PhenoWood – Process development for the production of phenolic compounds from wood

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- **Industry partner**
  - SunCoal
  - B+B Engineering

Aus Holz können durch die Depolymerisation des Bestandteils Lignin biobasierte phenolische Verbindung zugänglich gemacht werden. Das Verfahren der basenkatalysierten Depolymerisation (BCD) von Lignin, welches zur Bildung von monomeren sowie di- und oligomeren Alkylphenolen führt, wurde am Fraunhofer CBP etabliert und in den Pilotmaßstab übertragen.
Das Projekt umfasst die weiterführende wissenschaftliche Untersuchung der katalytischen Spaltung von Lignin, um ein tieferes Verständnis für den Reaktionsmechanismus während des Prozesses zu erlangen und Produktspezifikationen der Phenolderivate definieren zu können. Hierbei fokussieren die Untersuchungen auf ein material- und energieeffizientes Prozessdesign sowie die Bewertung und Umsetzung der technischen Machbarkeit einzelner Prozessschritte.

I. Project parameters

1. Topic, purpose and state of scientific knowledge

Topic of PhenoWood was the investigation of the continuous base-catalyzed depolymerization (BCD) of different types of lignin (Kraft and Organosolv), which is well known as the second most abundant terrestrial biopolymer and the only one high-available feedstock for aromatic molecules. The BCD reaction of lignin takes place under hydrothermal alkaline conditions at temperatures of 513 to 573 K, pressure of up to 250 bar and reaction times of 5 to 15 min (hydrodynamic residence time) [1]. The BCD leads to the formation of a complex mixture of phenolic compounds and by-products, based on a cleavage of different types of ether bonds in lignin, namely alkyl-aryl- and aryl-aryl-ether-bonds. Isolation and separation of the depolymerization products have been adopted to the purpose of balancing the main product fractions and by-products to propose a simplified kinetic model of the BCD, thus, to evaluate the process kinetics, activation energies and the process design of the BCD process. The main goal of the project is to gain a deeper understanding of the mechanism to facilitate a further scale-up of this process.

2. Interdisciplinarity of the project

The project Phenowood mainly addresses the pillar processing and conversion always considering the raw material nature and specification on the one hand and the economic consideration of the developed process on the other hand. However, within the framework of the joint project, individual partners do not consider the entire process chain from primary plant production to socio-economic evaluation of the applied methods and processes. The main focus of the processing / conversion pillar is inter-disciplinary in the fields of process engineering, chemical catalysis and analytical chemistry.

3. Innovativity of the research

The use of existing industry-relevant technologies for the hydrothermal conversion and product processing on the depolymerization of lignin and lignin-containing material streams to bio-based phenols is innovative and novel. The scientific challenge is to find reaction and process applications that can be transposed to industrial ones, i.e. which come close to continuous operation applying large capacities. Moreover, new products from lignin cleavage are available for different applications. Here, collaborated with associated partners for application testing are considered and ongoing.

4. Application-oriented research

Developments include technology demonstration in pilot scale, i.e. large scale prototype testing in intended environment close to expected performance is foreseen (TLR 5-6). Here we closely work together with users not only in the field of applications testing of the phenolic product but also for feedstock provision and plant construction and design. Relevant inputs from the external partners are included in the project design in order to enhance industrial implementation.

5. Relevance of the project for the bioeconomy, the ScienceCampus and the state of Saxony-Anhalt

The project is integrated in the Science campus focusing plant-based bioeconomy, especially the topic wood and waste wood usage is addressed. Companies from the fields of wood industry and pulp industry, plant construction and chemical manufacturers are relevant partners. There are already cooperation with companies from Saxony-Anhalt or supposed to be intensified.

II. Theory and methods

Lignin, major component of wood, has been appeared as promising resource for the production of high-value added phenolic compounds via depolymerization. Lignin is formed by three monomer units, namely *p*-coumaryl, coniferyl and sinapyl alcohol (see Figure 1). These units are linked by carbon-carbon- or ether-bonds leading to a complex, heterogeneous and highly branched structure [2].

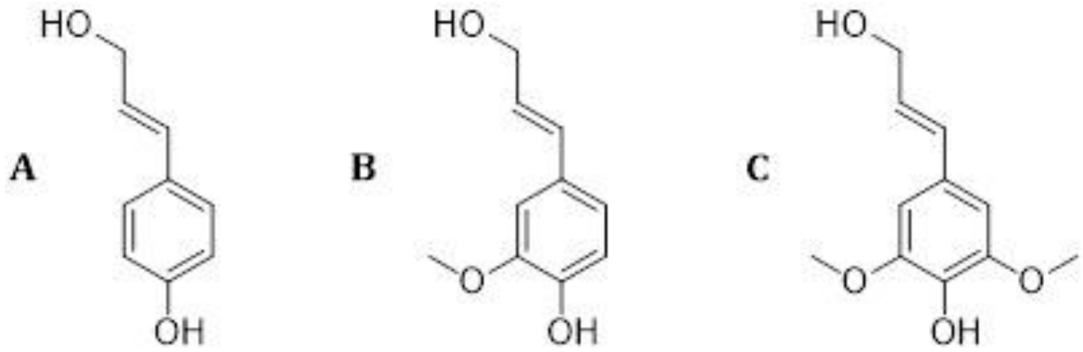

Figure 1: *Chemical structures of p-coumaryl (A), coniferyl (B) and sinapyl alcohol (C).*

During the last years, several methods to depolymerize lignin in different kind of ways have been developed [3]. The base catalyzed depolymerization of lignin in aqueous solutions of sodium hydroxide leads to a cleavage of ether-bonds in lignin and to the formation of a complex mixture of mono-, di- and oligomeric phenolic compounds as well as small organic and gaseous by-products (see Figure 2). An overview of the BCD is given by Rößiger et al. [4] and Otromke et al. [5].

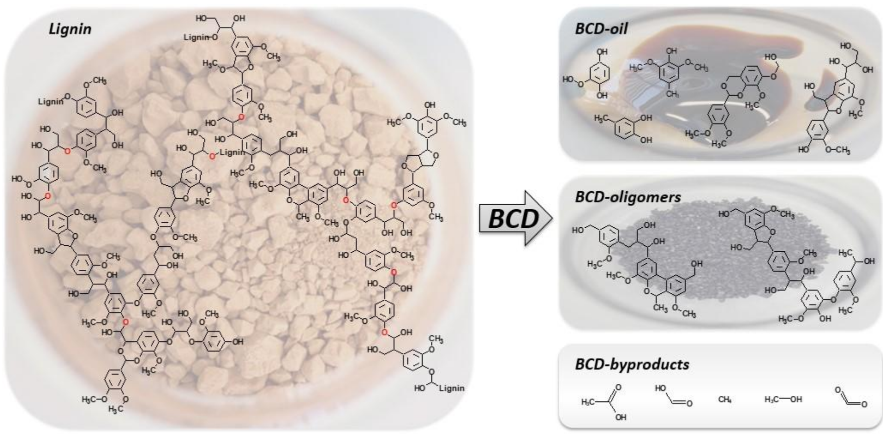

Figure 2: *Reaction scheme for the base catalyzed depolymerization of Lignin [4].*

To isolate and separate the product fractions in the mixture, a standardized procedure of the Fraunhofer CBP was applied. The procedure starts with an acidification of the product mixture, which leads to a precipitation of the oligomeric products (unconverted lignin and condensation products), which afterwards are separated from the liquid phase by filtration. The oligomeric products were dried and characterized by gel permeation chromatography to determine their molecular weight distribution. Mass loss during acidification by release of carbon dioxide was determined and used for the calculation of the gas yields. The supernatant contains small organic compounds (SOC, methanol, ethanol, formic acid and acetic acid), which were quantified by high pressure liquid chromatography (HPLC) and gas chromatography (GC). Furthermore, several phenolic monomers in the supernatant were quantified by HPLC. Afterwards, the supernatant was extracted with methyl isobutyl ketone and the combined organic phases dried over sodium sulfate. Following, the solvent was removed under reduced pressure to obtain the BCD-oil, which contains the phenolic mono- and dimeric compounds. For all product fractions (SOC, gas, oligomers and oil), the yield Y, with respect to the initial lignin (water- and ash free) was calculated.

III. Results and perspectives

1. Results

In AP1, the development of separation and purification technologies was in the focus of investigation. Here, it has been shown that the developed procedure for the isolation and separation of product fractions, as described above, facilitates to quantify the majority of educts and products (mass balances around 95 wt.%). Furthermore, it has been shown, that the separation of the precipitated oligomeric products can be eased by a short heat-up of the suspension, what could be explained by an aggregation of the lignin particles.

For an investigation and optimization of reactor technologies in AP2, residence time experiments were applied. These experiments have been shown, that packaging balls made of stainless steel or glass (diameter 4 mm) in the plug flow reactor (1 m length, internal diameter of 38 mm) of the pilot plant enables a laminar flow pattern, while a reactor without any packaging suffers in a more turbulent flow, which leads to higher residence times, hence, more undesired repolymerization reactions of the products.

AP3 addressed the optimization of the whole depolymerization process. Here, using design of experiments, a model equation for the yield of oligomers and oil in in dependence on temperature, mass flow of the reactants, reactor volume and sodium hydroxide concentration was determined. For instance, Figure 3 shows the influence of mass flow and temperature on the yield of oligomers. Here, high yields of oligomers have been obtained at low temperatures and high mass flows, while high oil yields have been obtained at high temperatures and low mass flows.

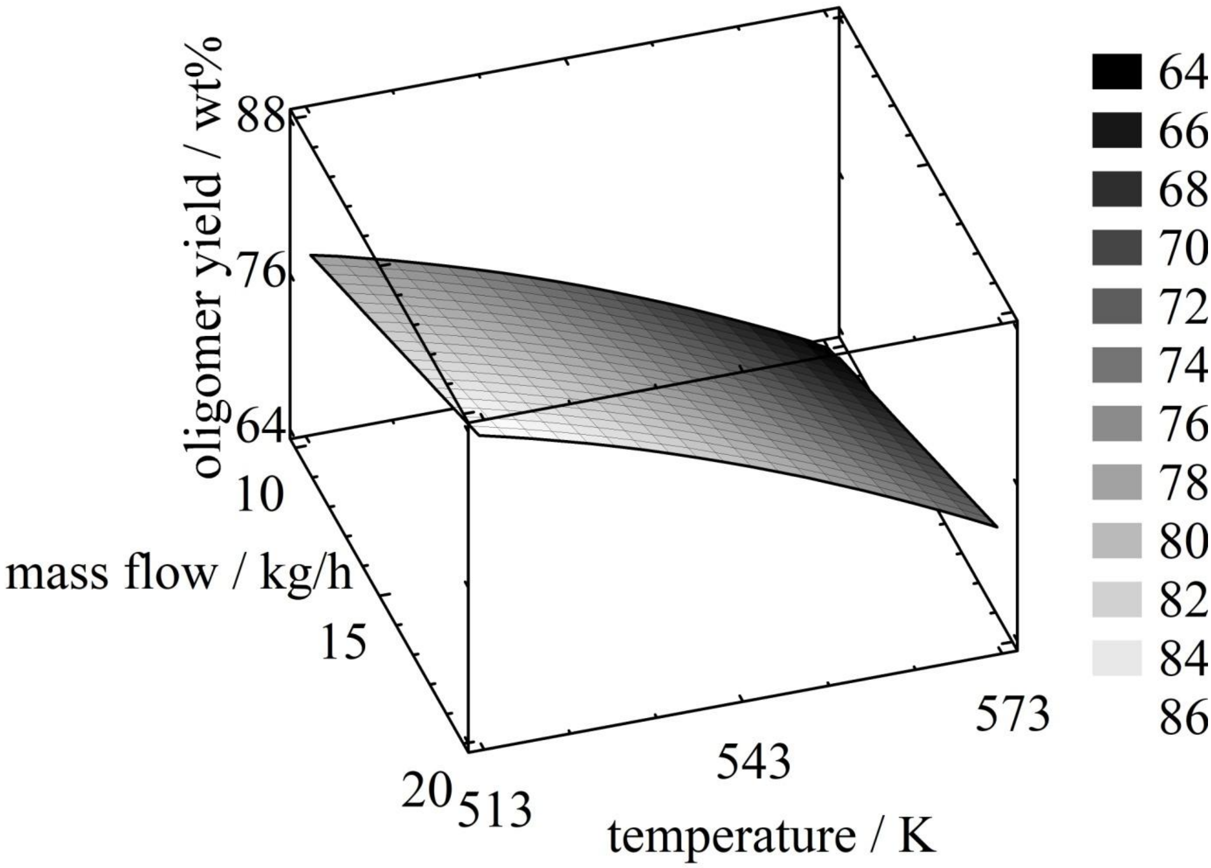

Figure 3: *Influence of mass flow of the reactants and temperature on the yield of oligomers, 1,67 wt.% NaOH, 5 wt.% Kraft Lignin, reactor volume 1 L.*

Further, to determine rate reactions and activation energies of the depolymerization reaction, a simplified kinetic model was proposed and evaluated (see Figure 4 left). From this model, activation energies of 37 and 22 kJ/mol for the BCD with 1.67 and 2.50 wt.% NaOH, respectively, were determined, which are in good agreement with values reported in the literature. For example, for the BCD with 1.67 wt.% NaOH and 5 wt.% kraft lignin, the time-dependent model fit of the oligomers, liquid products and gas and their experimental values is shown in Figure 4 right.

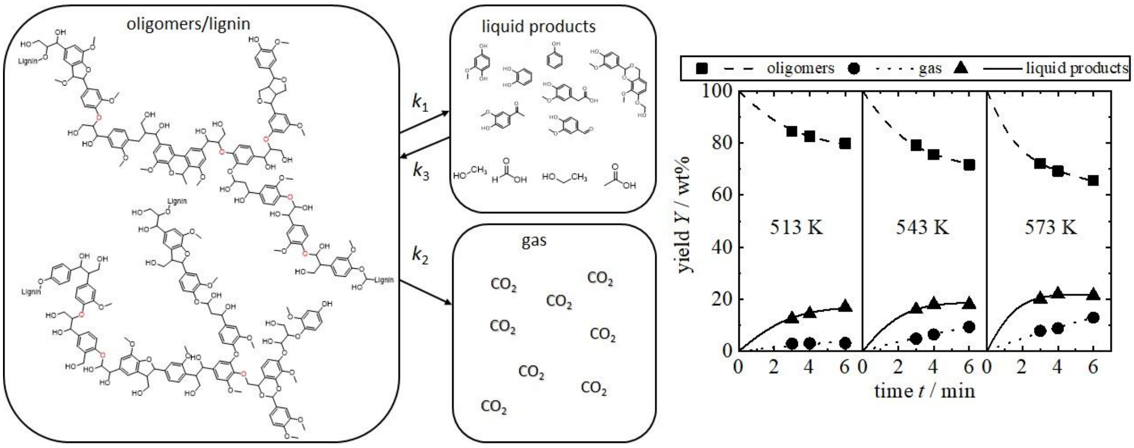

Figure 4: *Proposed simplified reaction network (left) and comparison between the time-dependent model fit (lines) of oligomers, liquid products and gas and their experimental values (symbols), 1.67 wt.% NaOH, 5 wt.% kraft lignin, reactor volume 1 L (right).*

Since an evaluation of the BCD process showed that sodium hydroxide has a noticeable impact on its economic balance and causes a significant carbon dioxide footprint [6], an additional aim of AP3 was to minimize the amount of sodium hydroxide. Several experiments have been shown that the NaOH concentration can be reduced to 1.25 wt.% with 5 wt.% lignin without the occurrence of technical problems like pipe- blocking in the pilot plant. Comparable experiments have been shown feasible with 10 wt.% lignin (Organosolv and Kraft) and 2.5 wt.% NaOH.

Analytical characterization of the phenolic compounds in AP4 compromises the quantification of main phenolic compounds and by-products. Besides identification of the major phenolic monomeric products phenol, guaiacol, catechol, vanillin and syringol, the HPLC analysis of further alkylphenols (e. g. ethylguaiacol) and vanillin derivatives (e. g. acetovanillone) was carried out.

2. Prospects for further external funding

The prospects for further external funding are very good. Follow-up project have already been drawn up and submitted. Close cooperation with industrial partners from pulp and paper industry as well manufacturing industry and application engineering is aimed at achieving industrial implementation of the process in medium term (5-10 years).

Index

Publications

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