KRAFT LIGNIN DEPOLYMERIZATION IN NEAR-CRITICAL WATER: EFFECT OF CHANGING CO-SOLVENT

TALLAL BELKHEIRI, LENNART VAMLING, THI DIEU HUYEN NGUYEN,[*]
MARCO MASCHIETTI,[*,****] LARS OLAUSSON,[**] SVEN-INGVAR ANDERSSON,[*]
LARS-ERIK ÅMAND and HANS THELIANDER[*]

*Chalmers University of Technology, Department of Energy and Environment,
SE-412 96 Gothenburg, Sweden*
[*]*Chalmers University of Technology, Department of Chemical and Biological Engineering,
SE-412 96 Gothenburg, Sweden*
[**]*Valmet Power AB, Box 8734, SE-402 75 Gothenburg, Sweden*
[***]*Aalborg University Esbjerg, Department of Biotechnology, Chemistry and Environmental Engineering Niels
Bohrs Vej 8, 6700 Esbjerg, Denmark*
✉ *Corresponding author: Tallal Belkheiri, Tallal.Belkheiri@chalmers.se*

As part of developing a process to valorize lignin in a pulp mill with lignin separation, the depolymerisation of lignin to valuable chemicals was investigated in near-critical water. This was done by using methanol as co-solvent and hydrogen donor, phenol to suppress repolymerization (e.g. formation of char), and ZrO_2 as a heterogeneous catalyst, with potassium carbonate as a co-catalyst. The reaction was carried out in a continuous flow fixed-bed reactor (500 cm^3), at 280-350 °C and 25MPa. An important aspect is to suppress char formation. Therefore, the char formation was studied by using different concentrations of methanol and phenol. The char yield varied between 14% and 26%. When using methanol as the only co-solvent, the char yield decreased with increasing methanol concentration. Adding phenol resulted in a further decrease. The reactor outlet consisted mainly of two liquid phases, an aqueous and an oil phase, mixed together. The chemical analysis of the aqueous phase showed the presence of mainly phenolic compounds, for instance guaiacol, catechol, phenol and cresol.

Keywords: LignoBoost, lignin conversion, hydrogen donors, char formation, phenolic compound, near-critical water

INTRODUCTION

To date, the pulping industries have been focused on manufacturing fibers and thereby mainly using the cellulose in the wood, while lignin has been mainly utilized as internal fuel. Accordingly, 55 million tons of lignin are produced per year as a secondary product in the pulping process.[1] Nevertheless, it contributes with 40% of the energy content of lignocellulose biomass.[1] It is separated in the pulping process from the other lignocellulosic constituents by means of physical and chemical processes, and these extraction procedures influence the structure, purity and properties of lignin.[2]

In the Kraft process, lignin is recovered in the "black liquor", which has been used as fuel to meet the steam and power needs of the pulping processes. Until now, many chemical conversion routes have been investigated with the purpose of increasing the value of lignin.

One such new method for the valorization of Kraft lignin is the LignoBoost process,[3] which has recently been commercialized. The LignoBoost process extracts high quality lignin from the black liquor, which gives new possibilities for expanding the pulp mill capacity at lower cost, and the potential for internal or external use of the lignin depending on the energy balance of the mill.

Several studies have shown that lignin is a promising source for further conversion to liquid fuel and phenolic compounds.[4,5] Therefore, many thermal, chemical and thermochemical processes for converting lignin into valuable chemicals have been investigated. For instance, Pińkowska *et al.*,[6] and Yong *et al.*[7] have shown lignin depolymerization in sub- and supercritical water for a range of temperatures from 473K to 663K. In these studies, water was considered as a reaction

medium. Moreover, water has many applications as a medium for chemical synthesis, waste destruction and biomass processing.[8] Supercritical water is an attractive fluid from a thermodynamic perspective due to the properties that it has, compared to other fluids, in supercritical conditions. For instance supercritical water has a lower dielectric constant, weaker hydrogen bonds, and high isothermal compressibility.[8] Thus, it is a suitable medium for biomass degradation reactions.

Supercritical water has, however, a drawback, i.e. that salts have a very low solubility. Therefore, near supercritical water is to be preferred in cases when inorganic salts are present: many inorganic salts have a reasonably good solubility and the water has properties that approach those of supercritical water.

The mechanisms associated with different homogenous[9,10,11] and heterogeneous catalysts[12, 13] for biomass conversion processes have been investigated. These studies have shown a char reduction and high phenolic compounds yields when suitable operation conditions are used. Different hydrogen donor solvents have also been investigated for the conversion of lignin, such as methanol, which has shown a high activity as a hydrogen donor.[14]

An earlier study[13] has shown that depolymerization reactions are promoted in the presence of homogeneous (K_2CO_3) and heterogeneous (Zirconia) catalysts. Phenol has the role of a capping agent to suppress char.[15] The objective of this study has been to examine the effect of methanol and phenol together with K_2CO_3 and Zirconia on the conversion of Kraft lignin into bio-fuel and small aromatic compounds in near critical water.

EXPERIMENTAL
Materials
Softwood lignin, extracted with the LignoBoost process in Bäckhammar, was used in all experiments. All the chemicals were used without further purification.

The heterogeneous catalyst used in the reactor was made of zirconia (ZrO_2) pellets from two suppliers: I) Harshaw Chemie BV, length: 3 mm, diameter: 3 mm, BET surface area 48 m^2/g and II) Saint-Gobain NorPro, length: 3 mm, diameter: 3 mm, BET surface area 55 m^2/g. Potassium carbonate (K_2CO_3, ≥99.5%), used as the homogeneous co-catalyst, methanol (≥98.5%) and phenol (crystallized, ≥99.5%), used as co-solvent, were all from Scharlau.

Apparatus and procedure
The experiments were performed in a continuous pilot plant (see Figure 1).

The system was composed of a fixed bed reactor (500 cm^3 Parr 4575), made of Inconel 600 and equipped with an electrical heating jacket; two high-pressure diaphragm pumps were installed, one used as a feed pump and the second as recirculation pump in order to rapidly heat up the fresh feed. The heating system was constituted of an electrical heating jacket around the piping, the feed tank and the reactor.

A run was carried out in the following steps.

First a lignin slurry was prepared, which was constituted of a mixture of lignin, K_2CO_3, methanol and deionized water. The mixture was dispersed by using an Ultra Turrax disperser for approximately 10 min at room temperature. Then phenol was added to the slurry in the experiments where it was used (A, D and E).

The system was heated up and pressurized to operating conditions (see Table 1) by using a continuous flow of deionized water. Then, the lignin slurry was continuously pumped by a high-pressure diaphragm pump at a flow rate of 1 kg/h. The mixture flowed through the catalyst bed for a residence time of approximately 11 min. The free volume of the reactor charged with the catalyst was 294 cm^3. The major part of the outlet was recirculated using a pump at a flow rate of approximately 10 kg/h.

The liquid products were continuously collected in sampling bottles every 40 min for analysis. Gas samples were collected in a gas bag (Tedlar sample bag, SKC) for a qualitative analysis.

After approximately 90 min from the start of the operation, the operating parameters became stable. The total run period was about 320 min with more than 180 min under steady state conditions. The shutdown operation began with cooling down to meet the conditions required for depressurizing. Then, the reactor was disassembled and the catalyst was recovered to measure the char deposited.

The collected samples of liquid products were separated by means of centrifugation.[13] The centrifugation resulted in an aqueous phase with a yellowish colour, and an oily phase with a black colour and high viscosity. However, in some experiments there was a water phase with solid particles instead of an oily phase.

Experimental conditions
In order to evaluate the effect of changing the ratio of methanol/water, it was varied from 0 to 3 by volume, in the presence of phenol, and for two ratios in the runs without phenol. The operating conditions for all runs are reported in Table 1. The reactor temperature and pressure were selected taking into account the near critical conditions for each ratio of water-methanol, with the critical point estimated using the "RefProp" program.[16] The K_2CO_3 amount in the

feed and the lignin amount were kept constant (wet lignin 170 g, K_2CO_3 34 g) for all runs.

Analytical methods
Characterization methods

Characterization methods as well as analytical apparatus have been previously reported in details by the authors.[13]

Regarding the analysis of the molecular weight distribution of the oily phase in Experiments D and E, a Gel permeation chromatography (GPC) was run with three series coupled columns Styragel HR2 (500-20 kDa), HR1 (0.1-5 kDa) and HR0,5 (0-1 kDa) with THF as eluent, calibration was made with polystyrene standard curve 480-19600 Da, and a UV-absorbance detector was used for detection at wavelength 280 nm. The samples (15-190 mg) were dissolved in 50:50 THF:DMSO, which was further diluted to 1 mg/mL with THF and analyzed with GPC/UV. The GPC

analysis was carried out by SP Technical Research Institute of Sweden.

Quantitation of char on solid catalyst

During the operation, char was formed due to the repolymerization of unconverted lignin and reactive light fraction. In order to quantify the char deposited on the catalyst, a regeneration procedure was carried out. The catalyst particles were recovered at the end of the cleaning procedure, and a portion of the catalyst was sampled. This sample was dried in an oven at 105 °C for about 24 h. After this, the sample was weighed. The catalyst sample was regenerated at 500 °C for 12 h to remove char. Afterwards the sample was cooled then weighed again. Thus by knowing the total mass of dry catalyst before the experiment in the reactor, the yield of char on a dry lignin basis could be calculated for each experiment.
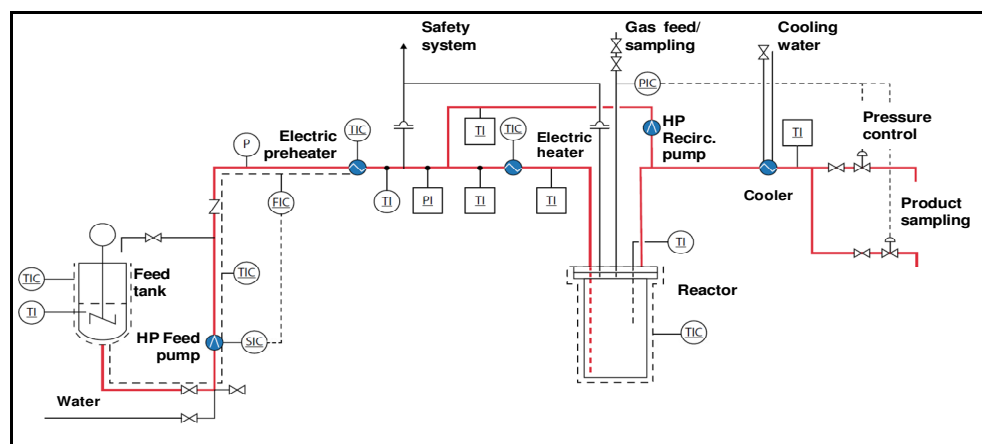

Figure 1: Pilot plant

Table 1
Operation conditions

	A	B	C	D	E
Temperature (K)	623	623	583	583	553
Pressure (MPa)	25	25	25	25	20
Methanol/Water*	0	0.064**	1	1	3
Methanol (%w/w)	0	4.1%	41%	39%	61%
Phenol (%w/w)	4.1%	0	0	3.9%	4.7%
K_2CO_3 (%w/w)	1.6%	1.6%	1.6%	1.6%	1.9%
Dry lignin (%w/w)	5.5%	5.5%	5.5%	5.3%	6.5%
Catalyst supplier	I	I	I	I	II

*Ratio by volume
**It is equivalent to 86 g of methanol. This is the same amount of phenol as used in previous tests

RESULTS AND DISCUSSION
Properties of the used LignoBoost Kraft lignin

The properties of the lignin used are given in Table 2.

Char formation

The effect of methanol and phenol on lignin conversion was investigated for different ratios of

methanol/water with (and without) phenol and the results are shown in Figure 2.

Table 2
Properties of LignoBoost Kraft lignin[13]

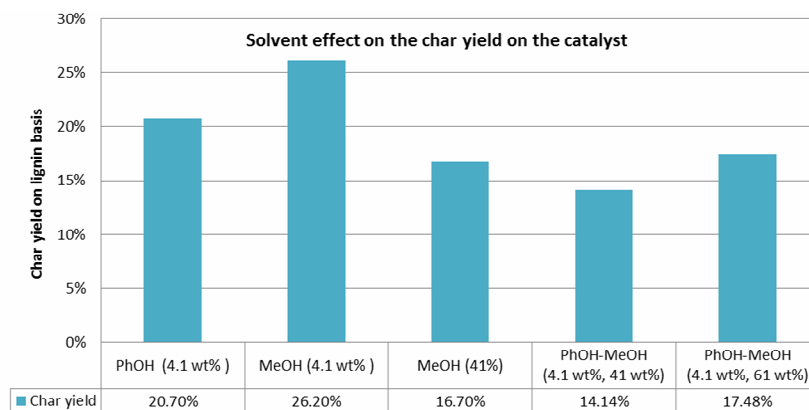| Lignin properties	Moisture (wt%)	Aromatics (wt%)	Aliphatics (wt%)	Molecular weight (g/mol)
	32.6	78	22	3900

Figure 2: Char yields for different methanol and phenol concentrations

Table 3
Mass fractions (%) of the main compound classes in the aqueous phase analysed by GCMS

Class	A	D	E
Phenol	1.96	1.96	3.14
Anisoles	0.001	0.19	0.21
Cresol	0.17	0.3	0.06
Guaiacols	0.05	0.19	0.26
Catechols	0.19	0.02	-
Dimers	0.006	0.4	0.52

By increasing the methanol to water ratio from 0.064 to 1 (by volume) without using phenol, the char yield on the solid catalyst decreased from 26.2% to 16.7%. By adding phenol and increasing the methanol/water ratio from 0 to 1, this char yield decreased further to 14.1%. However, by keeping the same phenol/lignin ratio and increasing the methanol/water ratio to 3, the char yield increased to 17.5%. In contrast, using methanol as a solvent created more clogging problems and variation in pressure during the experiments. An improvement during the experiments was observed when phenol was added, which prevented char formation. Thus, the phenol-methanol mixture showed a lower char yield on the solid catalyst and more stable operating conditions. It was observed that using

methanol led to the formation of a small amount of solid particles, it might be an oily phase with very high molecular weight (soluble in THF). Accordingly, less oil in the liquid phase was recovered or no oil phase was observed in Experiments B and C.

Chemical analysis

The aqueous phase also contained a considerable amount of methanol in Experiments D and E, but no accurate analysis was made of the methanol content.

Table 3 shows that an increase in the methanol concentration increased the amount of guaiacol and anisole to 0.26% and 0.21%, respectively. Furthermore, the phenol concentration increased to 3.14% in Experiment E, which had the highest

amount of methanol (61%) in the feed slurry. For the same amount of methanol (61%), the dimers fraction in the aqueous phase increased to 0.52%.

The largest amount of cresol (0.3%) was observed in Experiment D.

Table 4
Yields of oil, water soluble organics and char

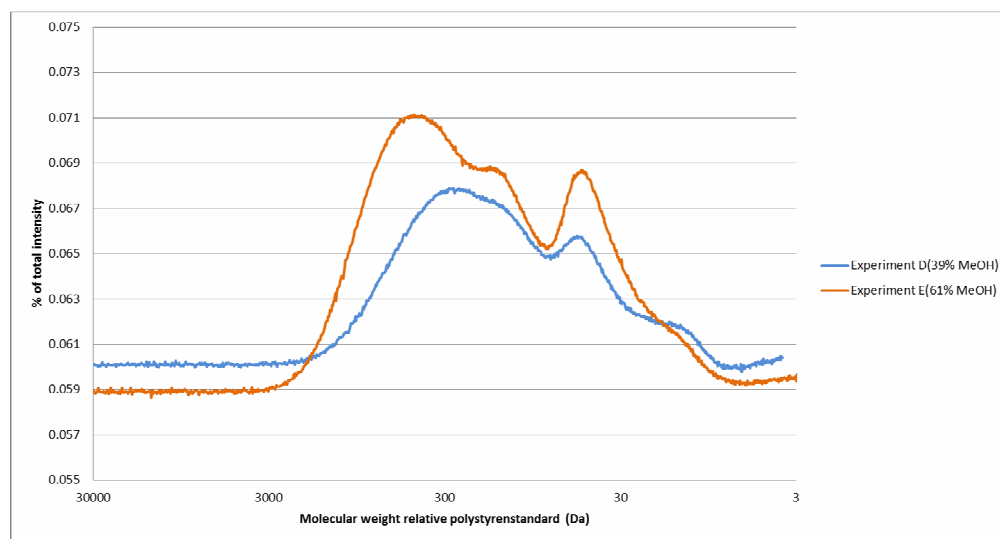|	A	D	E
$Y_{OIL \%}$	72.2	38.8	17.8
$Y_{WSO \%}$	9.7	24.0	17.8
$Y_{CHAR \%}$	20.7	14.1	17.5

Figure 3: Molecular weight distribution of the oily phase for different methanol concentration, according to GPC analysis

A qualitative analysis of the aqueous phase for Experiments B and C was carried out to identify the composition. The results showed the same class of compounds as in tests A, D and E (phenols, anisoles, cresols, guaiacols and other monomers and dimers).

The overall yield balance, Table 4, gave an acceptable discrepancy of ±2.6% for Experiment A, which is an accurate balance taking into account errors related to characterization methods and losses in the process. However, Experiments D and E have high errors (more than ±20%), which probably are mainly due to the oily phase nature in those tests, which was partly in solid form. Consequently, it was concluded that more oil in the solid phase was accumulated in the reactor system. It should also be noted that the catalyst used in Experiment E has another supplier than the other experiments. Tests have been carried out under equal conditions for the two catalysts and so far no indication of

differences has been observed. The highest oil yield was observed for non-methanol experiments. In addition the oil and water soluble organics yield were calculated on a phenol free-product basis.

A GPC analysis (see Figure 3) shows that the oily phase of Experiment E (61% methanol) has a higher average molecular weight than that of Experiment D (39% methanol). Since the average molecular weight of the lignin used is about 3900 Da (which corresponds to about 40 phenolic units), it can be concluded from the results in Figure 3 that all large lignin molecules have been depolymerized. Furthermore, the results presented in this Figure show that the major part of the molecules in Experiment D have a size corresponding to 1 to 5 phenolic units and the corresponding numbers for Experiment E are 1 to 10 units.

CONCLUSION

Lignin depolymerisation in this study showed an optimum point for char suppression, when both methanol and phenol were used. Nevertheless, the highest oil yield (72.2%) was obtained in a non-methanol test. Water soluble organics, such as monomers and dimers, represented about 24% in terms of the highest yield in the experiment with the methanol-phenol mixture. It was concluded that methanol as co-solvent improved char suppression moderately. However, it had a negative effect on oil yield when used in a high amount. On the other hand, phenol improved the oil yield.

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