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

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**ABSTRACT:**

As part of a project aimed at developing a process to valorize lignin in a pulp mill with lignin separation, the depolymerisation of lignin to valuable chemicals with a lower molecular weight was investigated in near-critical water. This was done by using methanol as co-solvent and hydrogen donor, phenol to suppress repolymerization, and ZrO2 as a heterogeneous catalyst. The reaction was carried out in a continuous flow pilot plant, with 1kg/h of the feed flow in a fixed-bed reactor (500 cm3), at 280-350 ⁰C and 25 MPa. An internal recirculation of the reaction mixture was set at approximately a rate of 10 kg/h.

Kraft lignin from a LignoBoost process was used as the feed material. It was dissolved in a solution containing water, methanol and phenol with potassium carbonate as a co-catalyst.

An important aspect of the development of this process is to suppress char formation, as it results in lower product value, catalyst deactivation and operability difficulties. 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 to the mixture water-methanol additionally improved further the char suppression.

The reactor outlet consisted mainly of two liquid phases, an aqueous and an oil phase together with minor amounts of gas. It was found that the amount of the oil phase increased with the amount of phenol. The chemical analysis of the aqueous phase was carried out with GC-MS, and showed the presence of mainly phenolic compounds, for instance guaiacol, catechol, phenol, cresol and some alkyl derivatives. Furthermore, it was observed that varying the concentration of methanol influenced the monomeric compounds distribution.

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

# INTRODUCTION

To date, the pulping industry has been focused on fiber manufacturing that mainly uses cellulose, while lignin has been mainly used as internal fuel. Accordingly, 55 million tons of lignin are produced in pulping process as a secondary product [[1](#_ENREF_1)]. Even though, it contributes with 40 % of the energy content of lignocellulose biomass [[1](#_ENREF_1)]. It is separated in the pulping process from the other lignocellulosic parts by means of physical and chemical process, and these extractions procedures influence structure, purity and properties of the lignin [[2](#_ENREF_2)].

Lignin is recovered in the Kraft process in the form of “black liquor” which has been used as fuel to generate the steam and power needs of the pulping processes. 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](#_ENREF_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 can be a promising source for further conversion to liquid fuel and phenolic compounds [[4](#_ENREF_4)] [[5](#_ENREF_5)]. Therefore, many thermal, chemical and thermochemical processes for converting lignin into valuable chemicals have been investigated. For instance, [Pińkowska](http://www.sciencedirect.com/science/article/pii/S1385894712001155) et al [[6](#_ENREF_6)], and  [Yong](http://pubs.acs.org/action/doSearch?action=search&author=Yong%2C+T+L&qsSearchArea=author) et al [[7](#_ENREF_7)] have shown lignin depolymerization in sub and supercritical water for a range of temperature from 473K to 663K. In these studies water was considered both as a medium and as a catalyst. Moreover, water has many applications as a medium for chemical synthesis, waste destruction and biomass processing [[8](#_ENREF_8)]. Super critical water is an attractive fluid from a thermodynamic perspective because of the properties that it exhibits, compared to other fluids, in supercritical conditions. For instance water has a lower dielectric constant, weaker hydrogen bonds, and high isothermal compressibility [[8](#_ENREF_8)]. Thus, it is a suitable medium for biomass degradation reactions.

The function of different homogenous [[9](#_ENREF_9)] [[10](#_ENREF_10)] [[11](#_ENREF_11)] and heterogeneous catalysts [[12](#_ENREF_12), [13](#_ENREF_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](#_ENREF_14)].

An earlier study, [[13](#_ENREF_13)], has shown that depolymerization reactions are promoted in the presence of homogeneous (K2CO3) and heterogeneous catalyst (Zirconia). Phenol has a role of capping agent to suppress char [[15](#_ENREF_15)]. The purpose of this study is to examine the effect of methanol and phenol together with K2CO3 and Zirconia on the conversion of Kraft lignin into a bio-fuels and aromatics ring.

# MATERIALS AND METHODS

## 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 (ZrO2) pellets from two suppliers: I) Harshaw Chemie BV, length: 3 mm, diameter: 3 mm, BET surface area 48 m2/g and II) Saint-Gobain NorPro, length: 3 mm, diameter: 3 mm, BET surface area 55 m2/g. The potassium carbonate (K2CO3, ≥ 99.5 %), used as the homogeneous co-catalyst, and the methanol (≥ 98. 5 %) and phenol (crystallized, ≥ 99.5 %), used as co-solvent were from Scharlau.

## Apparatus and procedure:

The experiments were performed in continuous pilot plant (See Fig. 1).

The system was composed of a fixed bed reactor 500 cm3 Parr 4575, made of Inconel 600 and equipped with an electrical heating jacket; two high-pressure diaphragm pumps, one 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.



**Figure 1**: Pilot plant

A run was carried out in the following steps:

First lignin slurry was prepared: It was constituted of a mixture of lignin, K2CO3, 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.

The system is heated up and pressurized to operating conditions (See table1) 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 flows through the catalyst bed for a residence time of approximately 11 min. The free volume of the reactor charged with the catalyst was 294 cm3. Part of the outlet was recirculated using a pump at a 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 90min from the start of the operation, the operating parameters had become stable. The total run period was about 320 min with more than 180min of the steady state period. The shutdown operation began with cooling down to meet conditions required for depressurizing. Then, the reactor was disassembled and the catalyst was recovered to measure the char deposited.

The collected samples during the operation were separated by means of centrifugation [[13](#_ENREF_13)]. Two phases were resulted from the centrifugation, an aqueous phase with a yellowish colour, and an oily phase with a black colour and high viscosity. Whereas, in some experiment there was water phase and a solid particle phase 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 with phenol present and for two ratios without phenol. The operation conditions for all runs are reported in Table 1. The reactor temperature and pressure were defined regarding the near critical conditions for each ratio of water-methanol, and the critical point was estimated using the “RefProp” program [[16](#_ENREF_16)]. The K2CO3 amount in the feed and the lignin amount were kept constant (wet lignin 170g, K2CO3 34 g) for all runs.

**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% |
| K2CO3 (%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 86g of methanol. This is the same amount of phenol as used in previous tests.

## Analytical methods:

### *Characterization methods:*

Characterization methods as well as analytical apparatus have been previously reported in details by the authors [[13](#_ENREF_13)].

### *Char quantitation:*

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 are recovered at the end of the cleaning procedure, and a portion of the catalyst is taken as a sample. This sample was dried in an oven at 105°C for about 24h. 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 mass fraction of the char determined on a lignin basis could be calculated from each experiment.

# RESULTS AND DISCUSSION

## Properties of the used LignoBoost Kraft lignin:

**Table 2** :The properties of LignoBoost Kraft lignin [[13](#_ENREF_13)]

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

## 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 fig 1.

**Figure 2**: Char yields for different methanol and phenol concentration.

By increasing the methanol to water ratio from 0.064 to 1 (by volume) without using phenol, the char yield decreased from 26.2% to 16.7%. By adding phenol and increasing the methanol/water ratio from 0 to 1, the char yield decrease 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 yields and better operating conditions. It was observed that using methanol lead 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 observed in some of the experiments, such as Experiments B and C.

## Chemical analysis:

**Table 3:** Mass fractions(%) of the main compounds in the aqueous phase

The aqueous phase also had a considerable amount of methanol in Experiments D and E, but the analysis of this substance thus far is not accurate enough to be presented.

|  |  |  |  |
| --- | --- | --- | --- |
| 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 |

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 had 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 the Experiment D.

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).

**Table 4**: Yields of oil, water soluble organics and char

|  |  |  |  |
| --- | --- | --- | --- |
|  | A | D | E |
| ***YOIL* %** | 72.2 | 38.8 | 17.8 |
| ***YWSO* %** | 9.7 | 24.0 | 17.8 |
| ***YCHAR* %** | 20.7 | 14.1 | 17.5 |

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 for Experiments D and E, it represented a high error balance (more than ±20%) due mainly to the oily phase nature in this test, which was in solid form. Consequently, it was concluded that more oil in the solid phase was lost inside the process. 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 have so far no indication of differences, but the analysis is not yet complete. 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.

# CONCLUSIONS

Lignin depolymerisation in this study showed an optimum point for the char suppression, when methanol and phenol were used. Nevertheless, 72.2% of the oil yield produced as the highest oil yield in a non-methanol test. Soluble organics such monomers and dimers represented about 24% as the highest yield in experiment with 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, whereas, phenol improved the oil yield.

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