energy use	Energy consuming process due to high temperatures	Exothermal process, low energy consumption
Carbon quality	Almost pure carbon, structure depend on processing conditions and e.g. tensioning of fibres during the process	Approximately 70-75% carbon, functional groups e.g. hydroxyl and carboxyl groups, amorphous structure, particles in micro and nanoscale
Yield	Carbon yield depends on precursor material	High mass yields, and carbon recovery

3 Summary of Experimental Work and Modelling

This chapter contains short summary of experimental work (3.1) and modelling (3.2) work carried out in BioPreCarb project.

3.1 Material and Product Demonstrations

Materials Demonstrations

Linear lignin for carbon fibres. Idea of the this demonstration was to verify the applicability of linear lignin as replacement of fossil-based materials in composites by producing long carbon fibre precursors from linear lignin using melt extrusion or various spinning techniques and carbonization. Linear lignin offers potential for lignin-based carbon fibres with enhanced mechanical properties. In this project, preparation of linear lignin was attempted by a method adapted from milled wood lignin (MWL) preparation, claimed to produce linear lignin. However, the method is not industrially applicable.

The linear lignin sample was relatively pure lignin with some xylan impurities. The average molecular weight of linear lignin was high compared to reference lignins soda grass (see Figure 4) and kraft hardwood lignin, indicating that linear lignin consists of larger molecules than either of the reference lignins. The molar mass of linear lignin corresponded to an average degree of polymerization (DP) of around 41. Linear lignin contained a high amount of β-O-4 lignin bonds, typical to native lignin. Thermal characterization indicated that melt-processing of this material is not feasible and, thus, only solution spinning methods suitable for fibre formation.
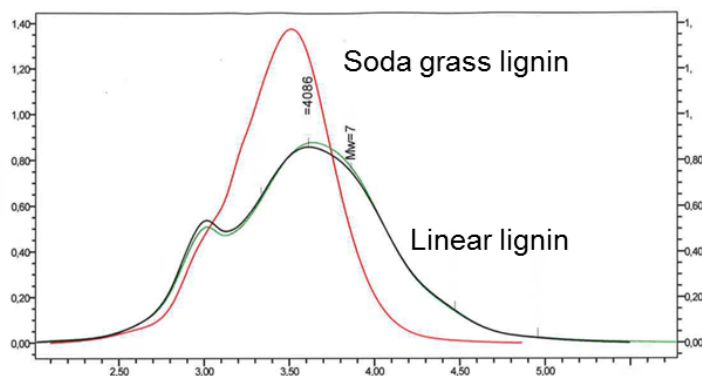

Figure 4   Molar mass distributions of linear lignin and soda grass lignin (data obtained from Liitiä et al., 2014).

Electrospinning trials of linear lignin indicated better spinnability compared to organosolv lignin used as reference and fibres were obtained in concentration below 50 wt% (see Figure 5). Preparation of sample suitable for carbonization was, however, unsuccessful. Fragility of fibres indicated that they would not have been good precursors for carbon fibres without additives.
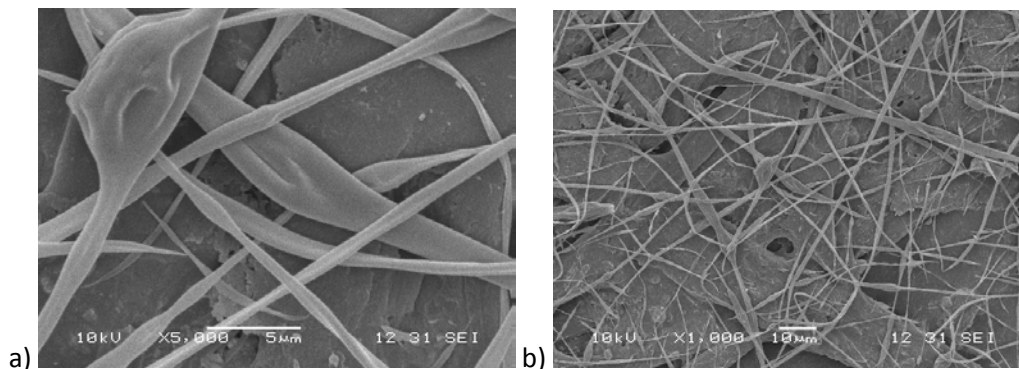
Figure 5   Appearance of electrospun linear lignin in concentration of 48 wt%. (a magnification 5000x and b 1000x)

Carbon foams. Idea of the this demonstration was to investigate possibility to produce carbon foams structures from lignin and other bio-based materials produced 1) via novel extrusion foaming technology and 2) 3D-printing, followed by high temperature carbonization. In addition we aimed for make less expensive carbon foams for high end applications, such as high temperature insulation, heat sinks, thermal exchangers, filters, fire and chemical resistant composites etc., using bio-based raw material and new processes in production of porous materials. Carbon foams are interesting application area since price of current carbon foams is high, upto 1000 €/kg. Therefore we studied possibilities to use relatively simple processes, extrusion foaming and 3D printing, for production of 3D precursor materials for carbonization. Challenge of extrusion foaming is that materials needs to be thermoplastic for processing, but not thermoplastic for carbonization. Cellulose acetate type of material, for example, requires processing, for example, deacetylation or stabilization prior to carbonization.

We were able to produce foam from cellulose acetate, but the structure was partly destroyed during carbonization due to its thermoplasticity (see Figure 6). Direct write 3D-printing was suitable for CNF pastes and we were able to produce precursor structures, which were not thermoplastic. We were able to make precursor and stabilize them (see Figure 7), but carbonization trial was unsuccessful. Even though we obtained some interesting preliminary results, but were not able to produce carbon foams with either types of precursors within this project.
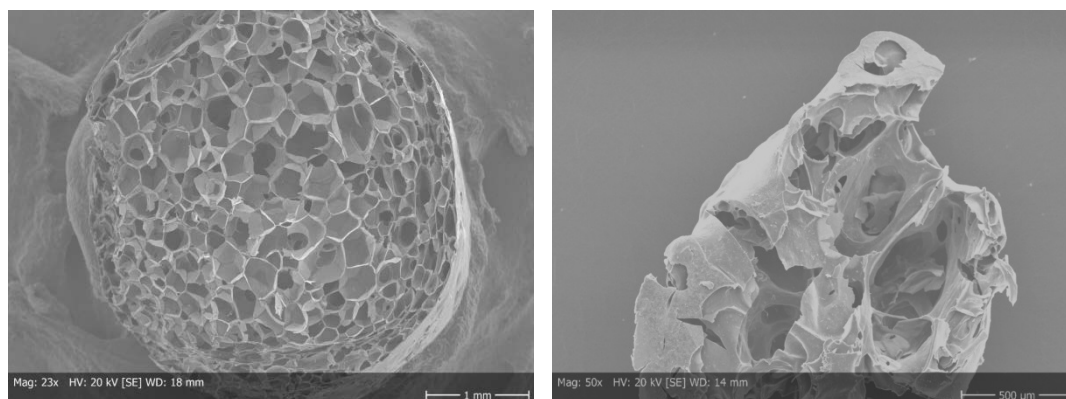

Figure 6   Cellulose acetate foam sample a) before and b) after carbonization. (Magnifications: x23 and x50)
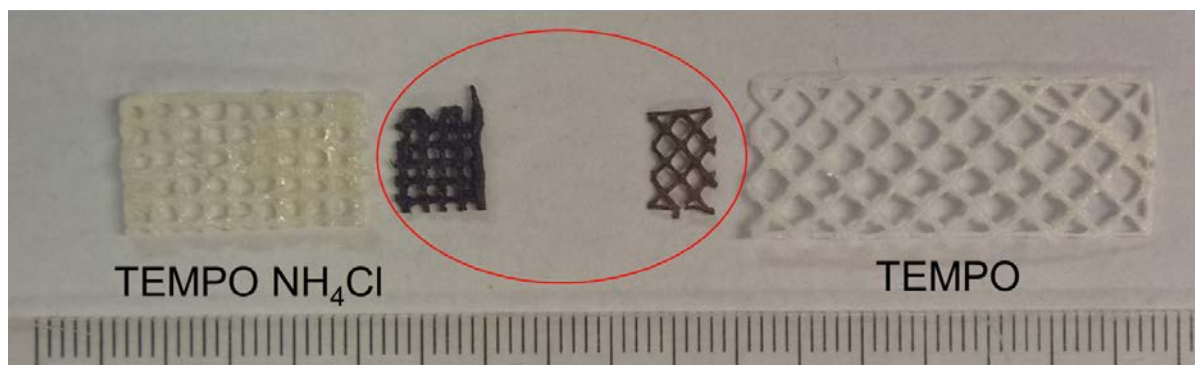
Figure 7   Stabilization trials of 3D printed objects from TEMPO CNF

Cellulose based carbon fibres. Idea of the this demonstration was to produce carbon and AC fibres from cellulose using wet-spinning, and further carding for making nonwovens, high temp carbonization and optional activation. We also studied use of chemical treatments for cellulosic raw material or precursor in order to increase carbon yield and activation stage in formation of cellulose based carbon fibres and fabrics for application such as composites for not-activated, and electrodes and possible also filters for activated carbons. Results of this study were used for validation of high temperature carbonization model.

Selected novel cellulose based precursors, cellulose carbamate and Biocelsol fibres, are more environmentally friendly than viscose. We were able to produce carbon and AC fibres and nonwovens from these materials using diammonium phosphate to increase carbon yield. Close-up image of carbonized fibres with and without impregnation are shown in Figure 8. Carbon fibres were not strong but had high electrical conductivity (between 3000-14000 S/cm) suggesting possible uses energy applications in certain type composites requiring heat or thermal conductivity. Carbon yield above 30 % was obtained with carbon fibres and considered sufficient by industry.
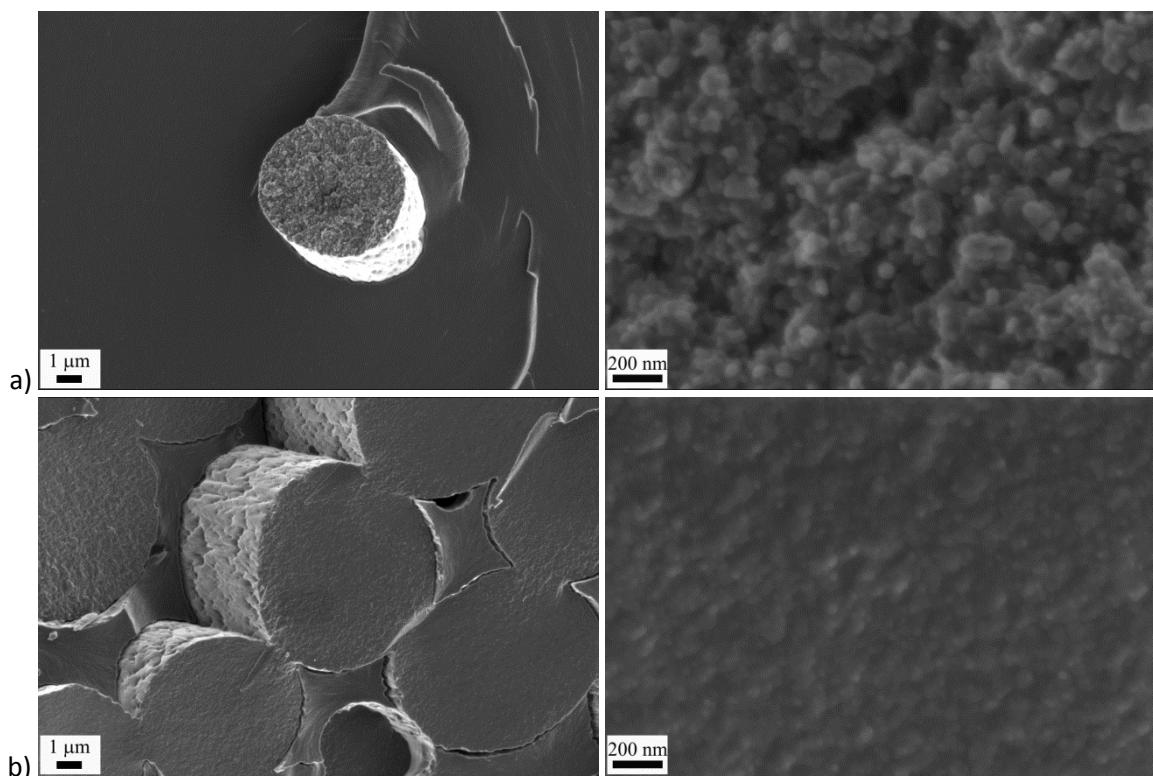

Figure 8   Appearance of the carbon fibres made using (a) untreated and (b) impregnated (2.5 % $(NH_4)_2HPO_4$) Biocelsol precursors

AC fibres had high specific surface area (1000-2000 m^2/g) in range of gas phase adsorption applications. Carbon yield of AC fibres was lower than that of carbon fibres, but still in best cases around 15 %. Appearance of precursor and AC materials are shown in Figure 9.
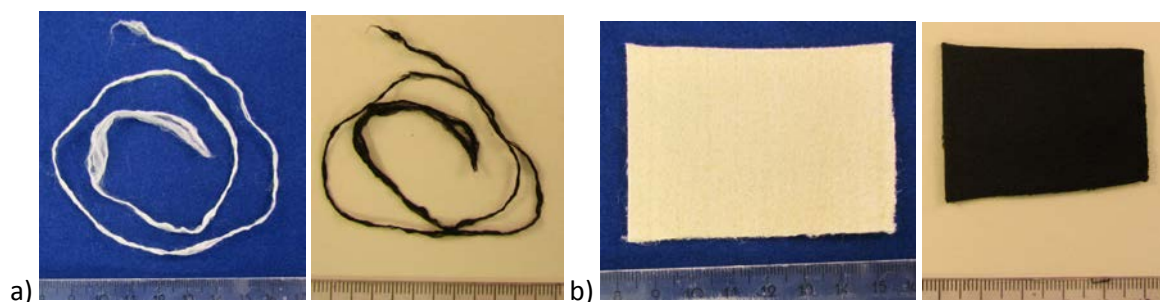

Figure 9 Appearance of AC samples before and after activation process a) Biocelsol fibre b) cellulose carbamate nonwoven.

HTC particles. Idea of the THC study was to produce various types of HTC particles from bio-based precursors and to produce experimental data for validation of HTC carbonization model. It was demonstrated that carbonaceous particles of different shape and size can be produced using HTC and different lignocellulosic raw materials. Spherical particles were obtained from glucose and hemicelluloses. Particles obtained by carbonization of kraft pulp and cellulose with short residence times were rod-like pieces having partly fibrous structure and fine-structure on the surface. With longer residence more spherical particles were also produced from kraft pulp. Particles from lignin in alkaline conditions, where lignin is partly soluble, adopted spherical structure. The particles formed from lignin in acidic conditions were sharp-edged clumps having partly smooth surface. The size of all these particles could be effectively reduced by microfluidizing reaching nano- and sub-micron-scale particle size. The shape of the particles appeared to remain intact during microfluidization (see Figure 10).
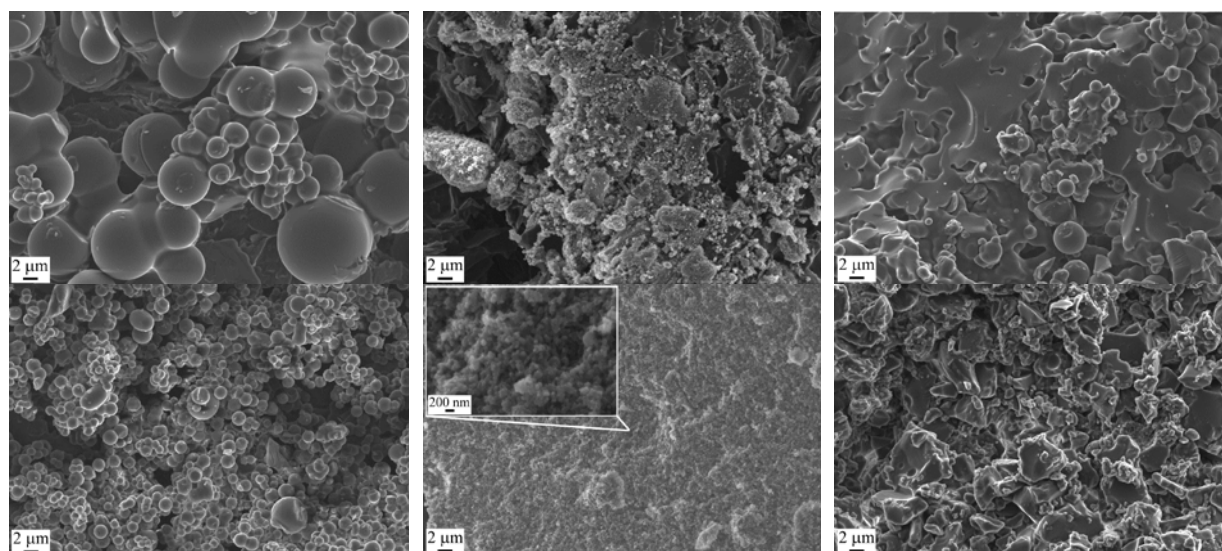

Figure 10 Appearance of HTC for glucose, kraft pulp and kraft lignin before (top line) and after (bottom line) microfluidization

The carbon content in the HTC-carbon particles reached ~70 % regardless of the original carbon content of the feedstock. Yields vary between 23 % and 73 % being higher for lignin than for carbohydrates in general. Glucose based and kraft pulp based HTC particles were used lubrication demonstration as lubrication additives and as fillers in low-friction coating, respectively.

Product Demonstration

HTC particles in lubrication. The applicability of biobased HTC carbon for tribology purposes was demonstrated by using the HTC carbon produced within the project as additives in mineral oil and in alternative carrier - deep eutectic solvent (DES). Furthermore, the effect of HTC carbon on friction properties of a coating was studied.

The measured coefficient of friction (COF) values of the lubricant with HTC additive were promising, see example in Figure 11. However, very little additional analyses on the lubricant and the coating systems were carried out in order to confirm and better understand the phenomena.

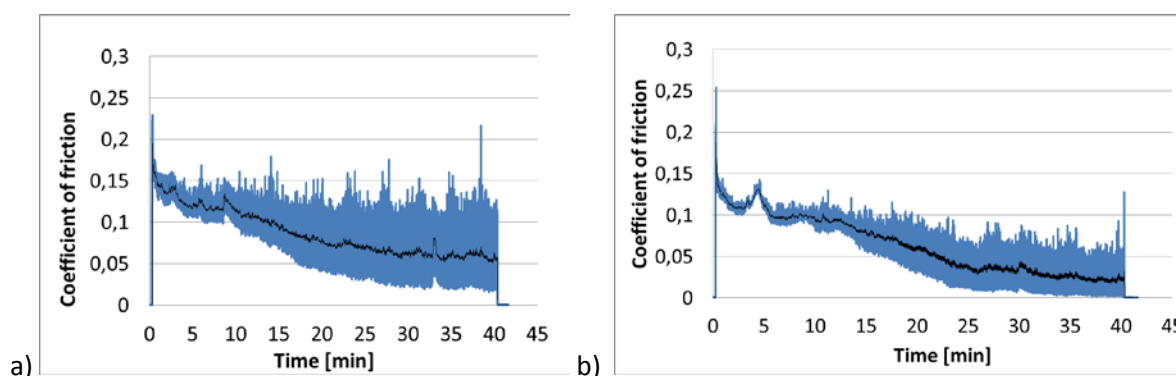a)   b)

Figure 11   The friction coefficient values for the Deep eutectic solvent (DES) lubricant systems: a) DES as such and b) the DES with HTC particles heaviest particles removed

In coating study it was quite evident that the Kraft pulp HTC particles improved the durability of a thin SiO_2 coating under compression and decrease friction of the coating (see Figure 12). In terms of lubricant solutions especially, more work is needed to find optimum particle and lubricant combinations, particle loadings, particle modifications etc.
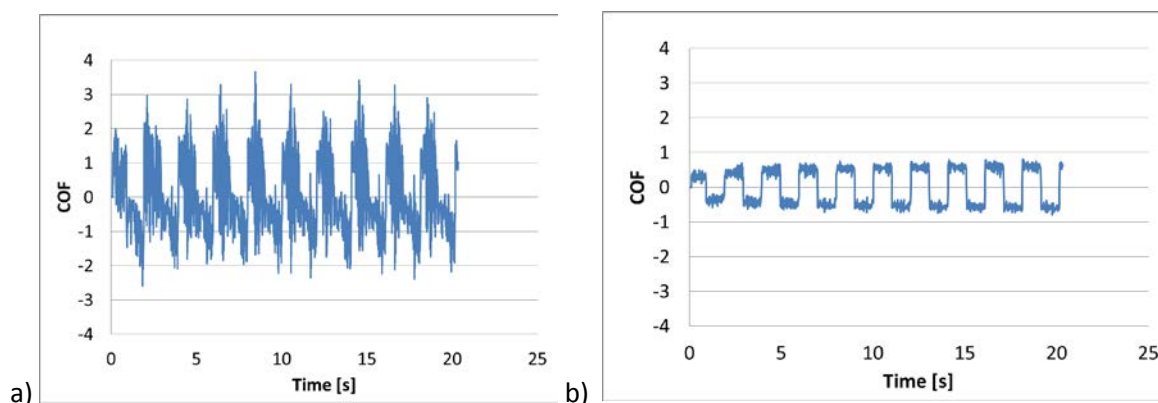
a)   b)

Figure 12   The friction coefficient values recorded for the sol-gel coating: a) without carbon particles, b) with Kraft pulp –based HTC particles

3.2   Modelling

In order to get better understanding of carbonization process we demonstrated the application of an atomistic modelling approach based on reactive molecular dynamics to the process of biomass carbonization (see Figure 13). The approach gives detailed insight into the decomposition and agglomeration reactions during carbonization. The quality and quantity of the end product can be analysed in terms of elemental composition, molecular size distribution, number of cyclic structural units, and overall structure.
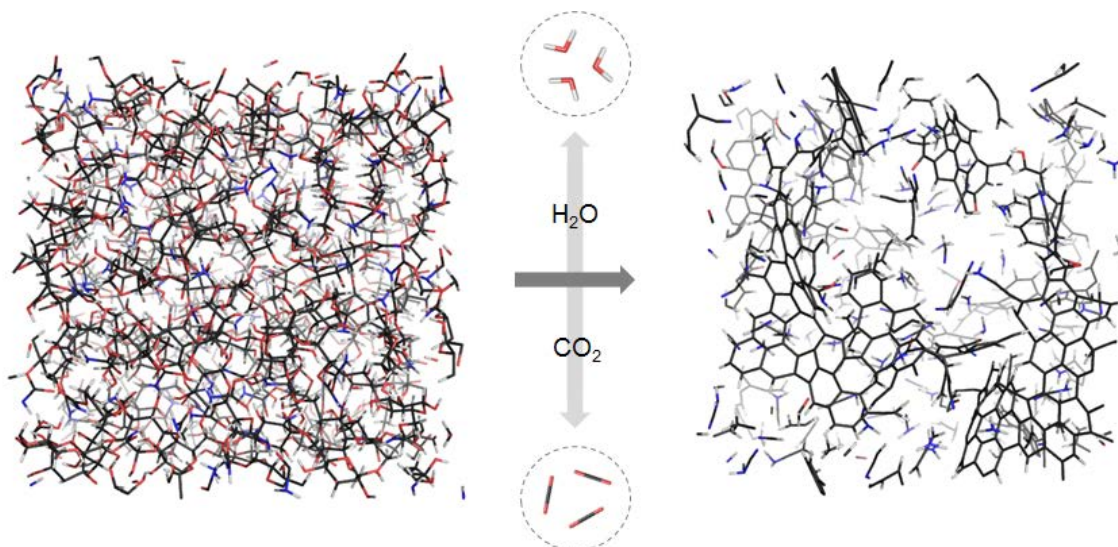
Figure 13   The reactive molecular dynamics (RMD) carbonization model: (left) initial configuration of 128 D-glucose molecules with one carbamoyl group per molecule and (right) final configuration after a 10 ns simulation at 2500 K with removal of inert gaseous species. Colour code: carbon in black, hydrogen in grey, oxygen in red and nitrogen in blue

For the carbamoyl group additive, both the number of carbon rings and the degree of carbonization increases for both half and one additive per glucose, but starts to decrease for two additives per glucose (see Figure 14). For two carbon monoxide additives per glucose, the number of carbon rings and the degree of carbonization increase considerably, whereas the hydrogen additive results in a slight decrease.
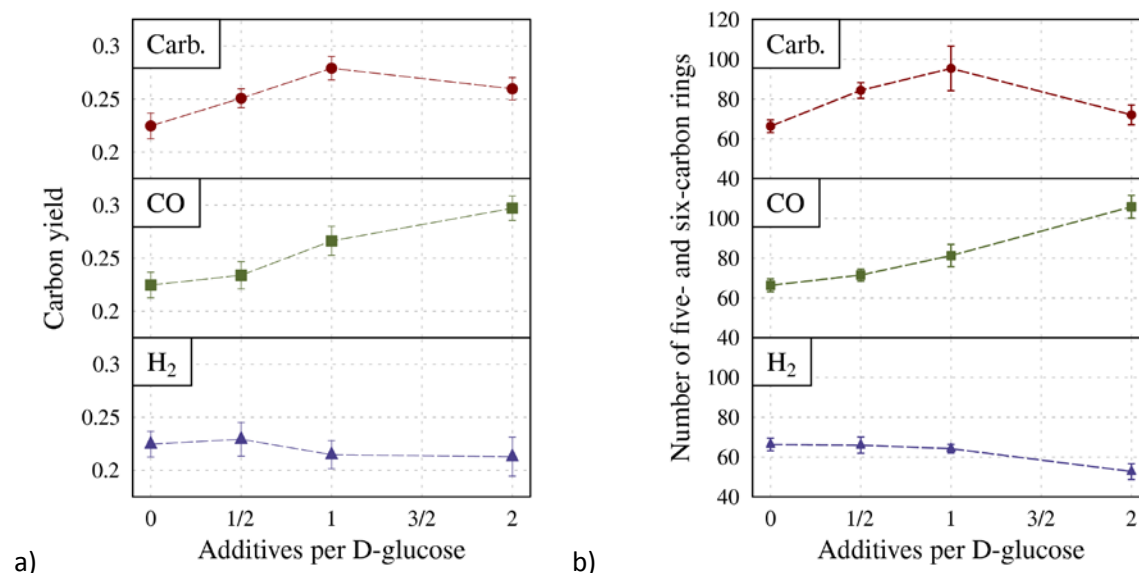

Figure 14   Results of the carbonization simulations: (a) carbon yield, and (b) number of five- and six-carbon rings. The leftmost marker in each plot represents the reference case of 128 D-glucose molecules

More details of the experimental and modelling work are available in publications.

1. H. Wikberg, A. Pasanen, P. Heikkilä, Bio-based tailored precursors for advanced carbons and applications, Carbon 2014, 29.6.-4.7.2014, Jeju, Korea
    Introduction to BioPreCarb project and carbonization methods, HTC examples from BioPreCarb projects

2. A.T. Pasanen, H. Wikberg, A. Paajanen, T. Pinomaa, J. Vaari, P. Heikkilä, A. Harlin, Carbon materials from bio-based and tailored precursors, Carbon Fibre Future Directions Conference 2015 February 24 - 27, 2015 Geelong, Australia

3. P. Heikkilä, K. Valta, M. Vehviläinen, T. Kamppuri, O. Orell, M. Kakkonen, A.T. Pasanen, M. Honkanen, A. Paajanen, T. Pinomaa, J. Vaari, M.Vippola, J.Vuorinen, A.Harlin, Carbonization of Cellulose Fibre Precursors: Experimental and Modelling Efforts, Carbon 2015

4. M. Honkanen, T. Kamppuri, M. Vehviläinen, P. Heikkilä, A.T.Pasanen, H. Wikberg, A. Harlin, J. Vuorinen, M. Vippola, Electron Microscopic Characterization in Bio-Based Tailored Precursors for Advanced Carbons and Applications -Project, Scandem 2015 - Annual Conference of the Nordic Microscopy Society during 9-11 June, 2015, Jyväskylä, Finland

5. P. Heikkilä, K. Valta, M. Vehviläinen, T. Kamppuri, O. Orell, M. Kakkonen, A.T. Pasanen, M. Honkanen, M. Vippola, J. Vuorinen, A. Harlin, Carbon Fibres from Regenerated Cellulose Fibre Precursors, NWBC 2015 - The 6th Nordic Wood Biorefinery Conference, 20-22 October 2015, Helsinki, Finland

6. H. Wikberg, T. Ohra-aho, M. Honkanen, P. Lahtinen H. Kanerva, A. Harlin, M. Vippola, C. Laine, Carbon materials produced by hydrothermal carbonization of potential pulp mill Streams, submitted 11 / 2015 to J. Mater. Sci.

7. Pinomaa *et al.* High temperature carbonization of cellulose using reactive molecular dynamics simulations, to be submitted e.g. to J. Phys. Chem. B in 2016

8. Heikkilä *et al.* about cellulose carbonization, expected in 2016Results of BioPreCarb cellulose material demonstration

4   Road Map

This technology roadmap describes a set of possible scenarios regarding the business development of specific technology area. Typical methods to produce such roadmaps can typically be divided into two classes: database analysis and expert interviews. In this project an approach has been to combine both methods. Scientific literature survey was performed together with meta-analysis of existing roadmaps in the field. These actions were done parallel with expert interviews. The process has been divided in to two phases: 1) collection of essential conditions and recruiting leadership, and 2) identifying product, critical system requirements, targets drivers and timelines.

This road-map report is divided into five cases within our projects focus areas. One of them is method oriented and four of them more products oriented, and depending on the case they can be more or less fixed for project focus areas, see Figure 15. Process oriented *HTC Process as Treatment for P&P Industry Side Streams* (Chapter 4.1) can be considered as one option for material source for the other two HTC related road-maps: *Lubrication Particles via HTC* (Chapter 4.2) and *Activated Carbon Particles from HTC Particles* (Chapter 4.3). Last two cases involve fibrous products involving high temperature carbonization process: *AC fibres from Cellulose for Added Value Applications* (Chapter 4.4) and *Reinforcing Bio-based Carbon Fibres for Composites* (Chapter 4.5).
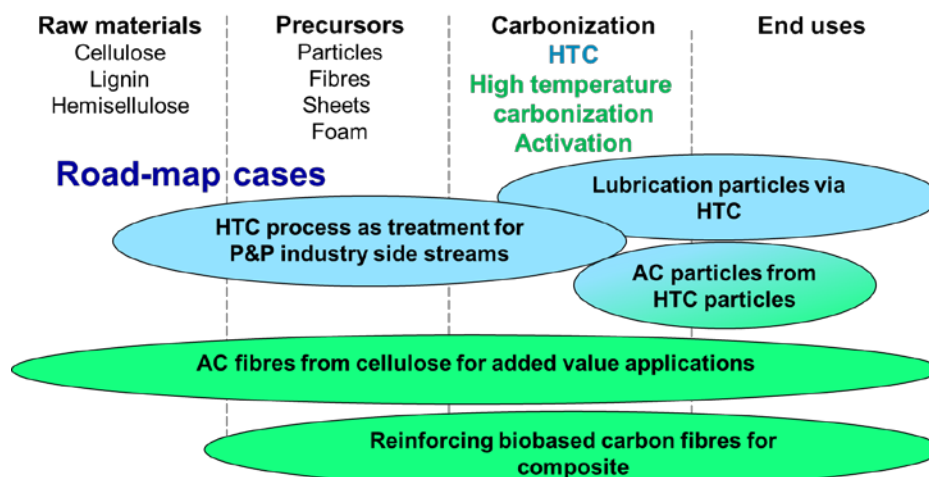

Figure 15   Project focus areas and cases studied in the road-map. Processes involving HTC are indicated with blue and involving high temperature treatment in green

Road-map was built by first collecting researchers view based on our own collective knowledge and literature sources. We wrote **introduction**, determined **essential conditions** and **product**, identified **value chain** and **critical system requirements**, reviewed **technology drivers** and **trade-off** and determined **questions** including critical research questions as well as questions to industrial partners. Road-map was then refined by industrial view which was collected from interviews of our IAB companies as well as other companies within carbon value chains. In general we obtained confirmation to our premise that in most carbon material applications price is the driving factor and bio-based origin as such is not a selling point if price is higher or no other benefit can be seen.

4.1   HTC Process as Treatment for P&P Industry Side Streams

Introduction

Hydrothermal carbonization (HTC) is a process that converts organic material into carbonaceous materials using mild processing temperatures (180-250°C) and water as the carbonization medium, under self-generated pressures. 'The great advantage of HTC is that wet organic feedstock (e.g.

organic waste) can be used without any special pre-treatment (e.g. drying) and so far no restrictions have been found regarding the composition of the organic matter' (Tesch *et al.*, 2013; Wikberg *et al.*, 2015a).' The carboneous product of HTC – referred to as 'HTC carbon' in this report has unique properties among others due to the presence of functional surface groups including hydroxyl, carbonyl, double bonds and enol structures (Kubo *et al.*, 2010; Titirici *et al.*, 2012). The hydrophilic-hydrophobic-properties can be tuned by subsequent activation. The advantage of the functional groups is on the one hand the option for further modification and on the other hand the possibility for forming aqueous dispersions or dispersions in other polar solvents. In other words, HTC carbon forms stable aqueous dispersions.

For this roadmap, HTC as future option for upgrading wet side products or side streams in the pulp & paper (P&P) industry to special carbons or their precursors is evaluated. These are lignin, other industrial sidestreams (prehydrolysis filtrate chosen for evaluation) and biosludge as shown in Figure 16.
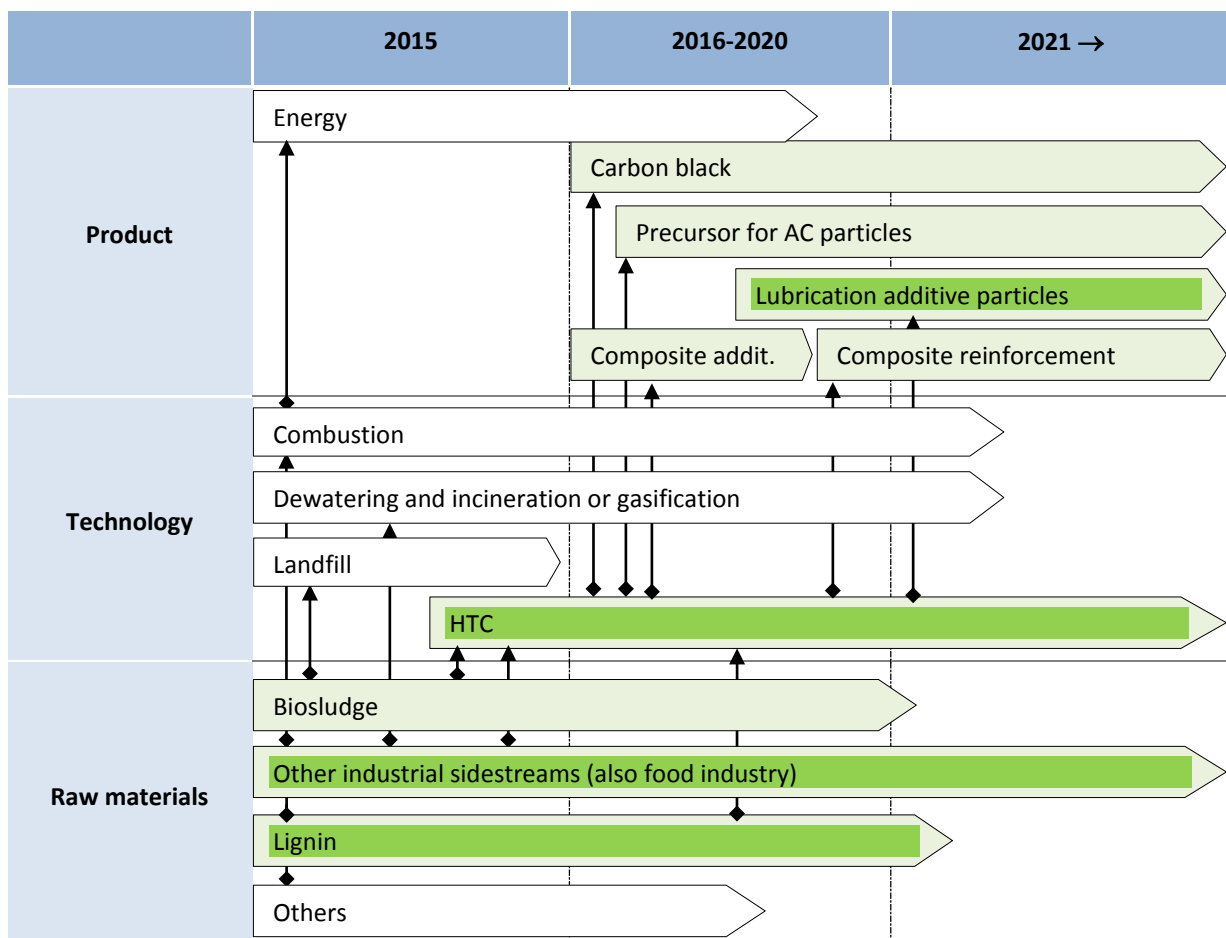

Figure 16   Road-map for industrial side-stream processing. Bio-based materials in light green and our projects focus with dark green background.

The HTC technology is established for sludge to produce dewatered HTC carbon product 'HTC biochar'. The availability of the process equipment opens the possibility to develop higher value products in the future. The general feasibility of HTC as an alternative for P&P industry sludge treatment has been evaluated in a recent diploma thesis (Child, 2014). In the cited thesis, it was estimated that the costs for HTC of P&P industry sludge are 13 €/t of wet sludge and the product 'biochar'. The HTC process from more pure products as pulp, lignin or isolated hemicelluloses has also potential to produce higher value products such as an adsorbent (activated carbon), biobased carbon black (Grönberg *et al.*, 2014), catalysis, energy storage, CO_2 sequestration and hybrid materials (Titirici *et al.*, 2012) as well as novel carbon material for electrodes/ supercapacitors (Falco

et al., 2013) and lubricant additives. In addition, an industry representative mentioned that there is very high demand for large (100 µm) spherical carbon particles for water filtration systems and currently no economical way to produce them. HTC could be the tool to produce these types of particles. In the project, HTC particles were tested as lubricant additive and as additives for wear resistant surfaces as outlined in the roadmap. It is estimated that HTC particles from lignin or side streams for lubricant applications still need considerable R&D and industrial lubricant producing partners to be realized in 5-10 years.

The main current use of lignin is combustion at the pulp mill for energy production. Wet waste streams are fed to e.g. to the water treatment (waste water) or landfilled, reused in agricultural or composting operations, incinerated or gasified (after drying), or treated in order to be used in a variety of soil enhancement (Child, 2014) as shown in Figure 69. Landfill of biodegradable, non-hazardous sludge of all types will no longer be accepted in landfills throughout the European Union after 2016 (EUR-Lex, n.d.), so there is a great need to find alternatives for their disposal or use.

HTC has many benefits as a method for sludge treatment as demonstrated already for municipal sludge treatment. The process is rapid (hours) compared to biological treatment options (days to months) – continuous HTC can process a sludge stream in 3 hours, be turned on and off instantly, and is not sensitive to biological disruptors, such as temperature, toxins or process fluctuations (Robbiani *et al.*, 2013). HTC breaks the organic matrix and forms hydrophobic carbonaceous product, biochar, enabling 60-70% dry matter content (compared to 30% dry matter content for raw sludge) (SunCoal, 2013; CarbonSolutions, 2015). Produced biochar is a hydrophobic, stable carbonaceous product that can be stored and transported (Buttmann, 2011; He *et al.,* 2013). All these aspects contribute in making HTC an attractive biosludge treatment alternative to the current practice of anaerobic digestion or simple dewatering. In the BioPreCarb project, HTC of sludge from e.g. P&P industry is not evaluated because sludge is an inhomogeneous raw material and is not expected to be suitable for producing high-value carbon products. A drawback of HTC for high value applications is that the carbon content remains moderate as described above.

Production of soil from organic waste by the HTC process has raised interest to tackle erosion of fertile soil (EC, 2011). The European Commission defined certain milestones to address the problem of soil erosion in Europe in 2011. The European companies active in HTC process development are mainly concentrating on converting wet organic waste to biochar for energy recovery. The economic viability is mainly based on renewable energy source regulations and subsidies. Most companies keep an eye on research in the soil application area in order to support evaluation of biochar potential for increasing soil fertility and/or carbon sequestration (Titirici, 2013). The expected price is however expected to be low and therefore there is no promising business opportunities expected.

The price for the HTC carbon process is preliminary estimated to be 60-100 €/ton HTC carbon excluding costs for the raw material under assumptions that have been published for sludge processing in a plan treating 52 000 tons sludge/year with sludge at 20% dry matter content (SunCoal, 2013; Wittmann, 2015).

Essential conditions

Potential of HTC has been reported for bulk application as well as for high-value products. The opening of the market for this new process for higher value products nevertheless demand the establishment of the HTC process in the market for bulk applications. In other words, there has to be a market pull for the process. In addition, there has to be a need for the P&P industry to treat side streams at reasonable costs and there has to be a market pull for the high-value products selected as potential case (see e.g. activated carbon in chapter 4.2 and lubricant additives in Tribology in chapter 4.2).

This will be the case under the following conditions for which evidence will be searched for P&P side stream treatment:

- There is a bottleneck for alternative treatments side-products/streams (e.g. combustion)
- The price for alternative uses is comparably low (heat value, bulk applications)[2]
- Potential side streams are composed partly of carbohydrates (>10-20 wt%), have a dry matter content of preferentially higher than 2-5 wt% and the content of inorganics and S are below a threshold limit (not fully defined)

The product

The product is the HTC process as a pathway from **wet** P&P side-products/streams to unique carbon products suitable for several end product applications. Special carbon products are evaluated in the following roadmaps, activated carbon powder / granules in Chapter 4.3 and lubricant additives in tribology in Chapter 4.2.

Identified value chain

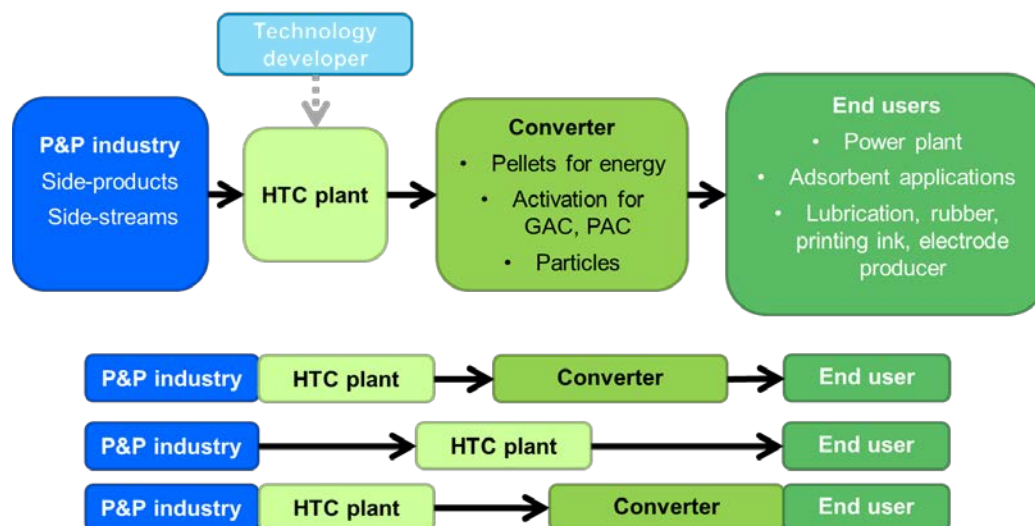Identified value chain and its variations are presented in Figure 17.

Figure 17   Value chain of HTC process

Critical system requirements

- Easy integration into existing mill infrastructure
- Cost-efficient, low need for personal costs and maintenance

Technology drivers

- Development of costs/prices for alternative products from side-products/streams
- Bottlenecks in combustion at pulp mills
- New business models

Trade-offs

The side-products/streams are utilized otherwise e.g. in the combustion or for the production of other products. This may be the case for lignin for which application studies are going on in many fields. SWOT analysis – comparison of HTC to other methods used in side-stream processing is shown in Table 13.

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[2] Needs information for costs and capacity of alternative from P&P industry

Table 13   SWOT analysis of HTC in side-stream processing

Strengths	Weaknesses
• Possibility to use wet feedstock • High raw material tolerance • Mild processing temperatures (180-250°C) and self-generated pressure • Local small plants are possible • Produces functional carbon materials with unique surface properties at high yields	• HTC process not established in P&P industry • R&D for high value products ongoing • Lacking know how of end use requirements in Finland
Opportunities	Threats
• Novel carbon products for large markets (>1 Mtons/a)/Large product portfolio • New business/emerging technology for P&P industry • High value carbon products (>1€/kg) for applications with tightening environmental regulations • Low production costs (60-100 €/ton HTC)*[3]	• Competition for the same feedstock • Demands commitment to long term R&D to enter the markets with the first product • Competition with oil-based products (low price at the moment)

4.2   Lubrication Particles via HTC

Introduction

The main function of lubricants is to reduce friction and wear. Thereby, energy and material savings are achieved. The consumption of lubricants is expected to reach 42 million tons by 2018 (Persistence, 2014). Mineral oil –based lubricants are dominating the markets. Conventional mineral oil –based lubricants are considered environmentally unacceptable due to their toxicity and low biodegradability. In addition, safe non-toxic lubricating alternatives are needed for certain applications (food and off-shore industry). The demand for bio-based lubricants and additives has been exceptionally strong in the Western European markets.

Addition of nanoparticles in lubricating oils is seen as a potential way to reduce interfacial friction and to improve the load-bearing tolerance of the surfaces in contact. Different solid additives have been used to enhance the performance of oil or water-based lubricant systems. Nanoparticles are attractive additives due to their advantageous physical and chemical properties. For example, carbon nanotubes have shown promising effects under boundary lubrication when used as additives in base oils (Dassenoy *et al.*, 2006).

In addition, nanoparticles such as graphene/graphite have been successfully used as additives in low friction coatings (Wang *et al.*, 2005). The network of sol-gel matrices are expected to form a feasible carrier for the carbon particles resulting in evenly distributed nanoparticle additives within the coating matrix.

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[3] Excludes costs for raw materials, price depends on size of production plant
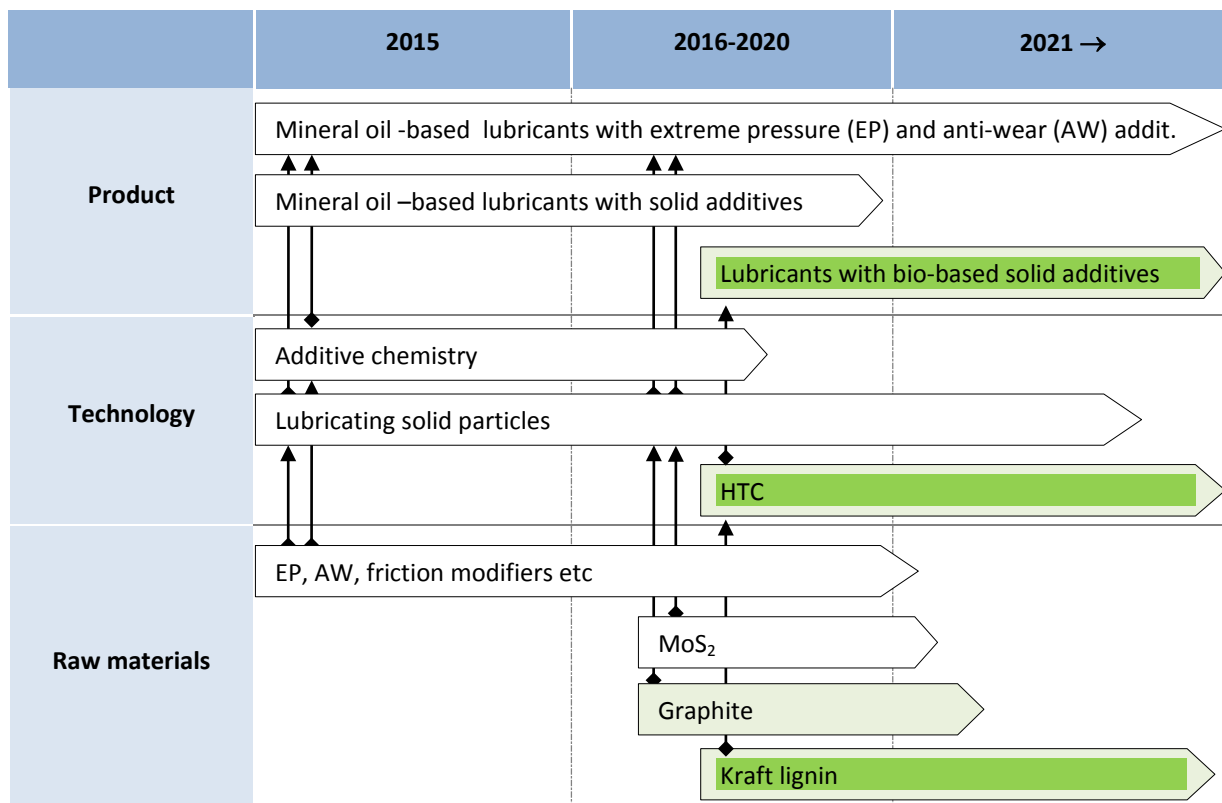
	2015	2016-2020	2021 →
Product	Mineral oil -based lubricants with extreme pressure (EP) and anti-wear (AW) addit.		
	Mineral oil –based lubricants with solid additives		
			Lubricants with bio-based solid additives
Technology	Additive chemistry		
	Lubricating solid particles		
			HTC
Raw materials	EP, AW, friction modifiers etc		
		MoS_2	
		Graphite	
		Kraft lignin	

Figure 18   Road-map for lubrication additives. Bio-based materials in light green and our projects focus with dark green background.

Essential conditions

It has been stated that lubricating solutions from renewable resources must have other advantages than price and performance in order to compete with mineral oil-based products. The competiveness of the green solutions lies on their superior ecological properties (Willing, 2001).

However, demand for green, environmentally friendly lubrication is increasing, especially due to public concern about environmental pollution. Water-based lubricants are needed for metal forming processes for cost savings. Legislation actions already in sight are bound to direct the development of lubricants and their additives towards non-toxic alternatives. Non-toxicity is particularly required for such targets as for food industry and off-shore industry.

There is also a great need to develop novel additive technology, since some additives are too coarse, irregular in shape or unevenly distributed within the lubricant matrix that severe abrasion of the surfaces occurs.

The product

Uniform spherical carbon particles for friction reducing additives originating from the side streams of the P&P or food processing industry:

- to be used as additives in lubricants
- to be used as additives in low friction coatings.

Identified value chain
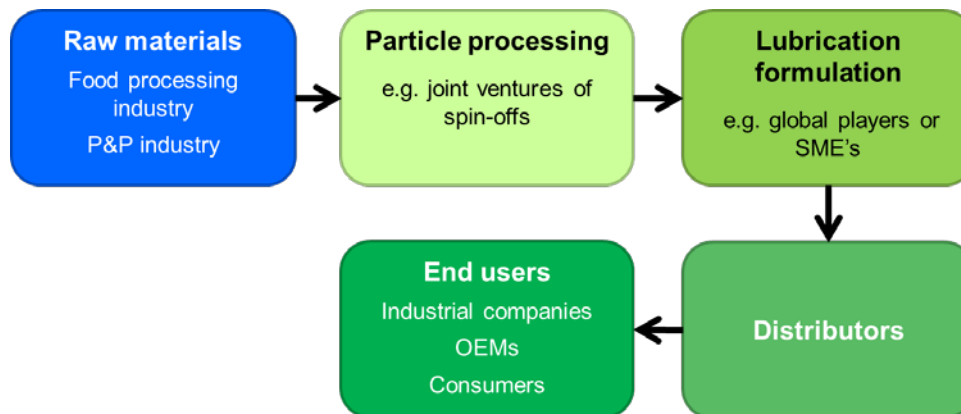
Identified value chain is presented in Figure 19.

Figure 19   Value chain for lubricant production

Critical system requirements

Carbon-based additive particles need to have suitable shape and structure that can provide low shear strength between contact surfaces either based on the rolling action (with spherical shapes) or formation of carbonous layers (e.g. onion-like-layered structures) on the surfaces. The optimum results are expected to reach when particles with narrow size distributions are used. Additives, which are too coarse, irregular in shape or unevenly distributed within the lubricant matrix, cause severe abrasion of the contact surfaces. The particles need to be compatible with the carrier fluid of the lubricant/coating matrix.

Technology drivers

There is an increasing need for novel additive technologies to replace conventional additive technology. The environmental sustainability, reliability and operation in extreme conditions will have more importance in the future. Regulation actions are expected to restrict the use of mineral oil –based lubricants. In addition, safe non-toxic lubricating alternatives are needed for specific applications, such as food industry, off-shore industry.

Trade-offs

The following solid/particle additives have been successfully used for different tribological applications:

- Carbon additives such as carbon nanotubes, graphene/graphite and even nano-diamond
- Polymeric solid additives such as PTFE particles
- Among inorganic particle additives promising results have been achieved with MoS_2, TiO_2 and SiO_2 nanoparticles (Peng *et al.*, 2009a & 2009b). NanoLub's (NanoMaterials Ltd.) spherical tungsten disulfide (WS_2) multi-walled nano-particle is an example of the commercial particle additives available (https://forum.lowyat.net/topic/3105204/all)

SWOT analysis HTC based lubrication particles is shown in Table 14.

Table 14   SWOT analysis of HTC based lubrication particles

Strengths	Weaknesses
• Utilization of industrial side-streams (food industry, pulp & paper) • Sustainable raw material (bio-based) • Non-hazardous additive.	• Thorough lubricant formulation required • Commercialization of the lubricants with new additives requires certification actions.
Opportunities	**Threats**
• New business opportunities • Market niche for lubricants needed in specific applications.	• Long production chain increases the price of the product • Technical performance is not adequate for extreme conditions.

4.3   Activated Carbon Particles from HTC Particles

Introduction

Adsorbents are materials having capacity or tendency to adsorb another substance. Selected gas and liquid molecules are adsorbed due the presence of porosity. Physical adsorbents are reversible and liquid can be extracted. Global market for adsorbents is around $2.8 billion in 2014: regionally North America 27 %, Europe 22 %, Asia-Pacific 39 %, South America 5 %, and rest of the world 7 %. Demand is increasing and increase is driven e.g. along with the new environmental regulations changed in 2011 and 2012. Lower demand in Europe due to its economic climate has recovered in 2013 due to an increased focus on wastewater treatment and air purification activities. Strong demand in developing regions, including the Asia-Pacific and South American regions, increased the demand for adsorbents, mainly active carbon adsorbents used in wastewater treatment and air purification. (BCC research, 2014b)

Table 15   Global market and sales volume forecasts for adsorbents (BCC research, 2014b)

	2013	2014	2019	CAGR 2014-19
Value	$2.7*10^9$ $	$2.9*10^9$ $	$4.0 \ 10^9$ $	6.7 %
Sales volume	$2.1*10^9$ tons	$2.2*10^9$ tons	$3.1*10^9$ tons	6.8 %

Activated carbon (activated charcoal) accounted for the largest segment of the global market for adsorbents in 2013 in terms of both volume (65.4 %) and dollar sales (65.6 %). The activated carbon segment of the adsorbent market is expected to continue to dominate the market through 2019. (BCC research, 2014b) Application areas include:

- **Environment**: removal of heavy metal ions and other toxic elements from aqueous solutions, VOC and other harmful compounds from waste/vent gases, toxic/harmful gases from air (breathing), removal of odour compounds for gases
- **Chemistry/oil refinement**: separation, ion exchange, recovery of selected components
- Medical/biological/dental/pharmaceutical: separation and purification processes
- **Food preparation and conservation**: purification of beverages, conversion and decolourization of sugar, and purification of oils
- **Energy related**: fuel storage, Hydrogen gas storage, electrodes, supercapacitors

Activated carbon is produced from carbonaceous source materials such as wood, coal or coconut shells. Precursor materials can be activated using physical or chemical activation. In physical

activation porous structure is produced using oxidizing atmosphere (CO_2 or steam) during or after carbonization, while in chemical activation raw material is impregnated with activation chemicals which produce porosity during thermal treatment. Physical activation is typically made by steam. However, in most cases higher specific surface and micro porosity can be achieved by CO_2 activation. Chemical activation is usually preferred in bulk applications due to lower temperatures and shorter time needed.

Activated carbon market is dominated by three large scale global corporations representing two thirds of global sales volumes. Top three companies are Calgon Corporation, Norit N.V. and MeadWestvaco Corporation, followed by Siemens Industry, Haycarb, Arkema, Osaka Gas, and Kuraray. Global markets are growing (CAGR 11 %) and are expected to cross 3 Billion $ by 2017. (ASDReports, 2013a & b). Powdered AC market segment is the fastest growing area within the global market (MarketsandMarkets, 2012). New low cost manufacturers are emerging and business opportunities are expected to be found from sustainability, new product developments, and new application developments (ASD Reports, 2013a & b). The major raw materials used for production powdered and granular AC are coal, wood, coconut shells, and lignite. Markets suffer periodical shortage of raw materials such as coconut shell charcoal which has led to increase in raw material prices. (ASDReports, 2013a & b)
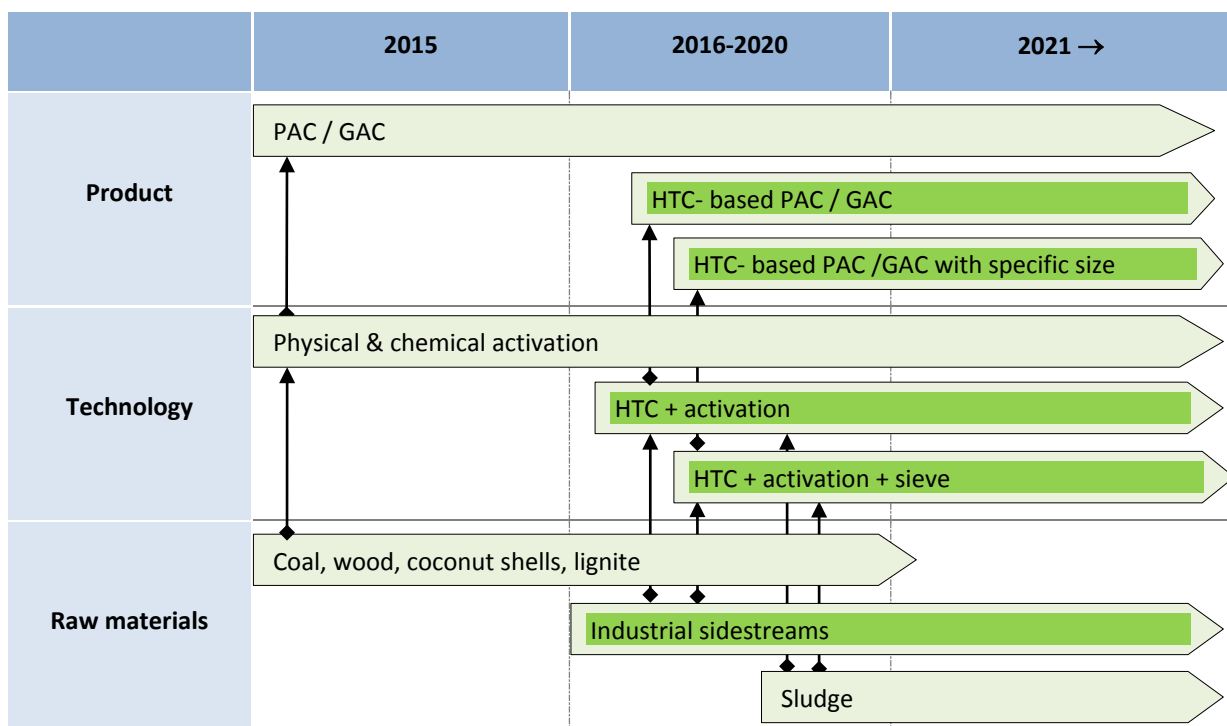

Figure 20 Road-map for activated carbon particles. Bio-based materials in light green and our projects focus with dark green background.

Essential conditions

End product requirements

- Market pull for adsorbents
- Price of HTC product as precursor for further activation to activated carbon products
- Quality of product from the precursor corresponds to requirements for activated carbon products

The product

Activated carbon powder / granules produced from particles obtained from HTC.

Identified value chain

Exemplary value chain for traditional PAC/GAC is shown in Figure 21. We see that HTC particles could be directly fed into activation unit.
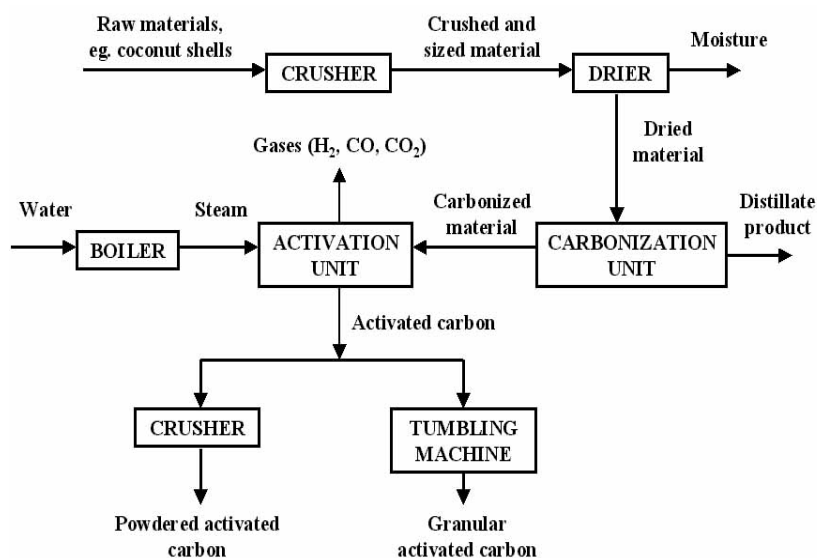

Figure 21   Process steps to AC powder and granules from agricultural wastes (Lartey et al., 1999)

Critical system requirements

- Activated carbon properties have to be achievable at competitive costs from the precursor obtained by HTC.
- Costs to produce activated carbon from P&P sludge or side streams (composed of benefit/costs for alternative use of raw materials and the costs for the HTC process) together have to be compared to costs for other raw materials as precursors for activated carbon.

Technology drivers

- Costs for precursors
- Shortage of raw materials for carbonization
- Legislation

Trade-offs

Activated carbon produced from various precursor materials including agricultural wastes, as well as other adsorbents. AC represents 66 % of adsorbents in 2014. Alternative products are listed in Table 16, and SWOT analysis HTC based AC particles is shown in Table 18.

Table 16   AC and alternative adsorbent products

Type	Market share	Properties or other info (BCC Research, 2014b)	Price min [web]
AC	66 %	Applications: adsorb nitrogen from air, water purification, removal of odors from gases, purification of He and cleanup of nuclear off-gases	200 $/ton
Molecular sieves (Zeolites)	19.2 %	Selectively adsorb molecules of a specific size, applications drying of gases, extracting oxygen from air, removing water from azeotropes, purification of hydrogen, separation of ammonia and hydrogen	50 $/ton
Silica gel	7.2 %	Strong desiccant properties; applications the control of relative humidity, drying of gases, refrigerants, organic solvents, transformer oils, etc.	500 $/ton
Activated alumina	3.3 %	Highly porous material; application drying of gases, adsorbents in transformer oils and removal of fluorine in alkylation process	100 $/ton
Others	4.1 %	Include clay, metal oxides, CB, and silica and alumina composites, calcium sulphate, and calcium oxide. Used for water purification, recovery and purification of steroids, removal of colors from syrups and organics from hydrogen peroxide	

Table 17   SWOT analysis of HTC based AC particles

Strengths	Weaknesses
• Carbon content of HTC particles already high, typically above 70 % • HTC particles provide precursor for AC as particle form with low size distribution	• Price and complexity of two step treatment (HTC + activation)
Opportunities	**Threats**

• HTC raw material can come from industrial side-streams
   • New steadily available raw material for AC production
   • Raw material with low costs
	• Low prices of competing adsorbents (zeolites, activated alumina, and others)
	 • Low price of competing raw materials

4.4   AC fibres from Cellulose for Added Value Applications

Introduction

Activated carbon (mainly activated charcoal) accounted for the largest segment of the global market for adsorbents in 2013 in terms of both volume (65.4 %) and dollar sales (65.6 %). The activated carbon segment of the adsorbent market is expected to continue to dominate the market through 2019. (BCC Research, 2014b) In filtration applications adsorbent-impregnated filter media is capable of removing foul odours and gaseous pollutants such as CO_2, CO, NO_2, SO_2 and VOCs from air streams (BCC Research, 2014a). Important issue in combining the adsorbent and nonwoven is that the media has to be engineered to minimize particle shedding. That can be challenging with the common product forms of activated carbon including extruded AC usually in the form of cylindrical pellets (mm range diameters), GAC and PAC.

Activated carbon is usually employed in powdered form, which cannot be easily processed into cloth, sheets or felt, which limits its use in high-volume applications. Activated carbon fibres, on the other hand, can be readily formed into cloth, sheets, and felt. As such, they are an ideal replacement for powdered activated carbon in many applications, such as bandages for malodorous wounds, dialysis

filters, air purification filters, liquid purification filters, radiation-proof filters, ozone eliminators for electrostatic copiers, masks for odour and noxious gases, chemical protective apparel, and cigarette filters. (BCC Research, 2013) Fibrous carbon better integrated into textile structure e.g. in filter to prevent shedding of AC material during product life-time (BCC Research, 2013).

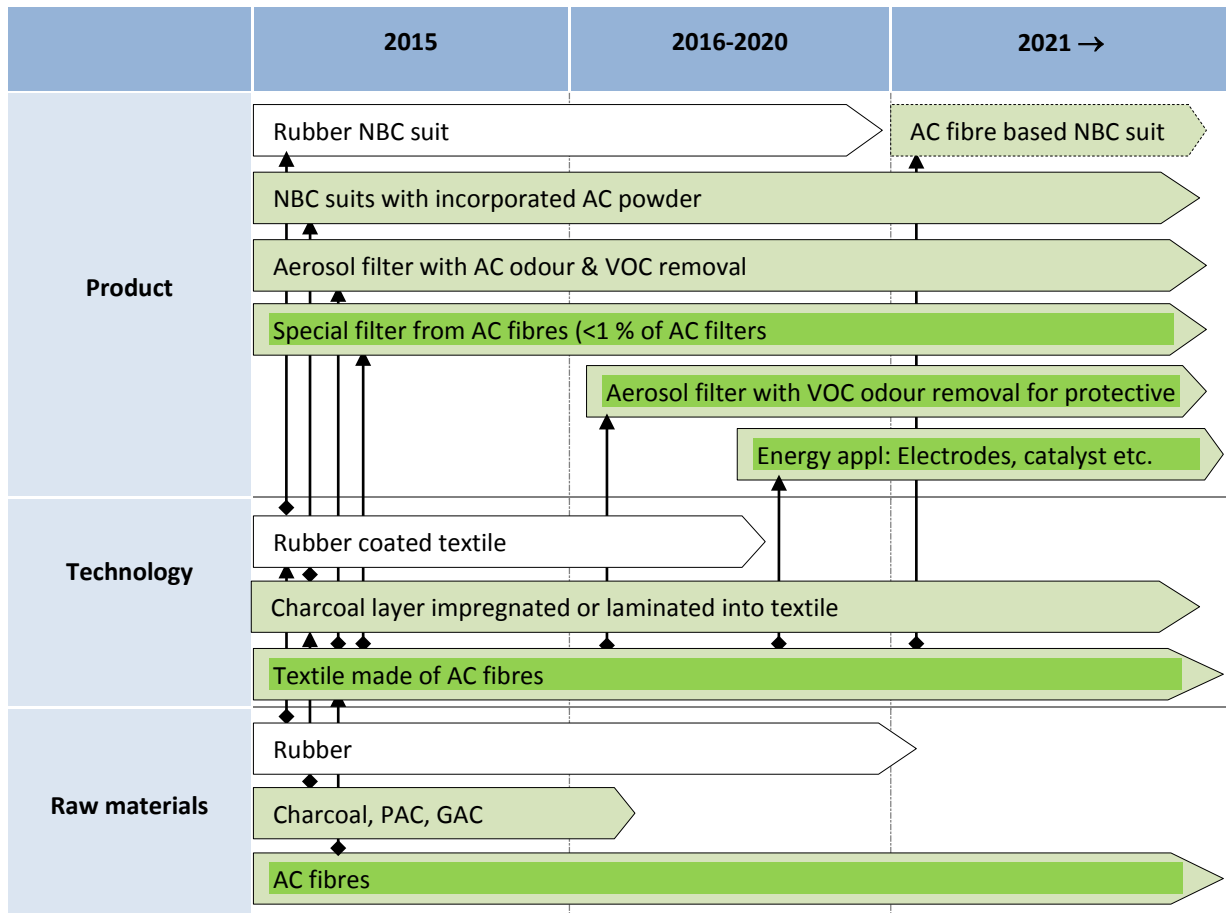|	2015	2016-2020	2021 →
Product	Rubber NBC suit		AC fibre based NBC suit
	NBC suits with incorporated AC powder		
	Aerosol filter with AC odour & VOC removal		
	Special filter from AC fibres (<1 % of AC filters		
		Aerosol filter with VOC odour removal for protective	
		Energy appl: Electrodes, catalyst etc.	
Technology	Rubber coated textile		
	Charcoal layer impregnated or laminated into textile		
	Textile made of AC fibres		
Raw materials	Rubber		
	Charcoal, PAC, GAC		
	AC fibres		

Figure 22   Road-map for activated carbon fibres for high dynamic adsorption capacity applications. Bio-based materials in light green and our projects focus with dark green background. Dashed line indicates something currently missing

Essential conditions

- Price of activated carbon fibres is high, application has to be high value added product, where function is essential over costs.
- Strength is required if material is exposed to mechanical forces

The product

Activated carbon structures: more options are fibres from cellulose and lignin, and nonwovens from cellulosic fibres.

Identified value chain

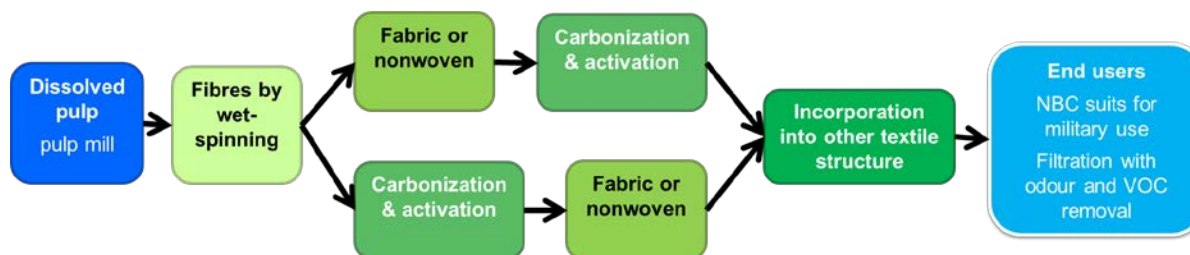We identified value chain for AC fibres and fabrics, see Figure 23.

Figure 23. Value chain for AC fibres and fabrics

Critical system requirements

- AC material should have high dynamic adsorption capacity and be breathable (for protective clothing) or have low pressure drop (for filtration applications).
    - Based on VTT earlier knowledge that is obtained.
- Strength critical when fibres not immobilized.
    - Based on expert discussions it seems that protective clothing application is not suited for such AC fibres, they are not stable enough mechanically. Several patents for this application (e.g. Böhringer & Varga-Molnar 2010; Blücher & Böhringer, 2007 & 2012).
- AC fibre structure needs to withstand lamination with hot adhesive nets: only melting allowed, no solvent residues or volatile compound release
    - release should be checked, this might limit the possible impregnation agents.

Table 18 Properties of AC materials in examples of different application areas and their requirements

Process	Surface area, BET[4] (m^2/g)	Porosity	Application	Other requirements and additional info
Liquid processes	500-1000	Mesopores and micropores	Water purification (40 % of AC use[i], removal of traces of odour/taste	Impregnation agent residues cannot be harmful, they need to be eliminated by washing
			Food and beverage production.	In addition to above, safety and compliance with regulation related to food production.
Gas:	700-1500	Micropores	Aerosol filtration (35 % of AC use[i]	No residues that can be removed as particles allowed. Dynamic adsorption capacity - low pressure drop.
High value, special applications	1500-2000	Micropores	Chemical (war gas) protective clothing	High dynamic adsorption capacity and breathability.
			Care of malodorous wounds, e.g. burn	Odour removal and breathability.
			Protection of museum pieces	High dynamic adsorption capacity and moisture control
Ref: [i] (BCC Research, 2014b)				

Technology drivers

Activated carbon adsorbents play an important role in the wastewater treatment of both municipal wastewater and industrial wastewater. The demand for water treatment applications has dominated

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[4] Brunauer-Emmett-Teller (BET) surface area

the demand for activated carbon adsorbents in 2013, and it is expected to drive the market for activated carbon adsorbents through 2019 at a CAGR of about 7.6 %. (BCC Research, 2014b). The market is expected to focus on quality and high-performance active carbon adsorbents in the next five years.

Production cost of ACF is high and therefore ACF is not feasible in applications, which can be implemented by standard activated carbon granules or powder. In addition to physical macro structure the pore structure of ACF is also typically different than in other types of AC. High micropore volume directly available at the surface usually enables high dynamic adsorption capacity, which can be utilized in very demanding application like protective clothing or applications where only very low pressure drop is allowed. Based on industrial interviews (Blücher, 2015)

Trade-offs

Filter structures with AC are typically formed with AC powder or granule layers impregnated and/or laminated to textile structure. In protective clothing formerly used rubber –NBC (Nuclear biological chemical protection) suit has been nowadays replaced similar structures with AC impregnated and/or laminated textile structures.

SWOT analysis of AC fibres and fabrics is shown in Table 18.

Table 19   SWOT analysis of AC fibres and fabrics

Strengths	Weaknesses
• Fibrous AC structure enable higher air flow compared to structure produced from AC powder • Not as fragile as AC monoliths • Versatility in production: carbonization either before or after textile production	• Complicated production chain leading to high price • AC fibres are not mechanically strong, require immobilization when fibres movable, breakdowns possible
Opportunities	**Threats**
• Better wearer comfort as NBC suit as current competition • Lower probability of shedding from filters compared to PAC and GAC	• Higher price compared to alternatives • Reliability in long term use NBC application can be questioned

4.5   Reinforcing Bio-based Carbon Fibres for Composites

Introduction

Global composite material industry reached 19.6 billion $ and market value of the end use products was 55.6 billion $ in 2011. The composite industries have accelerated approximately 6-8% annually. (Kazmierski, 2012) The division of the market segments in 2017 were estimated to be as shown in Figure 24.

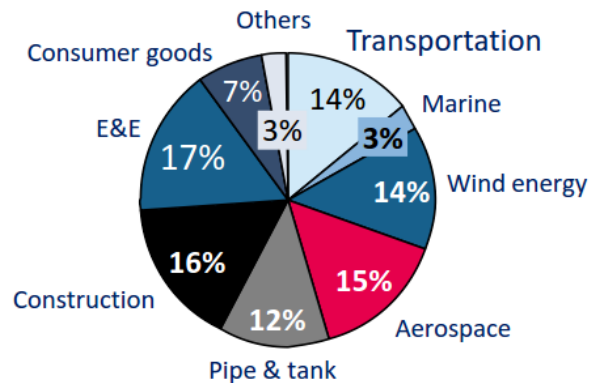## Global composite materials distribution ($ mil) by market segments in 2017

Figure 24   Distribution of the composite markets on different sectors (Kazmierski, 2012)

In several market studies it is estimated that transportation and especially automotive industry has great potential to increase significantly the polymer composite demand. (Kazmierski, 2012) Actually the markets in which the composites already have the largest markets (transportation, construction, pip&tank) have currently the lowest penetration of the materials compared to competing materials, such as steel and aluminium (Table 20) (Kazmierski, 2012).

Table 20   Composite penetration in various market segments (Kazmierski, 2012)

Market Segment	Composite Materials Market	Structural Materials Market (Steel, Al & Composites)	Composites Penetration	Performance Gap	Price Gap
Transportation	$2.8 B	$77.8 B	3.6%		
Marine	$0.5 B	$0.8 B	68%		
Aerospace	$2.3 B	$23.2 B	10%		
Pipe & tank	$2.6 B	$37.8 B	7%		
Construction	$3.4B	$85.1 B	4%		
Wind Energy	$2.4 B	$6.4 B	38%		
Consumer Goods	$1.3 B	$9.4 B	14%		

Composites Penetration Compared to Competing Materials (Steel & Al)

Carbon fibre is a fibre reinforcement used as high volumes in various range of applications, such as aerospace and automotive where low weight of the materials is essential. For example Boeing 787 Dreamliner utilizes already over 50 % by weight carbon fibre composite materials. (Liu *et al.*, 2014) The materials have excellent mechanical properties and low density allowing to especially in applications where excellent specific mechanical properties are required. Currently most of the commercial carbon fibres are produced form PAN-polymer, although pitch and viscose based fibres are also available.

The greatest restriction of more general utilization of carbon fibre based products is the high price of the fibre materials. The prize of the final product arises from several steps the dominating being the high price of the current PAN-precursor material. Because of that great efforts are currently used to develop new cheaper precursors for the materials of which bio-based products are one of the most interesting. (Liu *et al.*, 2014; Ashley, 2013; Eberle, 2013)

Cellulose is more affordable compared to PAN, and it decomposes and forms char instead of melting in high temperatures which is beneficial for carbon production manufacturing. However, naturally existing localized defects can cause inferior carbon quality. Crystalline structure and orientation of regenerated cellulosic fibres are not favourable for production of highly ordered i.e. strong carbon materials. Therefore, in production of high strength carbon fibres from regenerated cellulose fibres

require high temperatures (2,000°C) with simultaneous stretching (upto 300 %). That is because even though those having high degree of crystallinity, the crystal orientation is not in fibre axial direction. (BCC Research, 2013) Novel cellulose materials and or new spinning technigues could provide us more favourable structure of cellulosic fibres in the future.

Main process steps for production of regenerated cellulose based carbon fibres include dissolution, wet-spinning, oxidation (200°C-350°C), carbonization (1,000°C - 1,300°C), and optional graphitization at 2,000°C-3,000°C (C > 99 %) under tension and upto 300 % drawing for high strength applications. Current uses of cellulose based carbon fibres include carbon-phenolic composites with low thermal conductivity used in rocket nozzles and missile re-entry vehicle nosecones and heat shields. (BCC Research, 2013) High strength cellulose fibres are more thermally stable than PAN based one's, but due to the carbonization process requirements they are more expensive (BCC Research, 2014c).
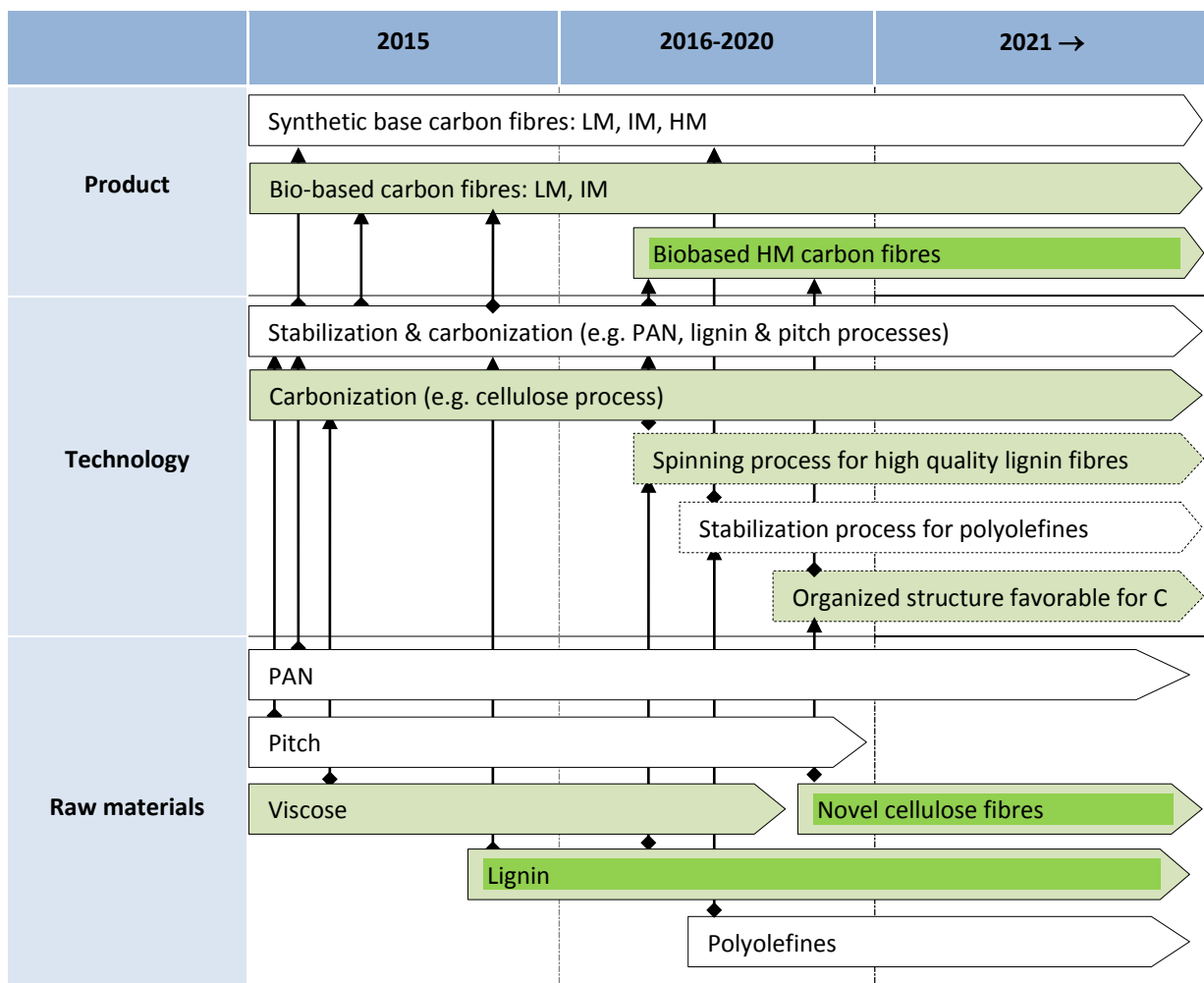
Figure 25   Road-map for carbon fibres. Bio-based materials in light green and our projects focus with dark green background. Dashed line indicates something currently missing

Lignin also has high carbon content and can be obtained by-product of the pulp and paper industry and thus would be interesting raw material option for carbon fibre production. Lignin fibres can be synthesized by melt-spinning followed by oxidative stabilization and carbonization. Poor mechanical properties of lignin based carbon fibres, partly caused by natural inhomogeneity of lignins, limits their use in structural applications, but show promise in highly porous activated carbon type materials (Chatterjee *et al.*, 2014).

There are currently lot of activities for resolving problems of lignin for MH carbon fibre production. Typically additional synthetic plasticizer needed for carbon fibre production from lignin (De Palmanaer *et al.*, 2015a). PAN is one option for this (Dodd & Straus, 2015). In recent study (Morris &

Weisenberger, 2015) lignin has been used to partly substitute PAN in carbon fibre precursors. It was noticed that displacing 6 % of PAN with lignin did not affect strength or morphology or fibres, but reduced shrinkage during stabilization and increased carbon yield. It was, however noticed leaching of lignin from fibre in the coagulation bath in wet-spinning is a challenge. (Morris & Weisenberger, 2015) Another blend polymers studied are polyethylene oxide and polypropylene (Anagnou *et al.*, 2015). Based on presentations given in Carbon 2015 conference, it seems that HM carbon fibres from lignin (or mainly lignin) precursors is not that far in the future.

Essential conditions

The average price of the produced cheapest carbon fibre is approximately 20 $/kg. Although carbon fibre composites are already used in the industry, such as in the first mass produced carbon fibre monocoque body vehicle BMW i3, it is estimated that approximately 50% decrease of the current cost of the reinforcements should take place for the carbon fibre composites to be introduced more generally in the automotive industry. In that case hugely increased demand for the material is to be expected, as sketched in Figure 26.

Global automotive production by car type	Expected vehicle production	Expected use of CF in cars	Demand for CF at 50% of current price (pounds)	Market for CF at 50% of current price ($M)
Super cars	6,000	100%	1.3 million	$7M
Super luxury cars	600,000	10%	101.2 million	$506M
Luxury cars	4 million			
Other/regular cars	92 million	1%	202.4 million	$1,012M
Total	**97 million**		**305 million**	**$1,525M**

Source: Lucintel, ACMA Composites 2012

Managed by UT-Battelle for the U.S. Department of Energy

3× current global CF demand for **all** applications; 10B lb potential automotive demand at full market penetration

Potential to reduce US petroleum demand by 2-3 Mbpd (~10-15%)

Figure 26   Estimation for the carbon fibre demand if the price decreased 50% (Eberle, 2013) CF = carbon fibre

In current manufacturing techniques of the commercial carbon fibre reinforcements, roughly 50% of the current price of the least expensive carbon fibres comes from the precursor as shown in Figure 27.
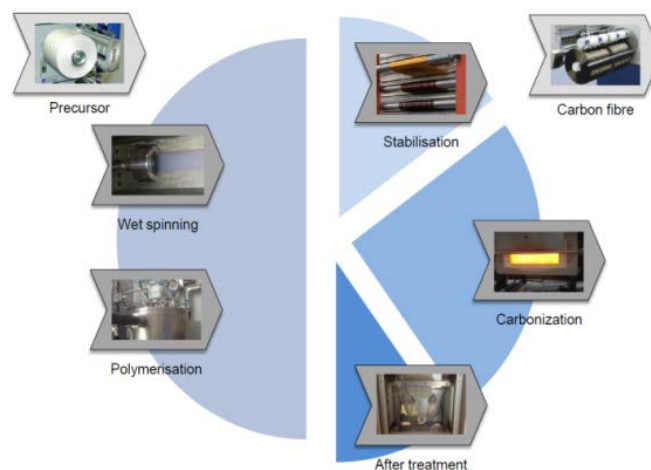

Figure 27   The effect of the various manufacturing steps on the PAN based carbon fibre price according to De Palmenaer et al. (2015a)

Several different precursor materials are studied and developed extensively. Some beneficial improvements can be achieved with development around PAN material, but to obtain significant decreases in the price the utilization of totally different precursors is required. Of the most potential precursors polyolefin based and bio-based materials are the most promising and studied. (Eberle, 2013)

Bio-based precursors, such as different lignins and celluloses are sustainable resource materials with low price and high volume. The availability of resources is abundant and their cost is largely independent of the oil prices. Challenges of lignin based carbon fibres include complex molecular structure of lignin, which do not form highly ordered precursors, and short chain length. Both of these factors affect mechanical properties of fibres and fragility of precursor fibres makes carbonization difficult. Some further development is needed in order to obtain good quality precursors from lignin and thus enabling carbon fibre quality. Based on literature review and discussions with companies it seems that best option for use of lignin is used is a mixture with other polymer. While using PAN as additional polymer has shown some promise (Dodd & Straus, 2015), there are also contradicting views based on notion that compatibility between lignin and PAN is limited (interviews).

The product

The final product will be the carbon fibre reinforcement but the actual product of the road map study is the bio-based fibre precursor for the carbon fibre manufacturers fabricating products for automotive industry.

Identified value chain

The value chain of the product begins from the harvester of the natural resource to the manufacturer of the final carbon fibre composite component, see Figure 28.
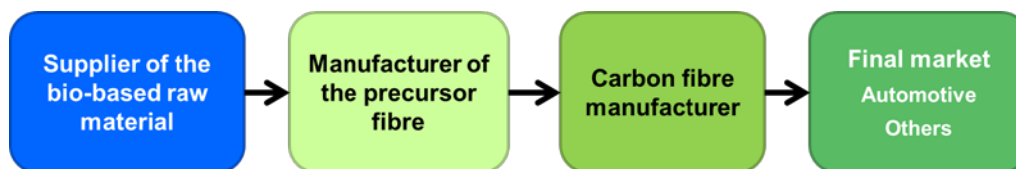

Figure 28 Value chain for carbon fibre composites

Critical system requirements

Currently the price of the precursor is the dominating factor hindering the utilization of the carbon fibre composites. It is told by the car manufacturers that the automotive industry targets 10-14 $/kg price after which the material and process compete the conventional materials and manufacturing techniques with metals. (Eberle, 2013) From the price of today's materials approximately 50 % comes from the precursors. If it is supposed that the complexity and thus costs of heat treatment steps in the manufacturing chain of the carbon fibre is relatively independent on the fibre precursor, it can be estimated that the maximum allowed price of the precursor fibre to achieve this target is approximately 5-7 $/kg.

The mechanical properties of the final carbon fibres if to be utilized similarly to current carbon reinforcements should reach 170 GPa and 1700 MPa so that automotive industry shows greater interests. (Eberle, 2013) One of the greatest disadvantages of the bio-based raw materials for carbon fibre production is their complex molecular structure that hinders the formation of highly oriented carbon structure required from the high performance fibres. So far the maximum tensile modulus and strength for lignin based carbon fibres that have been reported lie in the range of 85 GPa and 1700 MPa, respectively. (Downing, 2013)

Also stable raw material supply flow and the high quality of the raw material are of key issues in the industry which is difficult to overcome.

Technology drivers

By far the most important driver will be the cost reduction of the final carbon fibre reinforcement that is to be targeted by the bio-based materials. Current PAN-based fibres are eventually dependant on the oil price, so a technology driver would also be possibility to increase the independency to oil.

Trade-offs

Currently PAN-based standard modulus (SM) fibres are the most utilized carbon fibre type, which is used e.g. in sporting goods, automotive and industrial applications. Intermediate (IM) and high modulus (HM) fibres are used more or less in similar applications when improved properties are required with the cost of higher price. Ultra-high modulus (UHM) fibres are very expensive and utilized mostly in aerospace applications. Properties of the different carbon fibre grades are currently well known and recognized in markets, and e.g. changes in the fibre properties due to novel raw material such as bio-based precursors can be difficult to explain and introduce to market. Also the price of PAN-based fibres will decrease due to development of the utilization of textile PAN precursors.

Carbon fibres are also produced from pitch obtained from petroleum. Such produced fibres have very high stiffness and thermal conductivity and thus are used e.g. in satellite structures and thermal management applications such as space radiators and battery sleeves. On the other hand, low-quality pitch based fibres with cheap price are already used in construction industry in which the specific mechanical properties and not ultimate demand.

Table 21   Comparison of cellulose with PAN and pitch precursors in production of carbon fibres

Material	Yield [%]	Carbon fibre structure [i]	Carbon fibre properties[i]	Advantages	Disadvantages
PAN	50-60	Small crystalline sites. Partial ordering	Medium modulus, medium thermal conductivity, high tensile strength	High carbon yield upto 60 %, high quality fibres.	High cost 9.3 $/kg – more than half of carbon fibre production cost (17 $/kg), price fluctuates according crude oil price[iv]
Cellulose	18-22	Highly disordered amorphous structure	Modulus low, thermal conductivity very low, tensile strength generally low	Low precursor cost, purity and flexibility of resultant fibres[ii], low thermal conductivity, good thermal stability[iii]	Lower carbon yield compared to PAN & pitch, expensive post carbonization treatment with stretching needed for high strength[iv]
Pitch	80-90	Highly crystalline and ordered. Aromatic ring planes stacked together	High modulus, high thermal conductivity, low tensile strength	Most regular structure, inexpensive precursor [i]	processing pitch into a high-quality fibre is not inexpensive, converted into a mesophase, or a liquid crystal, before it is spun into a fibre[i]

Refs: [i.] (BCC Research, 2013); [ii] (Wu & Pan, 2002); [iii] (BCC Research, 2014c); [iv] (Dumanli & Windle, 2012)

Devolvement of polyolefin based carbon fibres seems to be driving faster than earlier mentioned timeline Figure 27a. First laboratory scale fibres produced in 2012 and pilot scale production (4 kg/hr) in 2014. In general polyolefin based carbon fibres can give higher carbon yield, 70 % compared to 50% in PAN, also raw material costs are around 1-2 $/kg compared to 5-10 $/kg for PAN. It has been reported that mechanical properties of polyolefin based carbon fibres are close to low end of the commercial carbon fibres, 170 GPa modulus and 1600 MPa tensile strength. In manufacturing of polyolefin carbon fibres main hindering factor is thermal chemical stabilizing of fibres. (Warren &

Naskar, 2012) One option for this is sulphonation (De Palmanaer *et al.*, 2015b). Also other synthetic polymers are studied for precursor use. One example being e.g. aromatic polymers such as poly[bis(benzinidazo-benzisoquinolinone)] (Tomita *et al.*, 2015)
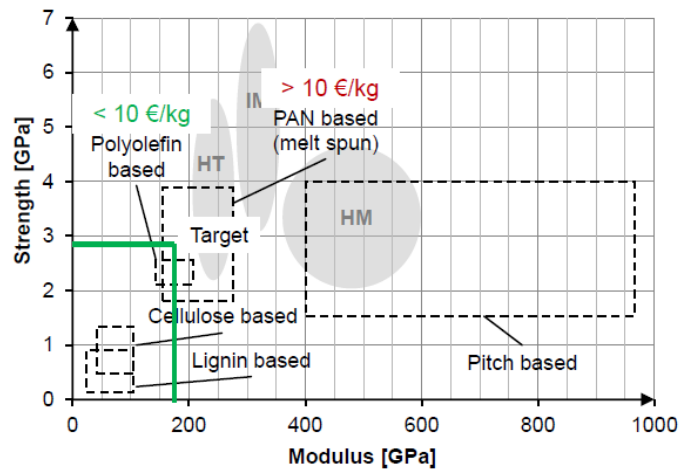

Figure 29 Mechanical properties of carbon fibres using different types of precursors according to De Plamenaer et al. (2015), HT = high tenacity, IM intermediate modulus, MH = high modulus

Table 22 Comparison of between of alternatives for PAN in carbon fibre production based on eight variables according to De Palmenaer et al. (2015a) , Rating: ++ very good, + good, o moderate, - poor, -- very poor

	Modified PAN	Polyolefin	Pitch	Lignin
Availability	-	++	o	+
Carbon content	+	++	++	+
Molecular structure	+	+	o	--
Spinnability	o	+	o	-
Convertability	o	o	++	-
CF-properties	+	+	++	o
Research activities	o	o	+	+
Costs	o	o	--	++

SWOT analysis bio-based carbon fibres is shown in Table 23.

Table 23 SWOT analysis bio-based carbon fibres

Strengths	Weaknesses
• Low price of lignin and cellulose compared to PAN • Low price of spinning of cellulose fibres compared to PAN spinning • Independence on oil • Availability	• Inhomogeneity of lignin raw material • Unfavorable molecular structure compared to synthetic materials, non-linearity of lignin and crystal orientation of wet-spun cellulose • Lower carbon yield compared to PAN
Opportunities	**Threats**
• Blending with synthetic materials to lower their cost (e.g. polyethylene+lignin)	• Polyolefin based precursors are developed • Unobtainable property targets despite the great research efforts

5   Summary and Conclusions

In this study we surveyed technological possibilities to obtain bio-based carbon business in Finland applying biomass derived polymers and precursor structuring prior to carbonization. We reviewed application requirements for carbon materials of several applications including high performance engineering materials as well as materials for high efficient separation and applied energy technologies. We made designs for novel carbon materials to meet these requirements based on our background knowledge of possibilities of wood based polymeric materials, precursor production and carbonization processes. Most promising carbon designs were selected for material demonstrations, and then further for product demonstration. Main outcome of the project was road-map for bio-based carbon materials. Case examples for the roadmap were selected based on our follow-up of industrial needs for tailored carbon materials as well as information obtained from material and products demonstrations done within the project.

Hydrothermal carbonization process (HTC) was found interesting to be utilized for pulp & paper industry side-streams. HTC could be used for processing lignin and other side streams in order to produce more added value compared to combustion. Experimental work showed that particles of different shapes and sizes can be obtained from bio-based raw materials using HTC.

Carbonaceous particles obtained from HTC can have various applications. We studied their use as bio-based additives in lubrication and evaluated possibility to use them as raw material for activated carbon (AC). There is an increasing need (and regulatory pressure) for novel additive technologies to replace mineral oil –based lubricants; safe non-toxic lubricating alternatives are also needed for specific applications, such as food and off-shore industry. Preliminary tests of HTC particles as lubricants showed promise in that application, which can be the topic of the R&D project. For AC application HTC particles from industrial side stream shows potential for low cost, stable feed of raw material, while plant based materials may have homogeneity as well as availability variation. That could be interesting option after wider commercialization of HTC process.

Carbon fibre market is expected to triple if carbon fibre price is reduced to half of the current price (20 \$/kg -> 10 \$/kg). Costs of precursor polyacrylonitrile (PAN) fibre currently contribute one half of carbon fibre price. Alternatives, also bio-based ones, are currently studied and developed around the world. Use of lignin and cellulose fibres as precursors for high modulus (HM) carbon fibres requires some further development and possibly also completely new technologies. We tested idea to use linear lignin for this, but the method was not feasible yet. Cellulose based AC fibres can be produced with existing technologies - in AC applications active surface area rather than the strength determines the function. We obtain as BET surface areas above 2000 m^2/g for cellulosic AC fibres and nonwovens within our experiments. Currently AC seems to be a more interesting application field for cellulose based precursors than HM carbon fibres. Modelling of cellulose carbonization indicated slight benefit of using new types of cellulose fibres instead of viscose for AC fibre production. Knowledge obtained from modelling as well as from experimental carbonization of bio-based precursors can be used for R&D projects.

References

Acmite (2011): Market Report: Global Catalyst Market.

Ahlroos T., Hakala T.J., Helle A., Linder M.B., Holmberg K., Mahlberg R., Laaksonen P., Varjus S. (2011) Biomimetic approach to water lubrication with biomolecular additives, *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology* **225**(10), 1013-1022

Anagnou S., Milioni E., Mpalias C., Kartsonakis I., Koumoulo E., Charitidis C. (2015) New precursors for the development of carbon fibers: the case of lignin, Carbon 2015, 12-17 July 2015, Dresden, Germany

ASDReports (2013a) Global Activated Carbon Market to Cross US$ 3 Billion by 2017, on-line[5] news, published 18 April 2013

ASDReports (2013b) Global Activated Carbon Market Forecast and Opportunities 2017, ASDR-60527

ASDReports (2012) Global desalination market to be worth $18.37bn in 2012, on-line[6] news, published 30 October 2012

Ashley S. (2013) Cutting costs of carbon composites, SAE International, on-line article 11618, published 27 Feb 2013, http://articles.sae.org/11618/

Awal A, Sain M. (2013) Characterization of soda hardwood lignin and the formation of lignin fibers by melt spinning, *Journal of Applied Polymer Science* **129**(5), 2765-2771

Babel K., Jurewicz K. (2008) KOH activated lignin based nanostructured carbon exhibiting high hydrogen electrosorption, *Carbon* **46**(14) 1948–1956

Babel K. (2004) Porous structure evolution of cellulose carbon fibers during heating in the initial activation stage, *Fuel Processing Technology* **85**(1), 75-89

Baik S., Yoon D., Lee H.I., Kim J.M., Lee G.S., Lee Y.Z. (2008) Frictional performances of activated carbon and carbon blacks as lubricant additives, *Tribology Transactions* **52**(1), 133-137

BCC Research (2014a) Nonwoven filter media: Technologies and global markets, AVM043E

BCC Research (2014b) Absorbent and Adsorbent Materials: Global Markets, PLS046B

BCC Research (2014c) Specialty Fibers: Technologies And Global Markets AVM060C

BCC Research (2013) Advanced Structural Carbon Products: Fibers, Foams & Composites, AVM038E

BCC Research (2011) Supercapacitors: Technology Developments and Global Markets, EGY068A

Buttmann M., (2011) Klimafreundliche Kohle durch Hydrothermale Karbonisierung von Biomasse, *Chemie Ingenieur Technik* **83**:1890-1896

CarbonSolutions (2015) HTC-applications, Available at http://www.cs-carbonsolutions.de/, accessed 17.1.2015.

Child M. (2014) Industrial-scale hydrothermal carbonization of waste sludge materials for fuel production, Diploma Thesis, Lappeenranta University of Technology, 109 p.

Cislo R. Kricinska I., Babel K., Koszewska M. (2004) Electrical resistivity of active carbon nonwovens, *Fibres & Textiles in Eastern Europe* **12**(3/47), 70-74

Chatterjee S., Jones E.B., Clingenpeel A.C., McKenna A.M., Rios O., McNutt N.W., Keffer D.J., Johs A. (2014) Conversion of Lignin Precursors to Carbon Fibers with Nanoscale Graphitic Domains, *ACS Sustainable Chem. Eng.* **2**, 2002–2010

Dassenoy F., Joly-Pottuz L., Martin J.M., Mieno T. (2006) Carbon nanotubes as advanced lubricant additives, *Carbon Nanotubes: NATO Science Series II: Mathematics, Physics and Chemistry* **222**, 237-238

De Plamenaer A., Seide G., Gries T. (2015a) Alternative ways to carbon fibre, Carbon Fibre - Future Directions (CF-FD) conference, 24-27 Feb 2015, Geelong, Australia

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[5] https://www.asdreports.com/news-1372/global-activated-carbon-market-cross-us-3-billion-201

[6] https://www.asdreports.com/news-860/global-desalination-market-be-worth-1837bn-2012

De Plamenaer A., Wortberg G., Seide G., Gries T. (2015b) Low cost carbon fibres from polyethylene, Carbon 2015, 12-17 July 2015, Dresden, Germany

Dodd A., Straus S.K. (2015) Determining what key attributes are needed for strong lignin-based carbon fibres, Carbon 2015, 12-17 July 2015, Dresden, Germany

Downing M. (2013) Lignin to carbon fiber, Renewable, Low-Cost Carbon Fiber for Lightweight Vehicles Workshop, 4-5 June 2013, Detroit, MI, US

Dumanli A.G., Windle A.H. (2012) Carbon fibres from cellulosic precursors: a review, *Journal of Materials Science* **47**(10), 4236-4250

Eberle C. (2013) R&D on low-cost carbon fiber composites for energy applications, Carbon fiber R&D workshop, 25-26 July 2013, Orlando, US

EC (2011) Roadmap to a Resource Efficient Europe, European Commission COM(2011), 571.

EUR-Lex. (n.d.). Council directive 1999/31/EC of 26 April 1999 on the landfill of waste. Retrieved 09/21, 2015, Retrieved from http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:31999L0031

Falco C., Sieben J.M., Brun N., Sevilla M., van der Mauelen T., Morall E., Cazorla-Amoros D., Titirici M.M. (2013) Hydrothermal carbons from hemicellulose-derived aqueous hydrolysis products as electrode materials for supercapacitors, *ChemSusChem* **6**(2), 374–82

Falco C., Baccile N., Titirici M.M. (2011) Morphological and structural differences between glucose, cellulose and lignocellulosic biomass derived hydrothermal carbons, *Green Chemistry* **13**, 3273-3281

Frank E., Hermanutz F., Buchmeiser M.R. (2012) Carbon fibers: Precursors, manufacturing and properties, *Macromoecular Materials and Engineering* **297**(6), 493-501

Frost&Sullivan (2008) Advances in Carbon Fibers for the Composites Industry, D16F

Frost&Sullivan (2009) Nanomaterials application road-map: The 2030 Scenario, DICF

Frost&Sullivan, (2011) Supply chain analysis of the automotive carbon fiber composites market, N9CB-39

Frost&Sullivan, (2012a) Top Tech Report--Materials and Coatings Cluster (Technical Insights), June 2012, D4A7-TI

Frost&Sullivan, (2012b) High-tech materials alert, 6th July

Freedonia (2012) World Filters to 2015 - Demand and Sales Forecasts, Market Share, Market Size, Market Leaders, Study #: 2856

Grönberg V., Wikberg H., Hentze H.P., Harlin A., Jääskeläinen A.S. (2014) Process for the hydrothermal treatment of high molar mass biomaterials. WO 2014096544 A1.

Guilminot E., Fischer F., Chatenet M., Rigacci A., Berthon-Fabry S., Achard P., Chainet E. (2007) Use of cellulose-based carbon aerogels as catalyst support for PEM fuel cell electrodes: Electrochemical characterization J Power Sources 166, 104-11

Guo F., Xiu Z.L., Liang Z.X. (2012) Synthesis of biodiesel from acidified soybean soapstock using a lignin-derived carbonaceous catalyst, *Applied Energy* **98**, 47–52

He C., Giannis A., Wang, J.Y. (2013) Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: Hydrochar fuel characteristics and combustion behavior, *Applied Energy* **111**, 257–266.

Heikkilä P., Shen Y., Grönroos A., Houni J., Sarlin J. (2013) Electrospinning of cellulose acetate and use of such fibers in membranes, The International Istanbul Textile Congress, 30 May – 1 June 2013, Istanbul, Turkey

Heikkilä P., Pasanen A.T., Kauranen P., Pere J., Mahlberg R., Räsänen L. (2012a) Sub-micron and nanosized specialty fibers by electrospinning, Electrospinning, Principles, Possibilities and Practice, 21-22 March 2012, London, UK,

Heikkilä P., Suurnäkki A., Pere J. (2012b) Water-based Electrospinning of Natural Polymers?, 243rd ACS meeting, 25-29 March 2012, San Diego, CA, US

Heikkilä P., Pasanen A.T., Virtanen S., Vähä-Nissi M. (2015a) Preparation of sub-micron carbon fibre web, Carbon 2015, July 12-17 2015, Dresden, Germany

Heikkilä P., Putkonen M., Pasanen A.T., Rautkoski H., Ihonen J., Vähä-Nissi M. (2015b) Fibrous and tubular support materials using in catalyst support materials for low-Pt PEM fuel cells for automotive MEAs, EFCD2015, 13-16 September 2015 La Grande Motte, France

Holmberg, K. (2009) Friction science saves energy. Tribologia – Finnish Journal of Tribology **28**, 16-25

Huang H.D., Tu J.P., Gan L.P., Li C.Z. (2006) An investigation on tribological properties of graphite nanosheets as oil additive, *Wear* **261**(2), 140-144

Inagaki M., Radovic L.R. (2002) Nanocarbons, *Carbon* **40**(12), 2279-2282

Ioannidou O., Zabaniotou A. (2007) Agricultural residues as precursor for activated carbon production, *Renewable and Sustainable Energy Reviews* **11**(9), 1966-2005

Ismail A.F., David L.I.B. (2001) A review on the latest development of carbon membranes for gas separation, *Journal of Membrane Science* **193**(1), 1-18

Jazaeri E., Tsuzuki T. (2013) Effect of pyrolysis conditions on the properties of carbonaceous nanofibers obtained from freeze-dried cellulose nanofibers, *Cellulose* **10**(2), 707-716

Jazaeri E., Zhang L., Wang X., Tsuzuki T. (2011) Fabrication of carbon nanofiber by pyrolysis of freeze-dried cellulose nanofiber, *Cellulose* **18**(6), 1481-1485

Jiang G., Huang W., Li L., Wang X., Pang F., Zhang Y., Wang H. (2012) Structure and properties of regenerated cellulose fibers from different technology processes, *Carbohydrate Polymers* **87**(3), 2012-2018

Johnson, M. 2010. High performance lubricants: Cost vs. performance, Tribology & Lubrication Technology, May 2010.

Kaburagi Y., Hosoya K., Yoshida A., Hishiyama Y. (2005) Thin graphite skin on glass-like carbon fiber prepared at high temperature from cellulose fiber, *Carbon* **43**(13), 2817–33

Kadla J.F., Kubo S., Venditti R.A., Gilbert R.D., Compere A.L., Griffith W. (2002) Lignin-based carbon fibers for composite fiber applications, *Carbon* **40**(15), 2913–20

Kazmierski C. (2012) Growth opportunities in global composites industry 2012-2017, Composites 2012, 21-23 Feb 2012, Las Vegas, NV, US

Keskinen J., Sivonen E., Jussila S., Bergelin M., Johansson M., Vaari A., Smolander M. (2012) Printed supercapacitors on paperboard substrate, *Electrochimica Acta* **85**, 302–306

Kim J., Lee J., Hyeon T. (2004) Direct synthesis of uniform mesoporous carbons from the carbonization of as-synthesized silica/triblock copolymer nanocomposites, *Carbon* **42**(12-13), 2711–2719

Kubo S., Kadla, J.F. (2005) Lignin-based carbon fibers: Effect of synthetic polymer blending on fiber properties. *J. Polym. Environ*. **13**(2), 97-105.

Kubo S., Tan I., White R. J., Antonietti M., Titirici M.M. (2010) Template synthesis of carbonaceous tubular nanostructures with tunable surface properties, *Chemistry of Materials* **22**(24), 6590-6597

Kuzmenko V. (2012) Carbon nanofibers synthesized from electrospun cellulose, Thesis, Chalmers University of Technology

Lartey R.B., Acquah F., Nketia K.S. (1999) Developing National Capability For Manufacture Of Activated Carbon From Agricultural Wastes, The Ghana Engineer, May 1999 http://www.africantechnologyforum.org/GhIE/ActCarbon.htm

Liitiä T., Rovio S., Tamminen T., Rencoret J., Gutiérrez Suárez A., del Río Andrade J.C., Saake B., Schwarz K., Vila Babarro C., Gravitis J., Orlandi M. (2014) Structural characteristics of industrial lignins in respect to their valorization, 13th European Workshop on Lignocellulosics and Pulp (EWLP), Seville, Spain, 24-27 June 2014

Liu C., Chang H., Kumar S. (2014) Carbon fibers and lignocellulosics, IPST Executive Conference, 13th March 2014, Atlanta, US

Lupo D., (2013) A printable supercapacitor as a storage unit in a RF energy harvester, 5th International Conference and Exhibition for the Organic and Printed Electronics Industry, June 2013, Germany.

Marchessault R.H. (2011) All things cellulose: a personal account of some historic events, *Cellulose* **18**, 1377-9

MarketsandMarkets (2012) Activated Carbon/Charcoal/Coal Market by Product (Powdered, Granular) & Application (Water Treatment, Air Purification, Automotive, Food & Beverage) – Global Trends & Forecasts to 2016, AD1577

Morris E.A., Weisenberger M.C. (2015)Solution spun lignin/PAN hybrid carbon fibers and their properties, Carbon 2015, 12-17 July 2015, Dresden, Germany

Nousiainen P., Vehviläinen M. (2009) Biocelsol - Biotechnological process for manufacturing cellulosic products with added value. 48th Dornbirn Man-Made Fibers Congress, Austria 16.-18.9.2009 11 p.

Peng D.X., Kang Y., Hwang R.M., Shyr S.S., Chang Y.P. (2009a) Tribological properties of diamond and SiO_2 nanoparticles added in paraffin, *Tribology International* **42**(6), 911-917

Peng D.X., Kang Y. (2009b) The tribological behaviour of modified diamond nanoparticles in liquid paraffin. *Industrial Lubrication and Tribology* **61**(4), 213-219

Peng Y., Hu Y., Wang H. (2007) Tribological behaviors of surfactant-functionalized carbon nanotubes as lubricant additive in water, *Tribology Letters* **25**(3), 247-53

Persistence (2014) Global Analysis of the Synthetic and Bio-based Lubricants Market, Persistence Market Research Blog, Jul 28, 2014, http://www.persistencemarketresearch.com/article/global-synthetic-and-bio-based-lubricants-market.asp

Robbiani Z., Hydrothermal carbonization of biowaste/fecal sludge, Master thesis, Swiss Federal Institute of Technology Zurich, 2013

Roberts A., Service D., Red C. (2011) 2011 Global Market Opportunities for Carbon Fibers: An Industry Evolving into High-Volume Processing, Composites World Conference's Carbon Fibers 2011, 5-7 December, 2011, Washington DC, US

Senatore A., D'Agostino V., Petrone V., Ciambelli P., Sarno M. (2013) Graphene oxide nanosheets as effective friction modifier for oil lubricant: materials, methods, and tribological results, *ISRN Tribology* ID 425809

Sevilla M., Fuertes A.B. (2009) The production of carbon materials by hydrothermal carbonization of cellulose, *Carbon* **47**(9), 2281-2289

Shannon M.A., Bohn P.W., Elimelech M., Georgiadis J.G., Marinas B.J., Mayes A.M. (2008) Science and technology for water purification in the coming decades, *Nature* **452**, 301–310

Spradling D.M., Amie D.R. (2011) Carbon foam from metallic salts of lignosulfonates, US 8034266 B2

SunCoal (2013) Boost Efficiency in Dewatering Industrial Organic Sludge, Available at http://www.suncoal.de/uploads/20130313_Sludge_Article_Final.pdf, accessed 17.01.2015.

Suss M.E., Baumann T.F., Bourcier W.L., Spadaccini C.M., Rose K.A., Santiago J.G., Stadermann M. (2012) Capacitive desalination with flow-through electrodes, *Energy & Environmental Science* **5**, 9511-9519

Sutherland K. (2008) *Filter and filtration handbook*, 5th ed. Elsevier Science, ISBN 1856174646, pp. 520.

Tesch W., Tesch P., Pfeifer C. (2013) Hydrothermal Carbonization: a feasible solution to convert biomass to soil? *Geophysical Research Abstracts* **15**, EGU2013-7266, EGU General Assembly 2013

Titirici M.M. (2013) *Sustainable Carbon Materials from Hydrothermal Processes*. John Wiley & Sons, Ltd.

Titirici M.M., White R.J., Falco C., Sevilla M. (2012) Black perspectives for a green future: hydrothermal carbons for environment protection and energy storage. *Energy & Environmental Science* **5**, 6796-6822

Tomita N., Sugimoto Y., Soneda Y., Yoshizawa N., Kodama M., Hatori H. (2015) Structure and mechanical characteristics of carbon fiberes from aromatic polymer precursors, Carbon 2015, 12-17 July 2015, Dresden, Germany

Transparency Market Research (2013) Technology trends in Lubricants (Mineral, Synthetic, and Bio-based) Market for Turbine oil, Compressor oil, Gear oil, Hydraulic oil, Bearing oil and Heat transfer fluid lubricant Applications - Global Industry Analysis, Size, Share, Growth, Trends and Forecast, 2012 – 2018, Online: http://www.transparencymarketresearch.com

Turunen S., Pykäläinen N., Sinkko T., Putkisto K., Mikkonen H., Peltonen S. (2009) Process for forming a pigment product from a cellulose derivative. WO2009144372 (A1)

Valta K., Sivonen E. (2010) Method for manufacturing cellulose carbamate, US 7 662 953

Valta K *et al.* (2011) Method for manufacturing cellulose carbamate solution US 8 066 903

Vehviläinen M., Kamppuri T., Rom M., Janicki J., Ciechańska D., Grönqvist S., Siika-Aho M., Elg Christoffersson K., P. Nousiainen (2008) Effect of wet spinning parameters on the properties of novel cellulosic fibres, *Cellulose* **15**(5), 671-680

Wang H., Xu B., Liu J., Zhuang D., Wie S., Zhang X., Jin G., Jiang Y. (2005) Microstructures and friction-reduction performances of the graphite coatings, *Materials Letters* 59, 1683-1686

Wang Q., Han X.H., Sommers A., Y. Park, T'Joen C., Jacobi A. (2012) A review on application of carbonaceous materials and carbon matrix composites for heat exchangers and heat sinks, *International Journal of Refrigeration* **35**(1), 7-26

Warren D., Naskar A.K. (2012) Lower cost carbon fiber precursors, Vehicle Technologies Office: 2012 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting 14-18 May 2012, Washington DC, US

Wikberg H., Grönberg V., Jermakka J., Kemppainen K., Kleen M., Laine C., Paasikallio V., Oasmaa A. (2015a) Hydrothermal refining of biomass - An overview and future perspectives, *Tappi Journal* **14**(3), 195-207

Wikberg H., Ohra-aho T., Pileidis F., Titirici M.M. (2015b) Structural and Morphological Changes in Kraft Lignin during Hydrothermal Carbonization, accepted to ACS Sustainable Chem. Eng.

Wittman, T. (2015) personal communication

Wu Q., Pan D. (2002) A New cellulose based carbon fiber from a Lyocell precursor, *Textile Research Journal* **72**(5), 405-410

Zhang W., Zhou M., Zhu H., Tian Y., Wang K., Wei J., Ji F., Li X., Li Z., Zhang P., Wu D. (2011) Tribological properties of oleic acid-modified graphene as lubricant oil additives, *Journal of Physics D: Applied Physics* **44**(20), 205303

Zou L., Li L., Song H., Morris G. (2008) Using mesoporous carbon electrodes for brackish water desalination, *Water research* **42**(8-9), 2340-2348