LigniMATCH

FUTURE USE OF LIGNIN IN VALUE ADDED PRODUCTS

- A ROADMAP FOR POSSIBLE NORDIC/BALTIC INNOVATION

LIGNIMATCH

LigniMatch is a joint industry-academy-project addressing environmental challenges at the same time as exploring the economic potential of a raw material that is abundant in the Nordic/Baltic countries – lignin. The project aims at evaluating possible upgrading of lignin that can be extracted from e.g. pulp and paper industry into value-added products that can substitute fossil-based alternatives.

Partners

LigniMatch is a collaborative project that combines the chemical industry and the forest industry in a new way.

Industrial partners

- Akzo Nobel Surface Chemistry AB
- Borregaard Industries
- Novozymes A/S
- Södra
- Volvo Car Corporation

Network organizations

- GMV Centre for Environment and Sustainability, Chalmers University of Technology and University of Göteborg
- Øresund Environment

Universities and research institutes

- Department of Chemical and Biological Engineering, Chalmers University of Technology
- Environmental Biotechnology and Biotechnology of Renewable Natural Resources, University of Helsinki
- Innventia AB (former STFI-Packforsk AB)
- Latvian State Institute of Wood Chemistry, IWC
- VTT Technical Research Centre of Finland

Deliverables

LigniMatch is a knowledge creation, dissemination and transfer project that builds on information in available literature and input from project partners. This summary report presents a roadmap for the future that highlights promising routes for new lignin-based products on the international market. The roadmap compiles inputs from the detailed technical reports delivered in the LigniMatch project during 2007-2009. For more information, see the project website at http://www.chalmers.se/gmv/EN/projects/lignimatch.

SUMMARY

Lignin is one of the main constituents in wood and is a raw material potentially available in large volumes in the Nordic/Baltic region. Development of its potential for value-added products has several possible benefits for the environment as well as for the economy. With a market for lignin-based products, fossil derived raw materials can be replaced at the same time as energy efficiency measures are encouraged in the pulp and paper sector, since an excess of energy can be taken out from the mills as lignin. Economically, lignin can be the basis of new innovation systems in the Nordic/Baltic region.

This roadmap aims at highlighting promising routes for implementation of new lignin-based products on the international market. It excludes applications that are already commercially available today, and focuses on applications that can be developed into new markets.

A wide range of potential lignin products were identified and evaluated within the LigniMatch project. In a process including studies of literature and patents, repeated partner meetings and electronic surveys, the following products were identified as the most relevant in the LigniMatch consortium to study further:

- Activated carbon
- Carbon fibers
- Phenols

After a more in-depth analysis of these systems in terms of energy and environment, market potential, and the innovation system, it was concluded that carbon fiber production was at present the most interesting route. It is recommended that a consortium is formed that can further explore this potential for the future use in e.g. the automotive industry. The roadmap ends with examples of roles in such a consortium.

INTRODUCTION

Lignin exists naturally in plants and trees and its complex chemical structure allows for use in a wide range of applications. The major sources of lignin are cooking liquors generated in wood pulping processes, e.g. black and red liquor. Black liquor is to date mainly used for energy conversion at the producing plant, but with the Lignoboost technology – a new Swedish-patented method – lignin can be isolated from the black liquor, resulting in both a raw material that can be used to produce value added products, and the opportunity to overcome equipment bottle necks when planning for capacity increases in the pulp mills. This opens up for development of the potential of lignin as a raw material for different products - a raw material that is potentially available in large amounts and that could provide large benefits for a range of actors in the Nordic/Baltic region.

Potential environmental benefits

The potential environmental benefits from finding alternative uses of lignin are extensive, and with a double effect. Lignin can be used to replace fossil based raw materials in a wide range of products, from plastics to individual chemical products and carbon fibers. Furthermore, if there is a market for lignin for such value-added products, the mills will also have an additional economic incentive to take measures for higher energy efficiency.

Roadmap to guide development in the Nordic/Baltic region

This roadmap aims at giving guidance on how to select and prepare for successful development and production of lignin-based products in the Nordic/Baltic region. The starting point has been the replacement of fossil-based products with lignin-based alternatives, of benefit for Nordic/Baltic actors, as well as for the environment. It focuses on three questions:

- During what conditions will it be beneficial to use lignin for other purposes than for heating?
- What fossil-based products will be most interesting to replace with lignin-based alternatives for the Nordic/Baltic actors?
- How can the development of lignin into value-added products be furthered?

The roadmap is directed towards potential actors in future innovation systems around value-added products from lignin in the Nordic/Baltic region, such as industry partners, network organizations, researchers and policymakers. The focus of the roadmap is on applications that can provide high value to the actors in the LigniMatch project. The roadmap contains a short summary of outcomes from the LigniMatch project and does not go into details on the technological, economical or ecological aspects of the routes presented. Those interested in further information are referred to the project webpage at: http://www.chalmers.se/gmv/EN/projects/lignimatch

Lignin supply

Lignin can be isolated through different extraction methods, resulting in various types of lignin with different characteristics. A large number of modification methods make it possible to derive a range of substances, materials and products from lignin. Examples are shown in Figure 1.

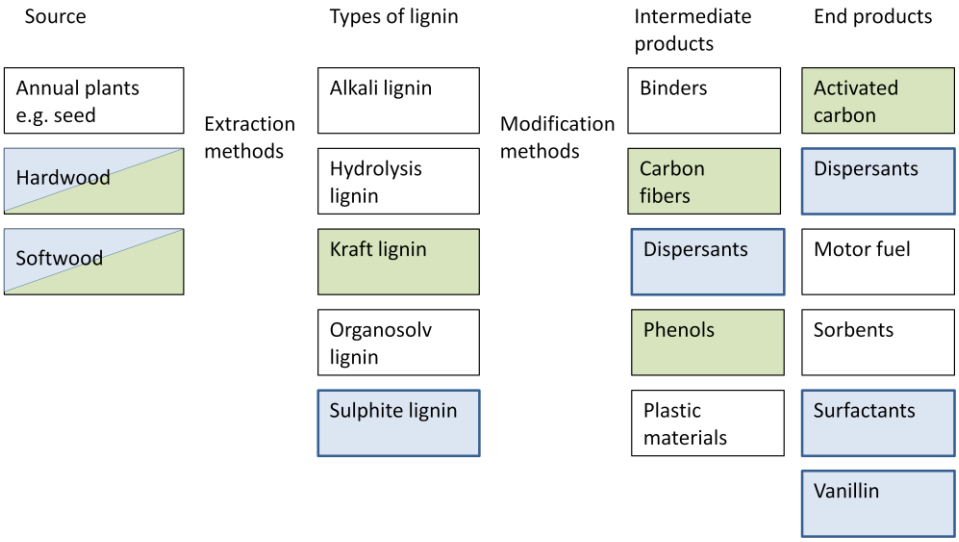


Figure 1. Sources of lignin, types of lignin potentially produced in industry and examples of intermediate and end products. Blue boxes represent product routes in commercial markets today. Green boxes show routes of most interest to develop further, as identified in the LigniMatch project.

The amount of lignin that will be available for value-added products is difficult to estimate. It depends primarily on the development of industrial activities within the pulp, ethanol and agriculture sectors, and on how much lignin that is ultimately isolated from different processes. The global pulp and paper production was approximately 160 Mtonne in 2000, with Swedish and Finnish industry contributing approximately 15% of this, i.e. 24 Mtonne. From this, the theoretical supply of lignin is about 8 Mtonne per year. However, today, most of the lignin is not isolated but instead used in the form of black liquor as internal energy input at the pulp mills.

LigniMatch has focused on applications that are possible to develop into new markets once the lignin has been isolated. Thus, the use for heating at the plant, or products on already mature markets, such as dispersants, surfactants and vanillin are not in focus. An interesting route for further development is the Lignoboost method for isolation of lignin from Kraft black liquor. The technique is available and most likely to be implemented in pulp mills in a few years. However, in order to make up for investments required, it is important that a future market for lignin exists.

Lignin-based products

In LigniMatch, products that might be of interest to develop for a future market were selected based on a survey of available literature and patents and a questionnaire sent to all project partners. This resulted in a wide range of possible lignin-based products:

Activated Carbon – Activated carbon can be made from many different sources, out of which lignin is one. It is used in a wide range of applications, e.g. cleaning of environmentally hazardous emissions to air and water.

Binders – Research and small-scale implementation exist on using lignin as a binder in e.g. construction materials, road making and feed pellets.

Carbon Fibers – Carbon fibers from lignin have attracted great interest in recent years as they have the potential to replace oil-based carbon fibers in materials that are strong and light for applications such as laptops and aircrafts.

Motor Fuel – To use lignin for production of motor fuel is currently attracting much interest. Many actors are working with the issue, but the application is not of central interest to the LigniMatch partners to date.

Phenol – Due to its complex structure, lignin can be used to derive phenolic compounds for use as building blocks in a wide range of chemicals.

Plastic materials – Lignin can be used to produce plastic materials. Small scale implementation already exists in e.g. the electronics industry and in concept cars. Lignin-based polymers are mainly used in combination with petroleum-based materials, e.g. to increase the biodegradability of the plastics. Although the idea of using lignin for plastics has been in the loop for many years, no commercial breakthrough has yet been recognized.

Sorbents – Lignin can be the basis of bio-sorbents for water and soil purification. Medical enterosorbents can be synthesized from hydrolysis lignin for e.g sequestration of bile acids, and have existed on a limited market. Lignin based ion-exchangers show high sorption capacity towards heavy metals such as Cu, Cd and Pb as well as organic pollutants (oil products, pesticides, etc). However, production has so far mainly been tested in lab-scale, and the production of bio-sorbents requires large amounts of chemicals.

Routes of interest in LigniMatch

As listed above, a wide range of potential lignin products were identified in the LigniMatch project. The selection of routes for further examination within LigniMatch was determined through an iterative process in 2007-2009 including repeated partner meetings and electronic surveys. The products of interest to investigate further were selected based on the following criteria:

- Products and processes are relevant to active partners
- Raw material availability and capacity of production lines should not constitute a barrier
- Property rights should be considered

Final selection of the three most attractive routes for a Nordic/Baltic roadmap was made by the LigniMatch partners, based on an interest in participation as an actor in a future innovation system, at the same time as selected products were perceived as having good future market potential in mainstream or niche markets. Following the above process, the products identified as the most relevant to the LigniMatch consortium were:

- Activated carbon
- Carbon fibers
- Phenols

These alternatives were chosen for further evaluation in a system analysis.

SYSTEM ANALYSIS OF THREE ALTERNATIVES

A basic system analysis was made of the selected products, with system delimitations and performance metrics discussed and decided on at LigniMatch partner meetings. Table 1 summarizes the characteristics of each alternative in terms of lignin availability, market and property rights, function, energy and environment and costs and competitiveness.

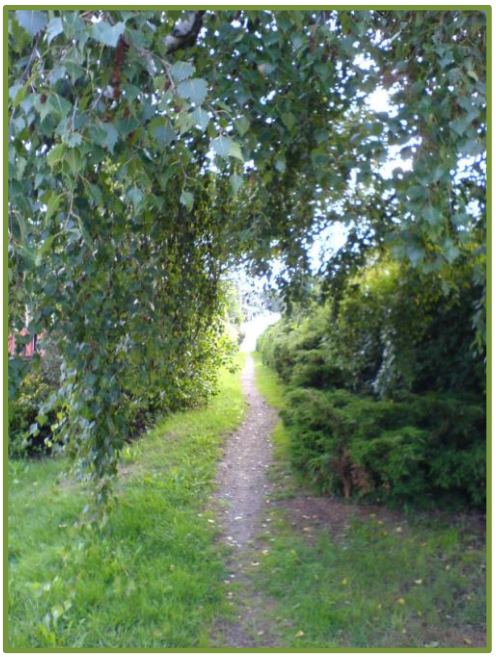
Other aspects of major importance for the future markets of these products are development in the world when it comes to e.g. political decisions, environmental awareness and shortage of oil.

Dependency on world market for oil and biomass

The preferred use of lignin is likely to depend largely on the world price of both biomass and of oil. Lignin is an excellent source of bio-energy and can always be traded on the basis of its energy content. At the same time, its competitiveness in replacing fossil based raw materials in various applications is highly dependent on the prize and supply of oil.

The importance of environmental awareness and political initiatives

Environmental awareness and political actions are important aspects influencing the potential market for lignin-based products. Political initiatives, such as strategies, large investment programs in environmental technology, and policy instruments that add costs or other burdens to fossil-derived products, may have a large impact on the market development.



REACH has been discussed as a possible barrier for future market development as all chemicals traded need to be registered and evaluated with considerable associated costs. This is not specific to lignin-based products, however, but can be a potential obstacle.

Table 1. Some characteristics of three alternative uses of lignin

System characteristic	Activated carbon	Carbon fibers	Phenol
Lignin source flexibility and availability	Flexible to different sources of lignin, e.g. kraft pulping, hydrolysis lignin, vanillin production byproduct (Vanicell), paper mill sludge and agricultural residues. Potential Nordic/Baltic lignin supply might be sufficient to cover the need on the European market.	Kraft-lignin and possibly organosolv-lignin. Theoretically, the pulp and paper industry can provide enough Kraft lignin to supply the current world market of 27,000 tonnes with carbon fibers from lignin from the Nordic/Baltic region.	Can be made from hydrolysis, sulphite and kraft lignin. Theoretically, enough wood is processed worldwide to cover the global phenol market.
Market	The market is enormous, covering a wide range of applications.	There is good growth in the carbon fiber market; 12% in average the last 23 years and expected to increase further. Current production capacity of PAN-fibers does not meet the demand.	Global market of 10.7 Mtonnes/year. Expected growth is 4.5% per year 2010-2015. Mainly local markets.
Property rights	Many patents taken on activated carbon in general in the 80's and early 90's but interest has taken another direction, especially taking into account biorefinery concepts and agricultural applications.	Large activity in research and patents showing wide interest for lignin based carbon fibers. Swedish patents exist that are of interest to develop further.	No patented process found for using lignin as a source for pure phenol.
Function	The raw material has a very large influence on the characteristics and performance of the resulting product.	General performance grade carbon fibers from Kraft lignin have been produced in lab-scale, using similar manufacturing processes as developed for PAN-derived carbon fibers.	Once produced and purified, the phenolic substances from lignin do not differ from the fossil derived ones.
Energy and environment	Chemicals needed as well as energy demand differ for different methods. However, energy demand for lignin-based products is not assumed to be higher than for other precursors in general, as similar processes are involved.	Lignin can replace fossil derived PAN as precursor, and when used to provide a strong composite material replace e.g. steel giving lighter products with less environmental impact. Carbonization of lignin can be more energy consuming than for PAN due to the higher inherent oxygen content. The use of solvents can be substantially reduced with a melt-spinning technique.	Lignin is the only natural biological aromatic polymer known. Environmental impacts depends on the energy demand for cracking the lignin, as well as catalysts (especially those containing Pb) and solvents needed in the production process.
Costs and competitiveness	Prices depend very much on application. Many alternatives to lignin as raw material for activated carbon exist and lignin is not supposed to be competitive unless some special characteristics or applications evolve.	The price of the precursor is important to keep carbon fibers competitive. Lignin is expected to be less expensive as precursor than pitch and PAN that are used today - especially if the oil price increases - and will be competitive if reliable quality can be achieved.	Processes result in a mix of phenols with an uncertain market value. Pure lignin-based phenol is expensive and not expected to be competitive compared to oil-based phenolics at today's price levels.

Activated Carbon

Activated carbon is a strong adsorbent due to large surface areas and pore volumes. It is used in a wide range of applications, making up a very large market globally. One major area of application is cleaning of environmentally hazardous emissions from air and water e.g. flue gas cleaning of municipal waste.

Many types of activated carbon exist

Activated carbon is currently offered in a vast array of product classifications, most of which are based on fossil raw material, but different renewable sources exist as well. Activated carbon from lignin is produced using chemical or physical activation. The prior is often preferred since this method can operate at lower temperatures and shorter time frames, which results in a less energy consuming process, but it also result in higher use of chemicals.

Possible niche market if the structure of lignin can be utilized

Although the technology to produce lignin-based activated carbon exists already today, it is not likely that lignin-based products will make up any large share of the total activated carbon market in the near future. Several other organic by-products exist that can be used, such as nut shells. Activated carbon from lignin sources is thus not likely to be unique on the market, unless niche markets can be found with specific surface properties by careful selection of lignin source, activation method and temperature. In this regard application of lignin derived activated carbons as a material for supercapacitor production should be mentioned – this type of material has been tested on the lab scale and exhibited superior qualities comparing to all other existing alternatives.

Carbon Fibers

Carbon fibers are used for light and strong materials in e.g. aerospace, defense, recreation and general industrial markets. Carbon fibers are currently produced in relatively limited quantities due to the high costs of the material, but are expected to see a rapidly growing market if the prices can be lowered, e.g. for use in lightweight and fuel efficient cars (carbon fiber composites have the potential to reduce vehicle weight by 50-60%). Most conventional production of carbon fibers today is based on fossil derived polyacrylonitrile (PAN). Lignin has gained a lot of attention as an alternative precursor as it has the potential of providing a less expensive material. The estimated annual growth for the carbon fiber composite industry for the period 2009-2015 is approximately 5-

25% depending on applications, with high growth in e.g. aerospace and windmill industry.

Possibilities to offer a less expensive precursor

Knowledge exists on how to produce general performance grade carbon fibers from Kraft lignin, using similar processes as developed for the manufacturing of PAN-derived carbon fibers. Key questions to address are related to implementation of lab scale methodologies into full scale industrial processes while still achieving the desired properties of the carbon fiber.

Cost reductions can be achieved by scaling up plant and production capacity with the current technology to reach a high volume production. With the high volume production scenario, the share of the precursor cost during manufacturing is increasing, making lignin even more interesting as it is expected to be less expensive as a precursor compared to PAN. A microwave assisted plasma conversion process (MAP) has also been developed that has the potential to further reduce production costs as well as processing time.

Great potential if robust production is achieved

The market price for today's production of carbon fibers from PAN for the automotive sector (using large tow fibers) is about $17-26/kg. It is estimated that lignin-derived carbon fibers would be attractive to the automotive industry when they can be produced and offered to the market at a price in the order of $6.5-11/kg. Currently, the estimated price for lignin derived carbon fibers produced with the MAP technique is in the range of $8.40-9.30/kg and expected to be lowered further by increased production speed (that also increases production capacity). As soon as the production techniques of carbon fibers from lignin are robust enough, this may well quickly take over a large share of the market.

Directives might have a large influence

New environmental and quality regulations from the EU could also have a large impact on the use of lignin-based carbon fibers in vehicles. The EU commission has adopted directives stating that 85% of vehicle components will have to be "recyclable" by 2015. The interpretation of this is not yet clear, but could open up for the use of renewable carbon fibers in several parts of a vehicle.

Phenol

Phenols constitute so-called platform chemicals from which a variety of new substances can be synthesized and then used in a wide range of products, e.g. automotives and textiles. Phenols are especially interesting as this application makes use of the natural aromatic structure of lignin; lignin is the only natural biological aromatic polymer. Phenols are currently produced from fossil oil. Phenols are flexible in terms of the source of lignin, and once produced, the phenolic substances derived from lignin do not differ from the fossil derived molecules.

Limited market for unpure phenols

The cracking of lignin results in a wide variety of aromatics, and the separation of those into pure compounds is a challenge. One approach is to produce a mix of phenolic compounds from lignin, but there seems to be no or very limited market for unpure phenols today. To get the quality required, the lignin derived phenol must be purified. The maximum theoretical yield of pure phenol from lignin is 60%, but in practice 40% is a more likely maximum yield. Based on the energy content of lignin and the current price of biomass for energy, lignin would cost about $330 per tonne. With a yield of 40%, this would induce a raw material price alone of the lignin-based phenol of more than $800 per tonne, which is on pair with the world market price of phenolic compounds today. The prize of conventional phenolics is however tightly coupled to the oil prize and changes with time.

Too high costs at current conditions

There is no process available today for the production of phenol from lignin, but there is some research going on in the field. With increasing population and industrialization, the market for phenolic compounds might well increase. Based on the immaturity of the technology and on the high expected costs for producing pure lignin, it is predicted to take a long time before lignin based phenolic compounds will, if at all, become a substantial alternative to fossil based phenols, even in niche products. This prediction may change e.g. with political incentives to replace or ban fossil derived products in certain applications, or if application areas can be found for a mix of phenols.

POSSIBLE DEVELOPMENT

The future market and the technology development for lignin-based products depend on a range of factors and is difficult to predict. To provide some guidance, a tentative estimate of possible trends in the future market development has been made for the three studied products, based on a qualitative evaluation of the aspects discussed in this roadmap (see Figure 2).

Lignin-based phenols are of great interest as lignin is the only known natural biological aromatic polymer, but the technology to produce phenols from lignin is immature and the cost to produce current quality demands is expected to be too high for a profitable market in the coming years. Possibly, this will change with a high increase in oil prices, or legal restrictions.

Activated carbon is much easier to produce, and it is already possible to make activated carbon from lignin. Due to the existing range of qualities and precursor alternatives, further studies are needed to see whether there exists a profitable niche market for lignin-based alternatives, for example use in supercapacitors.

Carbon fibers are expected to see a large market growth if the prices of the material can be reduced. Lignin is very promising in providing this less expensive precursor, as soon as large volumes can be produced at acceptable quality. Higher oil prices and carbon taxes can also drive this development.

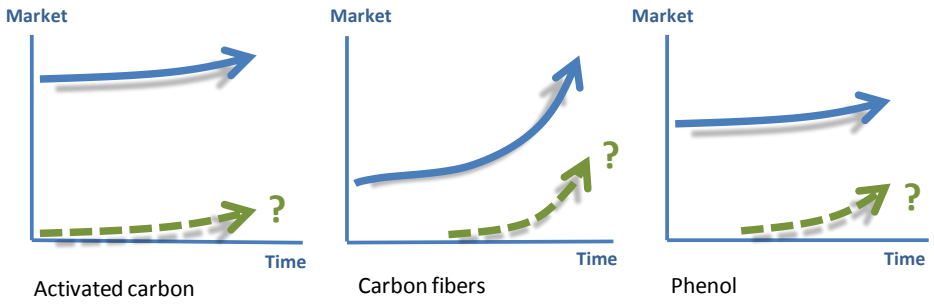


Figure 2: Tentative estimates of possible trends in the development of the overall market for the three studied products (blue), and the potential share of lignin-based ditto (green).

Carbon fibers – an interesting route

To provide an example of how the development of lignin for value added products can be furthered, carbon fibers were selected for further examination of possible ways forward. Apart from a possibly large market growth, lignin-based carbon fibers are also of interest because the properties and production processes of the material are similar to the PAN-based ones used today. This limits the investments needed, and makes the risk reasonable also for smaller actors. Another benefit of lignin-based carbon fibers is that it is used in high-value products, making it an interesting application for investments.

It is not necessary to wait for lignin-based carbon fibers to be of the exact same quality as that of PAN-derived. In some applications, e.g. the casing for electronics, properties such as low weight are more important than high quality. Typical early applications in cars can be found within interior details, seat casings, or as components in the floorspan, details that can be introduced as soon as the lignin-based material is available at the market.

Examples of roles in a consortium for further development

Presently, the global conventional carbon fiber industry is dominated by a handful of companies, based in Japan, Europe, the U.S. and Taiwan. There is to date no lignin-derived carbon fiber producer in the Nordic/Baltic region, but the region holds many actors that might be interested in participating in an innovation system around lignin-based carbon fibers for e.g. the automotive industry, within as well as outside the LigniMatch partner group (see Figure 3):

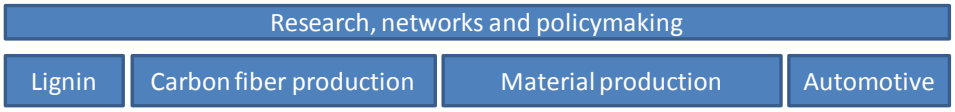


Figure 3. Examples of roles in a tentative innovation system for using lignin-based carbon-fibers in automotives.

Lignin production – The LignoBoost technology is under introduction in large scale, and will probably be established in the Nordic/Baltic region within a few years.

Carbon fiber production – There is to date no carbon fiber producer in the Nordic/Baltic region, but many actors are present that are knowledgeable around the various steps needed, including fiber production and spinning.

Material production – In production of the composite and in refining of the material, several actors with different competences might be needed. The technique to weave carbon fibers exists (e.g. in Nordic patents), which also opens up the possibility to use the more available large tows of carbon fibers (12k and more) while at the same time reducing quality requirements on

individual fibers. Actors with competences in specific segments have yet to be identified in order to complete the potential innovation system chain, e.g. from producers of the fibers, moulds and composites to manufacturers of ready-to-use products.

Automotive industry –The automotive industry, such as car manufacturers, has shown interest in using lignin-based carbon fibers in future vehicles. The interest from vehicle parts manufacturers need to be further investigated.

Research, networks and policymaking – The Nordic/Baltic region holds several important research milieus for research and testing as well as related networks and centras of excellence that can facilitate for innovation in using lignin-based carbon fibers in the automotive industry.

Actions by policymakers and governmental bodies are also important and can constitute both barriers and drivers for the innovation system. Anticipated environmental and quality directives will have a large impact depending on how they are designed and interpreted. Discussions should be initiated between industry and governmental bodies in order to examine this further. Funding for research, demonstration and full-scale plants is another powerful tool. For the supply of lignin, political incentives for general energy efficiency measures at the plants may also be of importance.

Nordic/Baltic lignin – an economic and ecologic opportunity?

LigniMatch is a joint industry-academy project aiming at creating a basis for efficient upgrading of the lignin fraction from pulp and paper industry into value added products that can substitute fossil-based alternatives.

Lignin has to date mainly been used for internal energy supply in the pulp and paper mills. However, the chemical structure allows for use in a wide range of applications. With the patented method LignoBoost, lignin can be isolated for use in different products, thereby potentially substituting fossil resources for e.g. plastics, carbon fibers and dispersants. In the forest industry intensive Nordic/Baltic region, a large supply of lignin can open up a wide range of possibilities that can provide economic growth at the same time as contributing to sustainable development. This joint economic and ecologic opportunity has been the focus of the LigniMatch project.

This roadmap aims at giving guidance on how to select and prepare for successful implementation of lignin-based products in the Nordic/Baltic region. Based on literature reviews, partner surveys, workshops and systems analyses of selected alternatives, the use of lignin for carbon fiber production is identified as an interesting route for the Nordic/Baltic actors. It is recommended that a consortium is formed that can further explore this potential.

LigniMATCH

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