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Valorisation of lignin – Achievements of the LignoValue project

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Abstract
Lignocellulosic biorefinery for production of biofuels, materials and chemicals requires valorization of all fractions including lignin. As a consequence of its poly-aromatic structure, lignin potentially serves as a source for aromatic chemicals. The developed biorefinery concept of the LignoValue project comprises two major steps:
(1) Organosolv fractionation of wheat straw and willow into (hemi)cellulose and high purity lignin.
(2) Further conversion of the isolated lignin via catalytic pyrolysis, supercritical depolymerization and partial hydrodeoxygenation (HDO) into different components like low molecular phenolic compounds, wood adhesives and fuel additives.
The cellulose fraction resulting after organosolv fractionation is effectively hydrolysed by enzymes for biofuel production. Quality assessment of the liberated lignins shows interesting characteristics for follow-up chemistry such as high purity, relatively low molar mass and polydispersity.
Catalytic pyrolysis in a fluidised bed at 400-500°C was found to convert organosolv lignin in 35-55% phenolic oil, 10% identified monomeric phenolic compounds, 10-20% water, 5-20% gas and 35-55% char. Supercritical depolymerisation of lignin in carbon dioxide based solvents resulted in a similar spectrum of products, however, at a lower temperature (ca 300°C) but at higher pressures. In both thermochemical processes the use of promotors or catalysts lead to an improved yield of the target monomeric aromatic products. Also the residual char fraction shows interesting properties for use in bio-char applications. Catalytic semi-continuous HDO of lignin in hydrogen atmosphere can be manipulated to yield both light oils or heavy oils as potential additives to fuels. Suitable catalysts were found to convert depolymerised lignin to phenolic oils in high yields. In this process no char formation is observed. The lignin oils were successfully tested on lab scale as partial substitution of phenol in resins for gluing wood panels.
The LignoValue concept is critically reviewed in a techno-economic analysis demonstrating the potential for further commercial development and adoptation of this innovative biorefinery process in Europe.

Introduction
Valorisation of lignin plays a key role in the further development of cost effective biorefinery processes for biofuels and the production of biobased materials and chemicals from lignocellulosic biomass. Today's increased demand for alternatives to fossil carbon based products, such as the production of transportation biofuels and bulk "green" chemicals, expands the interest and the need to added value to the unconverted lignin fraction. As a consequence of its poly-aromatic structure and large availability, lignin is the obvious candidate to serve as a future source for aromatic chemicals.

Lignin is found in trees and other lignocellulosic plant-based materials representing 15-25% of its weight and about 40% of the biomass energy content.
In biorefinery processes, lignin will be produced in large quantities, additionally to lignin production in the paper and pulp industry, and can serve as a future aromatic resource for the production of green chemicals [1].
Pre-treatment is a crucial step in the biochemical production of second generation biofuels since it is required to increase the accessibility of the cellulose polymers for subsequent enzymatic hydrolysis. Most pre-treatment technologies are optimized for sugar production only and produce a residue that is only suited for heat and power generation. However, to improve cost-effectiveness optimum valorization of all biomass fractions is required. Therefore, an organosolv fractionation technology based on ethanol-water was chosen with the aim to achieve full fractionation of all main constituents of lignocellulosic biomass including lignin, in a sufficient quality for further conversion into marketable products. Lignin conversion was studied via catalytic pyrolysis, supercritical depolymerization and partial hydrodeoxygenation (HDO) into different components like phenolic oils, low molecular phenolic compounds, wood adhesives and fuel additives [2].
For this study two model feedstocks were chosen, eg. willow and wheat straw which are common crops in The Netherlands. For the lignin conversion process development was mainly carried out using an organosolv lignin from mixed hardwoods (Alcell^{tm}) to get a good comparison with earlier work. Then the developed conversion processes were applied to wheat straw and willow organosolv lignin. Finally, the whole biorefinery concept studied in LignoValue including organosolv fractionation and pyrolysis was reviewed by comparing different scenario's with a techno-economic analysis.

Experimental

Organosolv fractionation

Willow and wheat straw were cut into pieces <2 cm and fractionated in 1L or 20L pressurized reactors with ethanol-water mixtures at 170°C - 200°C during 60 min at temperature [3,4]. The enzymatic digestibility of fresh and pretreated lignocellulose was measured with enzyme Accellerase 1500 (Genencore, Rochester, NY) at 50 °C at 35 FPU/gr dry substrate and incubation for 72 h. The enzymatic glucose yield was calculated on the basis of the mean glucose concentration in the hydrolysate as determined by HPAEC-PAD after 72 h and the glucan content of the substrate [3].

Lignin recovery and analysis

Lignin was precipitated from the organosolv liquor and the washing solution upon dilution with refrigerated water (water:solution 3:1 w/w). After sedimentation of the particles by centrifugation, the supernatant was decanted and the lignin was dried and weighted. Main lignin characteristics were determined as described previously [5].

Lignin conversion

1. Pyrolysis on lignin was conducted at 400 - 500°C in an 1 kg/h bubbling fluidized bed reactor with a cooled screw-feeder and integrated product recovery [6]. To support the process development analytical Py-GC/MS was carried out at 400 - 800°C [7].
2. Lignin was converted in a mixture of carbon dioxide/acetone/water under supercritical conditions (SCC) in a 100 ml PARR reactor at 300°C, 100 bar. Products were captured after pressure release in acetone for further analyses [8].

3. Lignin was converted by hydrodeoxygenation (HDO) in a 100 ml reactor at 350 – 400°C, 100 bar hydrogen pressure in the presence of a heterogeneous catalyst, e.g. Ru/C, with the formation of water and low molecular weight phenolics. Products were characterized as described earlier [6].

Lignin oil as wood adhesive
The lignin oil was obtained from a catalytic hydrotreatment of pyrolytic lignin, precipitated from a fast pyrolysis oil. Wood adhesive formulations with 50 and 75 wt% lignin oil were compared with a standard resin made with phenol-formaldehyde only. Wood veneers were glued with 150 g/m^2 resin with a contact interface of 25x25 mm. The specimens were hot pressed at 200°C under 3 MPa pressure for 5 min and tested according to European standard EN-314.

Techno-economical and socio-economical analysis of biorefinery concept
The different steps in the biorefinery concept were evaluated by a techno-economical assessment. At present, the lignin pyrolysis step was the most advanced technology and for this step 4 case scenario's were selected (Figure 7). A conceptual design based on a Pyrolysis Plant of 1000 ton/day of dry lignin includes mass and heat balances based on literature (petrochemical analogs) and lab-scale results was used.
To evaluate the economic potential the following assumptions were made:
Current cost level of a biorefinery lignin was set on ~350 €/ton.
Pyrolysis reactor was modelled as an 'average' state-of-the-art petrochemical fluid catalytic cracking (FCC) unit including primary downstream treatment (bio-oil and bio-char collection, dewatering). Downstream product upgrading equipment was modelled according to petrochemical analogs.
Socio-economic evaluation of this innovative biorefinery concept including lignin valorization was performed to identify the potential "set-up and location" for the whole process chain and identify chances and bottlenecks.

Results and discussion

Organosolv fractionation
Willow and wheat straw can be effectively separated by organosolv fractionation in ethanol-water mixtures in its major compounds. Temperature and catalysts have a clear effect on this fractionation. The temperature should not exceed 200°C as cellulose hydrolysis starts (Figure 1).
For willow and wheat straw maximum enzymatic cellulose hydrolysis was obtained with 0.02M HCl at the reaction conditions studied: liquid:solid : 9.6 kg/kg dry biomass, ethanol:water : 55-45% w/w, pretreatment severity: log R = 4.65. The obtained enzymatic glucose yield based the glucan content of the feedstock was 86 and 99% for willow wood and wheat straw, respectively (Figure 2).. These conditions lead to 73 and 83% hemicellulose hydrolysis, 51 and 68% delignification for these feedstocks. For acidic catalysts it was found that their effect was directly correlated to the pH, independently of the type of acid used.

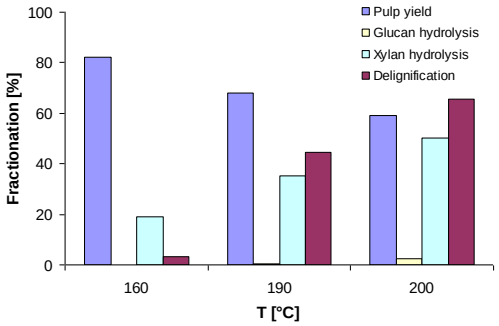

***Figure 1**. Effect of temperature on the organosolv fractionation of willow, EtOH:H_2O 60:40 wt%, 60 min*

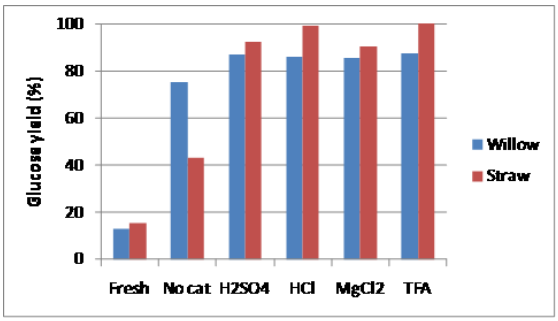

***Figure 2**. Effect of catalyst type on enzymatic digestibility of organosolv treated willow and wheat straw*

Organosolv lignin characteristics

From the organosolv black liquors lignin can be easily recovered with up to 70% yield from the original lignin in biomass. Organosolv lignins are relatively pure, >90 wt%, up to 96% for wheat straw lignin. Main impurity is oligomeric xylan. These lignins are sulphur- and ash-free and have a relatively low Mw 2000-3500 and narrow distribution.

Lignin conversion

Lignin pyrolysis

Py-GC/MS showed that a maximum yield of phenolic compounds was obtained at 600°C of 17.2% for Alcell lignin and 15.5% for soda non-wood lignin (Granit). Most of the phenolic compounds had an individual yield of less than 1%; however, for Alcell lignin, 5-hydroxyvanillin had a yield of 4.29 wt %, and for soda lignin, 2-methoxy-4-vinylphenol had a yield of 4.15 wt % on dry ash-free lignin [7].
Bubbling fluidized bed pyrolysis at 500°C resulted in good mass balances for 3 lignins studied with the highest oil yield of 55% for ECN wheat straw lignin (Figure 3). Pyrolysis oils contain a substantial amount of oligomeric lignin fragments. Granit soda lignin from grass/straw pyrolysis resulted in the highest monomers yield. Main aromatic compounds obtained from wheat straw lignin (ECN) and non-wood lignin (Granit) are guaiacols, for hardwood lignin (Alcell) mainly syringols. The pyrolysis results reflect the compositional differences between the lignins.

Lignin conversion under supercritical conditions (SCC)

Organosolv hardwood (Alcell) and wheat straw lignin (ECN) were converted to a total yield of identified aromatic compounds of 10% based on dry lignin together with 40-50% char, 10% gases and 30-45% phenolic oil with oligomers and monomers (Figure 4). Formic acid act as a hydrogen donor and increases the yield of aromatics. During this process a strong competition occurs between depolymerisation of lignin and recondensation of fragments. This leads to a residual lignin char fraction consisting of a substantially reduced oxygen content, improved thermal stability and a high content of carbon.

	ECN	GRANIT	ALCELL
Gas	15.1	15.2	20.7
Oil	54.7	47.6	38.9
Char	35.6	39.0	43.0
Balance	105.3	101.8	102.6
Water	23.9	17.1	14.5
Light ends	1.8	1.4	1.9
Guaiacols 	2.0	3.0	1.5
Syringols 	1.1	1.6	2.6
Alkylphenols 	0.6	1.1	0.3
Total catechols 	0.6	1.2	0.5
Monomers	7.8	11.2	8.5
Oligomers	21.4	18.0	14.0
Phenolics	29.2	29.2	22.5

***Figure 3**. Products from lignin pyrolysis, 500°C, fluidised bed*

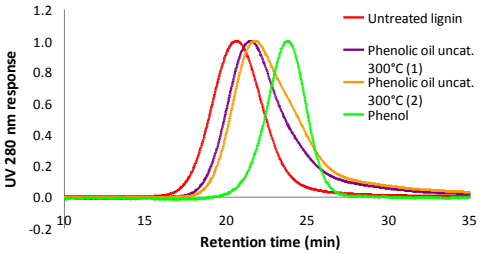

***Figure 4**. Effect of SSC treatment on molar mass of phenolic oil derived from lignin*

Hydrodeoxygenation (HDO) of lignin

Figure 5 showed that hardwood lignin (Alcell) was converted to a lignin HDO oil yield of about 70 % depending on the choice of catalyst. The highest alkylphenolic amount was achieved by using Ru/C. Under these conditions negligible char formation occurs. Lower molecular weight fractions of lignin lead to products with a higher H/C ratio and higher amounts of hydrocarbons.

Lignin oil as wood adhesive

Figure 6 showed that up to 75 wt% replacement of phenol in a PF-resin can be achieved with lignin oil to get sufficient glue strength of a plywood.

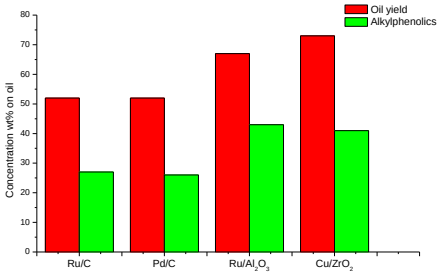

***Figure 5**. Effect of catalyst type on HDO of lignin to oil yield and alkylphenolics*

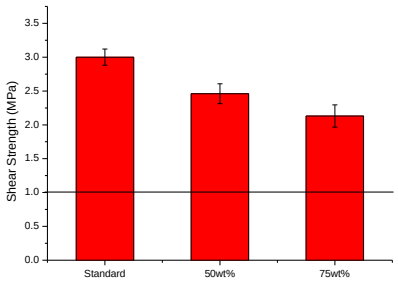

***Figure 6**. Strength of wood adhesive partially substituted by lignin oil*

Techno-economical and socio-economical analysis of biorefinery concept

Case 1. Lignin for fuel application was considered as not viable. Case 4 with the potentially highest value per ton lignin was considered as a long term option as downstream processing will be the determining factor and no sufficient lab-data is available (Figure 7).

Cases 2 and 3 showed realistic options and give directions to future biorefineries including lignin valorisation. These 2 cases will be further evaluated in the whole biorefinery concept (Figure 7).

Socio-economic analysis showed that Europe is well placed for a biorefinery with integrated lignin valorization. Ports in Europe, e.g. Rotterdam, are favorite locations as import of biomass and existing links with the chemical industry can be well integrated. For 100 PJ savings on fossil resources about 6 millions tonnes of lignin must be

valorized which need import of lignin containing rest streams. Use of the phenolic oil derived from lignin for resins or materials resulted in the highest impact.

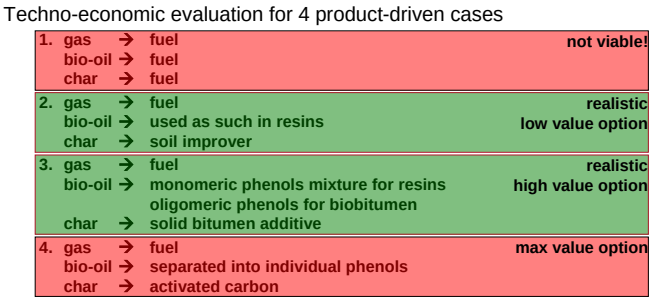

***Figure 7**. Scenarios for lignin pyrolysis products valorization*

Conclusions

Organosolv fractionation of willow and wheat straw in ethanol-water is effective.
The cellulose in pretreated biomass can almost completely be hydrolysed to glucose.
High purity organosolv lignin can be easily recovered up to 70%.
Catalytic pyrolysis and supercritical conversion of organosolv lignin lead to 40-55% phenolic oil, 40-50% char, and 10-20% gases. The phenolic oil consists of 10-20% monomers. Catalysts improve the overall conversion of lignin to monomeric phenolics.
Catalytic hydrodeoxygenation of lignin resulted in high oil yields (70%) with substantial amounts of alkylphenolics and hardly any char formation.
Lignin oil show high potential for use as replacement of phenol in PF-wood resins.
The first results of the techno-economic analysis of lignin pyrolysis show that using the phenolic oil for wood adhesives (resins) and bitumen together with the gases for fuel might give realistic scenarios for lignin valorization in a future biorefinery. This biorefinery can be implemented near a port in Europe to benefit from biomass import and chemical industry integrations.

Acknowledgements

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