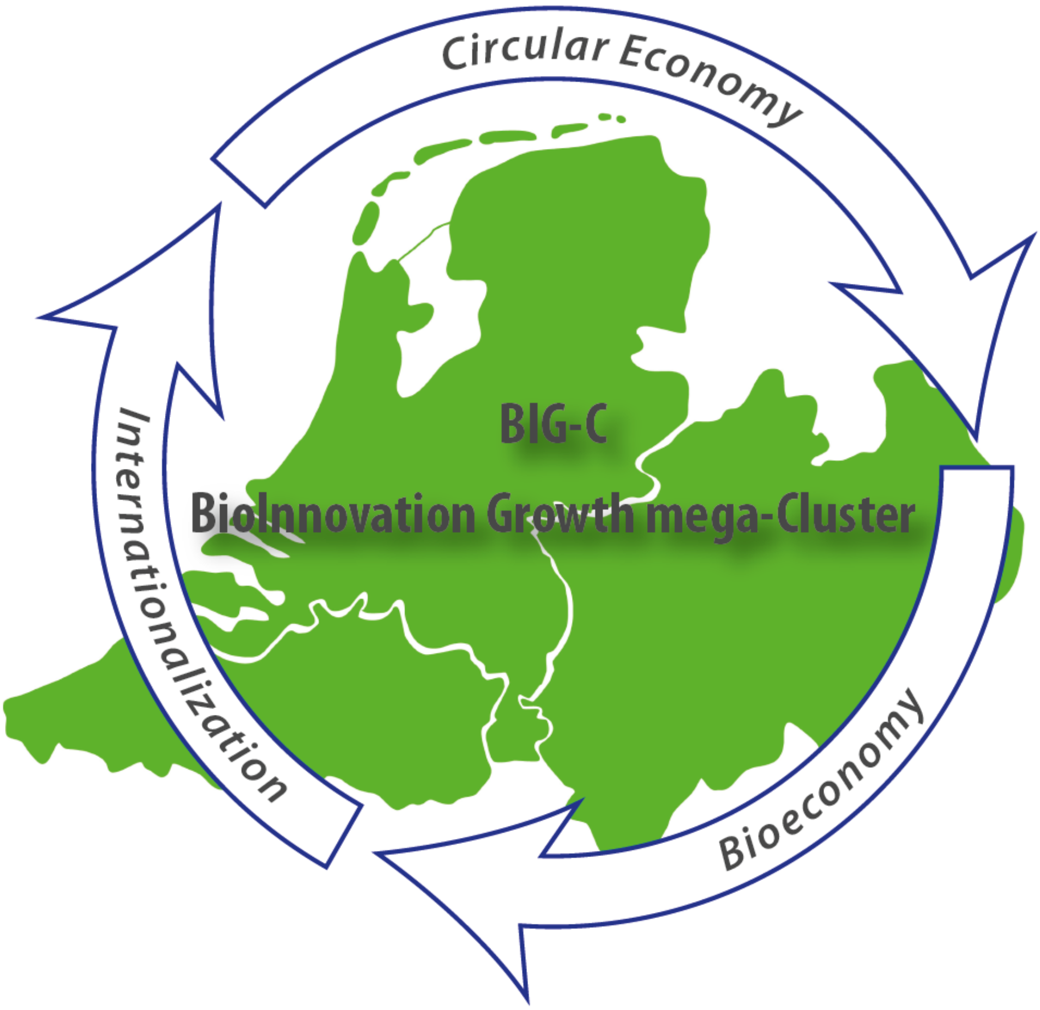
White paper

ALIGN
Aromatics from LIGNin

ALIGN – Biobased Aromatics from LIGNin



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Zusammenfassung

In dem vom BMBF geförderten Projekt ALIGN haben mehrere Partner aus Deutschland, Belgien und den Niederlanden " Biobased Aromatics from LIGNin " entwickelt. Das vorliegende Papier basiert auf einem Roundtable-Gespräch mit mehreren Experten zur Skalierung von Lignindepolymerisationsprozessen und Prozessen zur weiteren Verarbeitung von Lignin-haltiger Biomasse. Lignin muss als stoffliche Ressource genutzt werden, anstatt es zu verbrennen, um dringend benötigte aromatische Komponenten für eine zukünftige biobasierte Wirtschaft bereitzustellen. Da verschiedene Sektoren bereits um Holz und Lignocellulose konkurrieren, wird sich die Wettbewerbssituation durch den Eintritt der chemischen Industrie noch verschärfen. Daher sind flexible Verfahren, die verschiedene Arten von Biomasse nutzen, von Vorteil. Mehrere Entwicklungen werden neue Prozesse mit Lignin-haltiger Biomasse erleichtern: Maßgeschneiderte Vorbehandlungsstrategien, die reproduzierbare Ausgangsmaterialien liefern, präzise Analysemethoden zur zuverlässigen Bestimmung der gewünschten Parameter und robuste DSP-Technologien. Auf der Anwendungsseite kann Lignin eine breite Palette verschiedener aromatischer Monomere liefern, um die BTX-Fraktion zu ersetzen. Des Weiteren können die physikalisch-chemischen Eigenschaften von Lignin für UV-Absorptionsmittel, Antioxidantien, Klebstoffe oder Harze genutzt werden. Als letzter Anwendungsbereich wurde die Verwendung von minderwertigem Lignin als biobasierter "Füllstoff" identifiziert. Angesichts all dieser Möglichkeiten scheint die Zeit reif für einen kommerziellen Durchbruch für Lignin in naher Zukunft.

Summary

In the BMBF-funded ALIGN project, several partners from Germany, Belgium, and the Netherlands have collaborated creating “Biobased Aromatics from LIGNin”. This paper is based on a roundtable that was held with several experts on how to bring lignin valorisation to larger scale. It is crucial to use lignin as a resource instead of burning it to provide urgently needed aromatic components for a future biobased economy. As various sectors are already competing for lignocellulose and wood, the competitive situation will be worsened by the entry of the chemical industry. Therefore, flexible processes that utilize different types of biomass are advantageous. Several developments will facilitate new lignin-based processes: pre-treatment strategies that are tailored to the products and provide reproducible starting materials, precise analytical methods to reliably determine the desired parameters and robust DSP technologies. On the application side, lignin can deliver a wide range of different aromatic monomers to replace to BTX fraction. Another possibility is to utilize the general physio-chemical properties of lignin for UV-absorbance, antioxidants, adhesives, or resins. Another application field that was identified comprised the use of low-quality lignin as biobased “filling material”. Given all these possibilities, the time seems right for a commercial breakthrough for lignin.

Intent

In the past years, there has been a change of mind how to evaluate lignin. For a long time, lignin – as a very recalcitrant material - has resisted profitable exploitation. Therefore, it was perceived as waste material, e.g. in pulp and paper industry, and often burned to yield energy. Consequently, there has been the saying "You can make anything from lignin except money!". However, with an increasing demand for biobased materials and an uprise of new technologies, several promising approaches to valorise this abundant biopolymer have emerged.

In the BMBF-funded ALIGN project, several partners from Germany, Belgium, and the Netherlands have collaborated creating "Biobased Aromatics from LIGNin". In the final phase of the project, a roundtable was held with experts from the project and beyond from the Cluster of Industrial Biotechnology e.V. (CLIB) network. Based on this roundtable, the topic how to bring lignin valorisation to larger scale was examined in more detail. Accordingly, this white paper is not meant to give an all-embracing overview on lignin as there are several excellent scientific reviews (e.g., (1) (2) or (3)). Its purpose is to exemplarily address inherent challenges of lignin application, to classify ALIGN's achievements in this regard, and to point out possible further developments. Moreover, it will show the importance of public funding to close the gap between research and industrial application and will give recommendations for the overall process to bring biobased products to the markets.

ALIGN project

The ALIGN project was started in 2018 and focussed on upscaling three extraction processes that lead to both a high-value lignin fraction and a pure cellulose/sugar fraction: The LX process (LXP), an Organosolv process combined with base-catalysed depolymerisation (BCD), and the lignin-first process (LFP). The lignin fractions derived from the three processes differ in their composition regarding the degree of depolymerisation and functionalisation. Starting with this broad range of different lignin derivatives combined with tailor-made downstream processing (DSP) strategies, a wide variety of biobased aromatics (BBAs) with unique properties can be produced. These BBAs were applied as phenolic resins to produce high-pressure-laminates as well as substrate to produce natural vanillin for food and beverages. The ALIGN consortium covered stakeholders from the whole value chain starting from lignin extraction and conversion via DSP to application under the coordination of CLIB. Apart from the above-mentioned fields, the processes can be adjusted in future projects for a wide variety of applications in the aromatics sector ranging from fine chemicals to bulk products. These scientific results will be published separately in future.

Feedstock

All the experts of the ALIGN roundtable stressed how important it is to use the lignin as a resource. This would not only provide urgently needed aromatic components, but also decisively improve the economics of biorefineries and the bioeconomy.

First, it is important to compare the available supply with potential demands. There are several potential feedstocks for lignin. As widely known, plant biomass is built from three biopolymers: Cellulose, hemicellulose, and lignin. In general, eligible biomass can be classified as softwood, hardwood, and (lignified) grasses whereby the lignin is present in different concentrations and compositions. Moreover, lignin can be extracted from plant material residues that have undergone biogas fermentation as well as from municipal waste. In contrast to common crude oil, biomass is more difficult to transport (not fluid) and less energy-dense (higher water content). Although a transport system is already established for wood, this could pose an additional logistical challenge outside urban areas, especially for annual plants or grasses. Nevertheless, there are also good role models here, for example the sugar beet industry, where central sugar factories are supplied from the surrounding agricultural land.

There is already an immense amount of lignin produced: Estimations are that the global lignin production currently ranges around 100 million tons per year (2). However, most of it is thermically used (burned) und only 2% are seeing a chemical/material use in dispersants, coatings, adhesives, and surfactants. When compared to the current benzene-toluene-xylene (BTX) market which is sitting around 120 million tons per year (4), this is at least a similar order of magnitude. This is very significant, because with the expected decline in petrol production, new routes for aromatic base chemicals will have to be found. If other potential application markets for lignin such as bitumen replacement (world market estimated at 100 million t/a) or as additive for cement (world market estimated at 4.1 billion t/a cement (5)) become relevant customers, the actual demand of a fully bio-based economy could be significantly higher. On the other side, the increasing utilisation of lignocellulosic biomass (e.g. for biofuel fermentation) will inevitably also boost the lignin production massively in the next decades.

Looking at the long-term availability, the situation for plant biomass is initially different from crude oil. In contrast to crude oil, wooden biomass can obviously be regrown. However, depending on the plant species, regrowth takes a lot of time. Current innovations, especially for wooden biomass, can therefore only rely on the resources that were literally planted by previous generations. Thus, it is important to keep in mind that the lignin resource pool is large, but not inexhaustible: A too large withdrawal will clearly risk damaging the corresponding forest ecosystems and biofunctions which are also challenged by the imminent climate change.

Accordingly, it is clearly foreseeable that lignin will become too valuable for thermal conversion over the next decades and that there will be no "lignin for free", so all customers will have to pay a fair price even for low quality lignin. Various sectors such as the construction sector or the paper industry are already competing for woody biomass, and the competitive situation will be significantly worsened by the entry of the chemical industry. Therefore, flexible processes that could work with different types of biomass are advantageous. Nevertheless, it is also important to pay attention to raw material availability early in the planning of future processes and to consider gaining the renewable carbon from recycling streams or CO_2 utilisation instead.

Pretreatment

To access the industrial potential of lignin, pretreatment is the first process step and a very important success factor. Obviously, lignocellulose is a recalcitrant material by nature, so it is very important to find an energy-effective method to separate cellulose/sugar and lignin. In simple terms, first lignin has to be extracted (called pulping) and separated from the cellulose and hemicellulose. Subsequently, this lignin must be depolymerised to yield biobased aromatics (BBA). It is very important to understand that pretreatment massively influences the molecular composition, the chemical characteristics, and the physicochemical properties of the lignin and the biobased aromatics (6).

So far, traditional industrial processes are often focussed on the isolation of the other components of lignocellulose, while lignin is seen more as a side stream. This applies to pulp in the paper industry, for example, but also to the extraction of the cellulose C6 sugar fraction and the hemicellulose C5 sugar fraction in some biorefinery concepts to produce bioethanol. As a logical consequence, industrial applications could only rely on lower-quality lignin for a long time. In contrast, all three pretreatment technologies optimised in the ALIGN project were designed to generate high quality lignin (and have also succeeded in this regard).

Depending on the applied pretreatment, lignin may lose or gain some desired properties. To name the most prominent traditional method, sulphite pulping is applied in pulp and paper industry to create wood pulp. From this pretreament, ligno-sulfonate originates which has become water soluble due the addition of sulfuric groups. This can be helpful for some applications but makes it difficult to separate this lignin from aqueous solutions. Also known for long time and applied in paper production, kraft pulping with NaOH and Na_2S yields Kraft lignin which is also contaminated with sulphur. As sulphur (and other inorganic contaminations) can interfere with the subsequent conversion processes, other methods have been developed to avoid these problems. For non-wooden biomass, soda pulping is already used. For wooden biomass, different methods are in development: hydrothermal processes (using steam explosion or supercritical water), organosolv processes (using hot organic solvents such as methanol, ethanol, or acetone), and ionosolv methods (using ionic liquids) (7). These newer concepts envisage isolating high-quality lignin with tailor-made properties and without interfering impurities.

Depolymerisation can either take place as part of the extraction and fractionation process due to harsher conditions (pH, temperature…) or represent a subsequent, separate process step. In general, the catalytic depolymerization of lignin can be done either chemically or enzymatically (recent reviews can be found here (7) (8)). For application, the depolymerisation degree is an important key parameter because reactivity increases by depolymerisation as more functional groups become available.

In general, it can be recommended to have a flexible process that can operate with different kind of biomass feedstock and can handle seasonal changes as well as other challenges. For industrial purposes, pretreatment needs to yield reproducible and foreseeable results and defined molecules. To pose a reliable feedstock for the future industry, a deep understanding how the pretreatment process is operated to achieve the desired results is mandatory. For large-scale processes, a general recommendation is to „ Keep it simple, stupid! “ which means a minimum number of process operations and the use of robust technologies. Very expensive unit operations are only economic if the product is very expensive but cannot be applied in bulk processes. As shown in the ALIGN project, it is also important to minimize the application of chemicals and recycle the applied chemicals as much as possible to reach a sustainable and economic level. Energy efficient DSP methods such as membrane processes can help to reduce the footprint of new processes.

Given the significant effect of pre-treatment on the properties of lignin, it can be concluded that there will not be one “silver bullet” method for every conceivable application. Therefore, different kinds of pretreatment must be applied, adapted, and optimized for different kind of value chains. Organosolv lignin, for example, shows a good reactivity and is suitable for the preparation of biobased polymers such as phenol-formaldehyde resins, polyesters, polyurethanes or polyethers (7).

A special case is the pretreatment to create flavourings classified as natural from lignin for use in the food sector. Within the ALIGN project, natural vanillin should be produced on lignin-based biomass. However, the term natural can be understood in different ways: Natural product characterization may be understood as production from bio-based starting materials or in the sense of the EC Flavour Regulation. For vanillin, the latter one is far more challenging. Even though natural flavourings must be based on plant or animal source materials, the following processing steps are also subject to strict requirements that most industrial processes do not fulfil. Exclusion criteria can be, for example, too high temperatures or pressures, the use of solvents, or the use of chemical catalysts. Nevertheless, it is still valid that the high prices of some flavours such as vanillin would justify the efforts to adapt the process condistions. However, this should be understood as a special application in the high-price segment and requires tailor-made adaptations. During the ALIGN project, serious efforts have been undertaken to adapt the LX-process as a “natural” pretreatment process. However, the final decision of the responsible associations is still pending.

Upscaling

Over the past decades, numerous researchers and laboratory experiments have shown ways to extract, purify, and convert lignin. However, in order to finally realise the desired changes in the economy, these concepts must be transferred into industrial scale and application. A helpful indicator is the "technology readiness level" (TLR), which measures the degree of maturity from the idea to real application on a scale between 1 and 9. Often, increase in TRL is accompanied by an upscaling of the processes to larger volumes. Like in today's petroleum refineries, the economy of scale will also be a decisive factor in the bioeconomy to achieve competitive prices.

Despite extensive research, there are already a few commercial applications for the utilisation of lignin (1). In the current situation, smaller companies and start-ups find themselves in a classic chicken-and-egg problem. Particularly in the chemical industry and in the material sciences, validations on a larger scale are expensive. Theoretically, this money derived from investors. However, investors often want start-ups to prove that their product address a real demand on the market. In turn, this would require sufficiently large sample quantities to be delivered to potential customers (for which, again, an expensive scale-up would be necessary). Consequently, the TRLs between 4-7 are difficult to progress and are therefore referred to as the “valley of death”.

The expert workshop agreed that publicly funded projects should not only address basic research but can also provide crucial support to reach higher TRL. Such projects allow processes to rise sufficiently far up the TRL scale to find investors and prove their concepts to potential customers. At the same time, they bring together different partners and establish contacts between researchers, small companies, and large industrial interested parties. Therefore, public funding of scale-up projects such as ALIGN can initiate the first step to successfully “hatch the egg”. Nevertheless, it is important that the involved partners start already at a similar TRL at the beginning of a project when their milestones build on each other. However, secondary branches to create other products can still have a more exploratory character.

Analytics

In contrast to hemicellulose or cellulose, lignin is a very diverse molecule that cannot be assigned a clear molecular formula or schematic structure. Its aromatic components are linked in a variety of ways and differ between different plant species such as coniferous wood, deciduous wood, and grasses. Since the different pre-treatment processes, as mentioned above, strongly alter its structure on a macromolecular level and even on a molecular level, each lignin itself is initially a black box. Even if great efforts are performed to apply a reproducible pretreatment in the process, the resulting quality has still to be monitored continuously to guarantee the success of the subsequent industrial process steps.

In principle, this problem is not an unknown: crude oil is also a complex mixture of numerous compounds that must be purified, separated, and partly (de)functionalised by established process steps. Likewise, different crude oils differ significantly, for example in their viscosity or their sulphur content. However, the petrochemical industry has established ways to measure these parameters and to achieve desired properties through tailor-made blends.

For a commercial use of lignin, the black box must be assessed with precise and applicable analytics. Depending on the application area, these methods must enable the user not only to identify single monomers on a molecular level, but also to grasp the physio-chemical properties of the lignin (see next chapter).

Over the last years, a broad range of methods has been applied to characterize lignin monomers and oligomers. Applied methods include UV fluorescence spectroscopy (UV-FS), gas chromatography–mass spectrometry (GC-MS), gel-permeation chromatography (GPC), matrix assisted laser desorption/ionization – time of flight mass spectrometry (MALDI-TOF MS), and nuclear magnetic resonance (NMR) characterizations (9).

For the processed lignin, other global properties are also relevant for the later application. These include parameters such as solubility, temperature resistance, polarity, depolymerisation degree, and pH dependence. However, there is still an ongoing process to fundamentally understand which measurable properties of lignin can serve as sufficient parameters to deduce these (physio-)chemical characteristics.

With established measurements and analytical methods, defined lignin would ensure the reproducibility from early experiments onwards to production processes. Complementary to the petrochemistry, this also might enable the industry to create blends with certain desired properties to mitigate e.g. seasonal fluctuations.

Applications

During the ALIGN roundtable, the experts discussed that potential application for lignin could be divided into three areas: Interest in functional groups on a molecular level, in chemical characteristics of oligomers, and in physiochemical properties of larger lignin molecules.

First, lignin can deliver a wide range of different aromatic monomers. As already discussed, these monomers could potentially replace the BTX fraction in future days. Here, it is crucial which monomeric BBAs are formed and which functional groups they carry. Depending on their functional groups, these monomers can find use ranging from the cheapest basic chemicals to starting materials for high-priced fine chemicals. The cheaper the final products are, the greater the price pressure is on the processes. A promising option is the targeted conversion of individual molecules into high-priced products. At the same time, however, the quantities produced are relatively small. A good example of this is the conversion of monomers to natural vanillin, which has been the aim of the ALIGN project. This affects the previously mentioned points as follows: At high prices, the source of lignin can be chosen almost freely, as the raw material costs are less important. However, the quality of the raw materials combined with the pretreatment and DSP must ensure that sufficient quantities of the desired monomers are obtained. For such high-price markets, it was discussed that regulatory restrictions (pushes) and customer wishes (pulls) can influence their process design much more than cost reasons.

For the chemical industry, using lignin just because it is a bio-based replacement is less attractive than also exploiting its unique possibilities. Lignin-derived molecules show functional groups beside hydroxy groups that are not common and, therefore, open the possibility for a whole new chemistry, for example in the adhesive market. As already mentioned before, however, this requires a reproducible pretreatment and a depolymerisation without interfering substances. There have been several studies conducted how lignin can be biotechnologically valorised using microorganisms to produce polyhydroxyalkanoates, single cell oils, muconic acid, or vanillin, but these processes still seem to be on a low TLR (10).

The second principal target area for lignin application is to utilize the general physio-chemical properties of lignin. These characteristics are not tied to certain monomeric compounds but result from inherently heterologous nature the oligomers. Due to its aromatic compounds, lignin can absorb a broad spectrum of UV light and increase the UV-absorbance in sun protection, paints, and other applications (11). Aromatic rings with hydroxyl and methoxyl functional groups allow lignin to act as an antioxidant (12), while other molecular structures exhibit antimicrobial, antigenotoxic, or even antimutagenic effects. Like starch, lignin can also act as adhesive by itself. In ALIGN, one major success has been the replacement of formaldehyde compounds in low-viscosity lignin-based phenolic resins. During the roundtable, the experts agreed that there is a promising perspective in producing lignin blends similar to existing crude oil blends to tailor the physicochemical properties.

The last application field that was discussed comprised the use of lignin as "filler material". Low quality lignin can still act as biobased filler component to replace bitumen in the asphalt mixture where it shows promising results (13), to chemically stabilize problematic soils (14), or to improve the compressive strength of cement (2).

Given all these possibilities, the time seems right for a commercial breakthrough for lignin. Lignin will not only be used as a replacement for existing applications, but that new fields of application are also being considered, for example in the field of nanoparticles (15), hydrogels (16), battery storage technology (17), and 3-D printing (17).

General recommendations to bring bio-based products to the market

You can make money from lignin! However, it is necessary to identify the right feedstock, a KISS pretreatment, and a scalable process that match desired application.

International partnerships and networks are important to drive innovation and turn ideas into products.

The lignin resource pool is large, but not inexhaustible.

On a large scale, nothing will come for free, so your process concept should at least seem to be economically feasible if the best conditions are assumed.

Bio-based processes are NOT more sustainable than conventional fossil-based processes by themselves, so the rules of green chemistry (don't use toxic chemicals, avoid waste stream, recycle your materials...) must be followed from the start.

For the critical steps to overcome the TRL valley of death, funding can be an important tool for small companies.

When building the consortium, it should be ensured that the central partners start from similar TRL.

It is of great advantage to enrich consortia during the project with new associated partners to address unforeseen developments and exploit opportunities.

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