# CATALYTIC UPGRADING OF A SOLVOLYSIS LIGNIN IN A BATCH REACTOR

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## ABSTRACT

A prototype organosolv lignin was hydrocracked at temperatures in the 370-410°C range in the presence of tetralin, a hydrogen donor solvent. The effects of temperature and time were combined into a single severity parameter which was used to monitor the conversion of lignin to liquid and gaseous products, as well as the distribution of important liquid products. A nickel-tungsten catalyst was used in most of this work. At the highest severity of treatment, conversion of lignin did not exceed 50%. The high yields of either reactor residue (at low severity), or residual lignin (at high severity) suggests that the reaction conditions used were not sufficient to degrade the lignin to liquid and gaseous products. The distribution of liquid monomeric compounds was too wide and their yields were too low to warrant complete identification and quantification by capillary gas chromatography. However, from the relative abundance of representative peaks in the chromatograms of acetylated compounds in the methylene chloride solubles, syringols and guaiacols predominated at low severities of reaction. At high treatment severities, demethoxylated compounds (phenols, catechols and their methyl and ethyl derivatives) were the major liquid products. The addition of nickel-tungsten heterogeneous catalysts with either low (3%) or high (60%) Ni content only marginally improved the yields of monomeric phenolic compounds. However, much higher gas yields were produced when using the 60% Ni catalyst.

**Keywords:** hydrocracking, ALCELL® lignin, tetralin.

## INTRODUCTION

During the last two decades or so, the demand for alternative sources of chemical feedstock is increasing due to an increasing awareness of the depletion of fossil fuel reserves, in addition to increased demand and the dynamic political environment in some of the major oil-exporting countries. Also, the current climate and research emphasis on pollution reduction favours the search for alternative sources of raw materials and energy. A great deal of interest has been shown towards the utilization of woody biomass, a renewable resource. In the pulp and paper industry, lignin is the major by-product and is nearly always used as a low-grade fuel in the pulping processes. Lately, there is an increasing trend to use a portion of the lignin as raw material for higher-value added products[1-3].

Structural models of lignin by a number of workers[4,5] all show it to be a complex, 3-dimensional polymer of phenylpropane units linked together by carbon-carbon and ether bonds. The high content of aromatic units in lignin suggests it might be a source of raw material for the production of useful phenolic compounds. Hydrocracking has been the subject of many investigations and appears to be a promising route for production of useful low molecular weight phenols from lignin. Hydrocracking is commonly practiced in modern petroleum refineries for converting various hydrocarbons of higher boiling ranges into more valuable products. Catalysts for hydrocracking have dual functions, consisting of hydrogenation metal(s) on an acidic cracking base. Commonly used hydrogenation components include cobalt, tungsten, palladium and nickel. The cracking component may consist of amorphous silica-alumina of various compositions. In any hydrocracking process, disposable and inexpensive catalysts are highly desirable.

In lignin hydrocracking, lignin typically depolymerizes into a wide slate of products, which can generally be classified into solids, liquids and gases. Product yields and distribution depends on the severity of the reaction conditions and type of catalyst employed. At hydrocracking conditions, $\beta$-O-4 aryl ether and unstable carbon-carbon bonds in the lignin are cleaved, and subsequent hydrodealkylation leads to rupture of the alkyl side chain groups linked to the aromatic rings. Also, it is customary to utilize solvents in amounts ranging from 1-3 times or more than the lignin. In the former cases, excellent hydrocracking solvents (e.g. phenols) are commonly used. However, these solvents typically react with the lignin, especially at hydrocracking conditions, making subsequent analysis of products rather complicated. In order to alleviate analytical difficulties and other disadvantages, tetralin was used in the present study. The advantages of tetralin as a hydrogen-donor solvent include: its high boiling point as well as its ready release of hydrogen atoms at hydrocracking conditions leading to formation of naphthalene, a relatively stable compound. The use of tetralin in lignin hydrocracking has been investigated by Davoudzadeh et al.[6], Connors et al.[7] and Schultz et al.[8]. However, the use of lignin as a raw material for chemicals continues to be restricted by the nature of current commercial delignification processes which render the lignins so isolated unreactive towards further processing into useful products.

A survey of the literature shows that the majority of studies on the production of chemicals from lignin have primarily focussed on technical lignins derived from the commercial pulping of softwoods. These lignins have a predominantly guaiacyl structure. A need for more investigations into the depolymerization of hardwood lignins (syringyl structure) to low molar mass chemicals is thus warranted for a more complete picture on this subject to be made. Moreover, the "new" lignins from steam treatments and solvolysis processes deserve attention not only because these wood fractionation technologies promise to be strong candidates for future commercial pulping processes, but the characteristics of these lignins so far suggest that they could offer more potential as chemical feedstocks than previously isolated lignins.

The objective of the present work therefore is to investigate the depolymerization patterns of a novel solvolysis lignin "ALCELL® lignin" via catalytic hydrocracking in tetralin. This lignin is produced semi-commercially using a novel ethanol-water based pulping process, the Alcell* process. A second objective is to correlate the yields of products using a severity parameter which embodies the effects of temperature and time of reaction.

## EXPERIMENTAL

### Materials

**Lignin:** ALCELL® lignin was supplied by Alcell Technologies Inc., Newcastle, New Brunswick (CANADA), where it was isolated from a hardwood mixture in a demonstration scale facility[7]. This lignin, available as a free flowing powder of 20-40 $\mu$m median particle size range, is hydrophobic and has a weight average molar mass of less than 2000 g/mol. Other typical characteristics of ALCELL® lignin have been presented elsewhere[9,10].

**Chemicals:** The following reagents used were:

- -1,2,3,4 Tetrahydronaphthalene (tetralin) (Analytical Grade) from Aldrich Chemical Co., Milwaukee, Wis., USA.
- -Acetone (Reagent Grade) from J.T. Baker Inc., Toronto, Ontario, Canada.

- -Diethyl ether (Reagent Grade) from VWR Scientific, Dartmouth, N.S., Canada.
- -Sodium hydroxide (Reagent Grade) from J.T. Baker Inc., Toronto, Ontario, Canada.
- -Hydrochloric acid (Reagent Grade) from J.T. Baker Inc., Toronto, Ontario, Canada.
- -Magnesium sulphate (Reagent Grade) from Caledon Laboratories Ltd., Georgetown, Ontario, Canada.
- -Methylene chloride (Analytical Grade) from BDH Inc., Dartmouth, N.S., Canada.

**- [*] Alcell is a Registered Name Owned by Repap Enterprises Ltd., Montreal, QU., CANADA.**

The monomers used as reference compounds for product identification by gas chromatography were of Analytical Grade and purchased from Aldrich Co. or Alfa Chemicals Co., both located in the USA. The chemicals were used as received.

**Catalysts**: - Nickel-Tungsten (6% Ni-19% W) mounted on silica alumina; 2 mm. dia. by 3 mm. length (Harshaw Catalysts, USA).

- Nickel on silica alumina (60% Ni) powder; surface area = 200 $m^2/g$ (Johnson Matthey, USA).

**Experimental Set-up and Run Procedure**

All experiments were performed in a 500 mL capacity batch autoclave equipped with a magnetic stirrer. A schematic diagram of the reactor is shown in Figure 1. Heat-up is provided by an external high capacity heater in addition to a specially built internal cartridge heater which had to be immersed in the reactant solution to prevent it from burn-out. The reaction is quenched by running cold water through cooling coils inside the reactor. The bomb has a 500 °C and 34.47 MPa rating. Both heat-up and cool-down periods are regulated using a PID (Model No. 4840) temperature controller.

A typical run procedure for the experiments was to load the autoclave with 20 g of lignin, 250 mL solvent, and 1 g of catalyst. After the reactor was sealed, tested for leaks, and pressurized (if necessary) with hydrogen to 10 kg/cm$^2$, the contents were agitated at 300 rpm. Heat-up was initiated by switching the controller on, which was pre-set to the desired reaction temperature. The reaction temperature was attained within 30-50 minutes. Runs were conducted at reaction temperatures of 370, 390, and 410 °C for each reaction time of 15, 30, and 60 minutes. During each run, the reaction temperature, time, and pressure were manually recorded every 3 to 5 minutes.

The reaction was terminated by quenching the autoclave with cold running water inside the coils. The reactor contents reached 100 °C inside 10 minutes; agitation was stopped when this temperature reached 50 °C. To ensure that both the reactor and its contents were sufficiently cold for handling, the reactor was immersed in a cold water bath for one hour before disconnecting the gas and water inlet and outlet piping on the unit.

The total volume of the gases produced was estimated by bubbling it through a flowmeter prior to venting it to the atmosphere outside. The flowrate was kept essentially constant by checking it approximately every minute and adjusting it accordingly. An average reading was calculated.

## Product Separation

After the reaction products were cooled to room temperature and the total gases quantified and vented, the products were separated as depicted in Figure 2. In all the runs, the reactor contents were comprised of a liquid mixture with some insoluble material. After decanting and filtering the tetralin solution, the insoluble matter inside the reactor and on the filter were thoroughly washed with diethyl ether and the wash combined with the tetralin solution. The reactor was finally washed with acetone and the "acetone-solubles" were dried at 80°C overnight. The remaining solid residue plus that on the filter paper less the amount of catalyst added are termed "reactor residue".

Diethyl ether was added to the tetralin mixture such that the total quantity of ether was *ca.* 200 mL. This mixture was then extracted 3 times with 15 wt% NaOH solution. In this manner, all the tetralin and its multifarious products remained in the ether phase and was thus separated from the reaction mixture. These ether solubles were discarded and not analyzed any further in this work. The combined alkali extracts were acidified to pH 1-2 with 20 vol% HCl and filtered. The insoluble precipitate was termed "residual lignin". The filtrate was extracted with methylene chloride (4X) until the solvent added was visibly colorless. A small amount (about 1 g) of $MgSO_4$ was then added to the combined $CH_2Cl_2$ extracts to remove any water remaining. After filtration and evaporation of the methylene chloride using a rotary evaporator, a fraction termed "methylene chloride solubles" was recovered.

HPSEC Procedure: A Waters liquid chromatograph connected to a Waters NEC 80486 data system was used. Three stainless steel columns (300 x 7.5 mm) connected in series and packed with ultrastyragel spherical particles of porosity $10^4$, 500 and 100 Å were used. A UV monitor (277nm) was used for detection. A constant flowrate through the system was maintained by a single piston, reciprocating pump. The following operating conditions were employed: eluent, degassed tetrahydrofuran (purged with $N_2$); temperature, 25 °C; injection volume, 100 $\mu$L; flow rate, 1 mL/min. A relative calibration curve was obtained using monodisperse polystyrene standards (Polymer Laboratories, England, UK). A third order polynomial of the form $y = ax^3 + bx^2 + cx + d$ best describes the relation between the log of the actual molecular weights of polystyrene standards (y) and their retention times (x). The following coefficients were calculated: a = -0.00021, b = 0.0283, c = -1.279, d = 20.64. These gave a fit with a correlation coefficient of 0.99. The size exclusion volume ($V_o$) for the column system was 6.4.

## RESULTS AND DISCUSSION

In the present work, experiments were conducted to study the effects of reaction temperature and time on the yields of reaction products and their distribution arising from the catalytic hydrocracking of ALCELL® lignin produced on the semi-commercial scale. The effect of these two reaction variables is combined into a single severity parameter, the reaction ordinate $R_o$, whose derivation and applicability have been described elsewhere[11]. It can be used as a mapping tool not only to correlate experimental data but to effectively plan a series of experiments in important temperature-time regimes in hydrotreatment work[12]. In the present work, the reaction ordinate used is given by:

$$R_o = \int_o^t \exp\left(\frac{T-150}{13.25}\right) dt$$

where:

T = reaction temperature, $^oC$

t = reaction time, min.

If a coordinate such as this one is not used, a complex non-homogeneous kinetics scheme would be required to adequately correlate and interpret the numerous reactions occurring simultaneously during depolymerization studies of complex polymers such as lignin.

Conversion of lignin to liquid and gaseous products was calculated as follows:

$$\text{Conversion (\%)} = \left[\left[M_i - \left(M_{RR} + M_{RL}\right)\right] / M_i\right] \bullet 100$$

where: $M_i$ = mass of initial dry lignin, g

$M_{RR}$ = mass of reactor residue, g

$M_{RL}$ = mass of residual lignin, g

Unless it is stated otherwise, 5 wt% of the Ni-W catalyst was used in the experimental runs. Nickel-tungsten catalysts have been used previously in catalytic hydrocracking. In a patent by Engel et al.[13], a Ni-W catalyst (0.6% Ni and 6% W - as oxides) on a silica-alumina support produced very high (> 40 wt%) yields of phenols. However, the reaction conditions were very different from ours. A key difference was the use of phenol as the solvent at high hydrogen pressures instead of tetralin at little or no initial hydrogen pressure. Also, Benigni and Goldstein[14] hydrotreated thiolignin in water using a similar Ni-W catalyst as in the present work. Liquefaction and distillation yields obtained were reportedly low to moderate when compared to the other catalyst systems they tested. Again, differences in reaction conditions, materials, and separation procedures used between these works and the present precludes any comparison to be made.

## Effect of Severity

As shown in Figure 3A, the conversion of ALCELL® lignin to liquid and gaseous products increases rather dramatically with increasing severity of reaction. However, even at the highest severity conditions employed here, conversion of lignin did not exceed 50%. Figure 3B shows the dependence of the reactor residue remaining inside the reactor on the severity of treatment. Also, (residual lignin) the lignin recovered as an acid precipitate after reaction is plotted on this figure as a function of severity. As seen, the residual lignin remains essentially constant for the range of severity studied. However, the reactor residue decreases noticeably with increasing severity. The high yield of this material at low severity suggests that recondensation reactions dominate any hydrocracking ones. This highly condensed residue is due to the inadequate amount of hydrogen radicals released by the solvent to stabilize the unreduced lignin fragments under these conditions. However, at high severity, significant hydrocracking occurs as reflected by the low (~10 wt% or less) amount of reactor residue recovered. Domburg et al[15]. has noted that char formation from lignin under mild reaction conditions is a consequence of the cleavage of labile lignin bonds like alkyl-aryl ether linkages and the resulting formation of more resistant condensed structures.

As shown in Figure 4A, the methylene chloride solubles are low at about 5 wt% for low severeties then remain at about 7 wt% for medium to high severities, except in one case, where the methylene chloride solubles are highest at 10 wt%. This data point corresponds to an experiment conducted using a residence time of 60 minutes at 390°C. However, the yields of liquid monomeric phenolic components in the methylene chloride solubles were all too low to warrant a detailed identification and quantification of all the peaks in the chromatograms. As we will see later, only the relative abundance of the major classes of these compounds will be discussed.

Total gas production is seen in Figure 4B to steadily increase with increasing severity of treatment. The yield of gases produced from the thermolysis of a kraft lignin in tetralin at hydrocracking temperatures has been reported by Connors et al.[7] to strongly depend on the treatment severity. Due to lack of a gas chromatograph, we did not identify nor quantify the gaseous components produced in our runs.

## Methylene Chloride Solubles

In the present work, the GC method was intended to detect and monitor classes of phenolic compounds identifiable in the methylene chloride soluble faction. Due to the wide slate and low abundance of the compounds present in the samples, only the relative abundance (not absolute amounts) were determined. A previous study[16] using the DB-5 column has demonstrated that response factors are not far from unity for the majority of compounds (acetates). The relative abundance is taken as the % area of each compound derivative identified and calculated from the total area of chromatographable compounds (excluding peaks attributed to the acetylating agents). Table 2 gives the relative abundance of each compound as a function of treatment severity. As seen: (i) phenols increase somewhat from low to high severity; (ii) guaiacols and syringol predominate at low severity but diminish or disappear altogether at high severity; (iii) catechols predominate at high severity but are almost absent at low severity; (iv) alcohols, aldehydes and aromatic ketones, on the other hand, are abundant at low severity, but only traces occur at high severity.

### Effect of Catalyst

The effect of no catalyst addition is illustrated by the data from Run 1, shown in Figures 3 and 4 as shaded square points. For a given reaction severity, conversion of lignin moderately increased from 20% to 24% with the catalyst. A somewhat higher amount of reactor residue (coke) is obtained than if the catalyst is added (compare Runs 1 and 3). The catalytic effect is more obvious by the increased yields of both methylene chloride solubles and gas produced when the catalyst is present. It should be noted that 5 wt% (based on lignin) of catalyst was used in this work. Increasing the amount of catalyst by 3 times in Run 12 at the same severity as in Run 3 (see Table 1) did not significantly affect the distribution and yield of products, except that there was a moderate increase (8%) in the residual lignin precipitated and a lower yield of reactor residue. The amounts of total gas produced and methylene chloride solubles were similar from both runs. This suggests that increasing the amount of catalyst increases the degradation of the lignin to a lower molecular weight, re-precipitable lignin, but is relatively ineffective in further depolymerizing this lignin to low molecular weight fragments recovered as methylene chloride solubles or gas. No further experiments were performed on the effect of varying the amounts of catalyst.

To determine the effect of nickel as the hydrogenating component, a catalyst comprising 60% nickel on silica-alumina was used in two experiments. The first experiment, conducted at 390 $^oC$ and 30 min. reaction time, resulted in a lignin conversion of 24% with only 5% of methylene chlorides extracted. Most of the starting lignin (61%) was recovered as a residual lignin, with a reactor residue of only 15% from this experiment. However, the gas produced in this run was the highest (at 8100 mL) of all the runs. The second run was carried out at the same reaction temperature but for 15 minutes reaction time. Conversion of the lignin to liquid and gaseous products was determined to be 17%, and the amount of methylene chloride solubles produced was 4%. Also, for this experiment, more reactor residue (21%) and residual lignin (62%), was obtained than in the previous experiment. These results are as expected since at shorter reaction times, less lignin will be degraded to lower molecular weight products, whether these are in the solid, liquid, or gaseous phases. The effect of nickel is reflected by the much higher amount of gases produced for a given severity, evident when comparing the above values of gas produced from the two runs with those presented in Figure 4. Even at the highest severity of treatment utilized in this work using the catalyst containing 5% Ni, gas production is only about 50% of that produced in either of the two experiments.

High Pressure Solvent Elution Chromatography: Analysis by HPSEC of the acetylated residual lignins after hydrocracking was performed as described elsewhere[17]. As shown in Figure 5, ALCELL® lignin is extensively decomposed into smaller fragments during hydrocracking. The chromatogram of the original lignin is multimodal with a large excluded peak whose maximum corresponds to a molecular weight of 3080 g/mol. However, this peak is completely absent in the chromatograms of all the residual lignins recovered after depolymerization of ALCELL® lignin. Also, the lower molecular weight area (800 to 200 g/mol) is much more enhanced, indicative of extensive degradation of the starting lignin during hydrocracking. The multimodular distribution exhibited by the initial ALCELL® lignin has also been observed for other organosolv lignins isolated under different solvolysis conditions[18,19]. Thus, this seems to be a common characteristic of organosolv lignins.

Table 3 represents the molecular weight values $M_w$ and $M_n$, polydispersity, as well as their corresponding degree of polymerization (DP) calculated on the basis of a monmer having a molecular weight of 205 g/mol. It should be mentioned at this point that since the molecular weights discussed throughout the present work were obtained using monodisperse polystyrene standards for calibration, these values should only be considered as relative, and not as absolute values.

Molecular weights throughout this article are therefore "apparent molecular weights". As seen, all the residual lignins are comprised of oligomers with average molecular weights of a few hundred and rather narrow molecular weight distributions. With increasing hydrocracking severity, the molecular weights of the residual lignins decrease, suggesting that the lignin is increasingly depolymerized.

Yields of the analysed hydrocracked lignins RL-1, RL-2, and RL-3 were found to be: 46%, 43%, and 38% respectively. On the other hand, the yields of the corresponding reactor residues were much lower and found to be 39%, 30%, and 13% respectively.

Hydrogen Pressure: To assess the effect of hydrogen addition, a run was conducted at a reaction temperature of 390 $^{o}$C for 30 minutes, which are reaction conditions identical to those used in Run 3. However, hydrogen was added to the autoclave up to a pressure of 10 kg/cm$^2$ prior to heat-up. Conversion was found to be higher at 30% instead of 24% from Run 3. Also, in both runs, the yield of methylene chloride solubles was almost identical at 6%. The most dramatic effect of hydrogen addition was, however, on the yield of reactor residue (coke). In Run 3, almost 40% of the lignin remained in the reactor as a residue but this fraction was only 11% when hydrogen was added. Clearly, the presence of hydrogen suppressed the formation of reactor residue to a significant extent. As suggested by Domburg and Sharapova[20], the formation of coke may proceed via intermolecular dehydrogenation, and that hydrogen may also act to capture active intermediates, leading to coke with lesser amounts of hydrogen. Thus, the reason for the reduction of cracked products, particularly the methylene chloride solubles, at higher hydrogen pressure may also be attributed to this stabilization.

## Acknowledgements

The author would like to thank Alcell Technologies Inc., Newcastle, New Brunswick (Canada) for supplying the sample of ALCELL® lignin. Financial contributions from the Natural Sciences and Engineering Council (NSERC) of Canada is deeply appreciated.

## REFERENCES

1.Chum, H.L., Johanson, D.K., Black, S., Ratcliff, M., and Goheen, D.W. "Lignin Hydrotreatment to Low-Molecular-Weight Compounds", Chapter 2, in Advances in Solar Energy-An Annual Review of Research and Development, Vol. 4, (K.W. Boer, Ed.), Plenum Press, New York, pp. 91-171 (1988).

2.Yoshida, H., Morck, R., Kringstad, K.P. and Hatakeyama, H. "Kraft Lignin in Polyurethanes. I. Mechanical Properties of Polyurethanes from a Kraft Lignin-Polyether Triol-Polymeric MDI System". J. Appl. Polym. Sci., Vol. 34, pp. 1187-1198 (1987).

3.Feldman, D. and Baskaran, A. "The Effect of Adding Lignin to Poly(Dimethyl Siloxane)-Poly(VinylChloride) Blends", J. Adhesion, Vol. 27, pp. 231-243 (1989).

4.Freudenberg, K., "Lignin: Its Constitution and Formation from p-Hydroxycinnamyl Alcohols", Science, Vol. 148, pp. 595-600 (1965).

5.Sakakibara, A., "A Structural Model for Softwood Lignin", Wood Sci. Technol., Vol. 14, pp. 89-100 (1980).

6.Davoudzadeh, F., Smith, B., Avni, E. and Coughlin, R.W. "Depolymerization of Lignin at Low Pressure Using Lewis Acid Catalysts and Under High Pressure Using Hydrogen Donor Solvents", Holzforschung, Vol. 39, No. 3, pp. 159-166 (1985).

7.Connors, W.J., Johanson, L.N., Sarkanen, K.V. and Winslow, P. "Thermal Degradation of Kraft Lignin in Tetralin", Holzforschung, Vol. 34, pp. 29-37 (1980).

8.Schultz, T.P., Preto, R.J., Pittman, J.L. and Goldstein, I.S. "Hydrotreating of Hydrochloric Acid Lignin in a Hydrogen-Donor Solvent", J. Wood Chem. Technol., Vol. 2, No. 1, pp. 17-31 (1982).

9.Pye, E.K. and Lora, J.H. "The Alcell™ Process - A Proven Alternative to Kraft Pulping". TAPPI J., pp. 113-117 (March 1991).

10.Lora, J.H., Creamer, A.W., Wu, L.C.F. and Goyal, G.C. "Chemicals Generated During Alcohol Pulping; Characteristics and Applications", 6th International Symposium on Wood and Pulping Chemistry (Proceedings), pp. 431-438 (1991).

11.Overend, R.P. and Chornet, E. "Heavy Oil Cracking: The Case for Non-Homogenous Kinetics", Can. J. Physics, Vol. 68, pp. 1105-1111 (1990).

12.Thring, R.W., Chornet, E. and Overend, R.P. "Thermolysis of Glycol Lignin in the Presence of Tetralin", Can. J. Chem. Eng., Vol. 71, pp. 107-115 (1993).

13.Engel, D.J., Steigleder, K.Z. and Ellyn, G. "Hydrocracking Process for Liquefaction of Lignin", US Patent No. 4 647 704 (March, 1987).

14.Benigni, J.D. and Goldstein, I.S. "Hydrogenation of Kraft Lignin", J. Appl. Polym. Sci., No.

36, pp. 477-488 (1971).

15.Domburg, G., Rossinskaya, G. and Sergeeva, V. "Study of Thermal Stability of Beta-ether Bonds in Lignin and its Models", in Proceedings of the 4th International Conference on Thermal Analysis, Budapest, Vol. 2, p.211-220 (1974).

16.Thring, R.W., Chornet, E. and Overend, R.P. "Analysis of Phenols from Lignin Depolymerization by Capillary Gas Chromatography", J. Chromatogr., No.467, pp. 441-446 (1989).

17.Thring, R.W. and Griffin, S.L. "The Heterogeneity of Two Canadian Kraft Lignins", Can. J. Chem., Vol. 73, No. 5, pp. 627-631 (1995).

18.Chum, H.L., Johnson, D.K., Tucker, M.P. and Himmel, M.E. " Some Aspects of Lignin Characterization by High Performance Size Exclusion Chromatography Using Styrene Divinylbenzene Copolymer Gels", Holzforschung, Vol. 14, No. 2, pp. 97-108 (1987).

19.Thring, R.W., Chornet, E., Bouchard, J., Vidal, P.F. and Overend, R.P. "Evidence for the Heterogeneity of Glycol Lignin", I & EC Research, Vol. 29, pp. 232-240 (1991).

20.Domburg, G. and Sharapova, T.E. "Formation of Intermediate Structures During Thermal Conversions of Lignin. 4. Features of Competing Degradation on Condensation Reactions", Khim. Drev., Vol. 4, pp. 56-65 (1982).

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| Run No. | Lignin[1] (g) | Tetralin (ml) | Catalyst (g) | T (°C) | t (min) | $\log_{10}(R_o/\text{min})$ |
|---|---|---|---|---|---|---|
| 1 | 19.0 | 250 | 0.0 | 390 | 30 | 9.42 |
| 2 | 19.1 | 250 | 1.0 | 390 | 15 | 9.25 |
| 3 | 19.1 | 250 | 1.0 | 390 | 30 | 9.45 |
| 4 | 19.0 | 250 | 1.0 | 390 | 60 | 9.71 |
| 5 | 19.1 | 250 | 1.0 | 410 | 15 | 9.91 |
| 6 | 19.0 | 250 | 1.0 | 410 | 30 | 10.12 |
| 7 | 19.0 | 250 | 1.0 | 410 | 60 | 10.34 |
| 8 | 19.2 | 250 | 1.0 | 370 | 30 | 8.75 |
| 9 | 19.1 | 250 | 1.0 | 370 | 60 | 9.02 |
| 10 | 19.4 | 250 | 1.0 | 370 | 15 | 8.50 |
| 11 | 19.0 | 250 | 1.0 cr | 400 | 30 | 9.74 |
| 12 | 19.0 | 250 | 3.0 | 390 | 30 | 9.40 |
| 13 | 19.0 | 250 | 1.0 untr | 390 | 30 | 9.41 |
| 14 | 19.0 | 250 | 1.0 | 390 | 120 | 9.96 |

[1] dry basis; cr = crushed; untr = untreated.

Table 1. Experimental conditions for the hydrocracking experiments.

| Compound | Relative Abundance, % | |
|---|---|---|
| Phenols | Low Severity<br>(log $_{10}$(R$_o$/min) = 8.5) | High Severity<br>(log$_{10}$(R$_o$/min) = 10.34) |
| 1. phenol | tr | 2.7 |
| 2. o-cresol | tr | 1.2 |
| 3. m-cresol | tr | 2.2 |
| 4. p-cresol | tr | 2.4 |
| 5. 4-ethylphenol | tr | 1.1 |
| Guaiacols | | |
| 6. guaiacol | 9.3 | 6.5 |
| 7. 4-methylguaiacol | 9.3 | 6.1 |
| 8. 4-ethylguaiacol | 2.8 | 9.3 |
| Syringols | | |
| 9. syringol | 21.6 | 6.8 |
| Catechols | | |
| 10. catechol | 12.6 | 21.9 |
| 11. 4-methylcatechol | 7.4 | 11.5 |
| 12. 4-ethylcatechol | 5.8 | 6.7 |
| Aldehydes | | |
| 13. vanillin | 7.5 | tr |
| 14. syringaldehyde | 3.0 | 1.6 |

Table 2.Relative abundance of classes of identifiable phenolic compounds in the methylene chloride solubles produced at low and high severity.

| Sample No. | $M_w$ (g/mol) | $M_n$ (g/mol) | d |
|---|---|---|---|
| RL-1 | 830 | 430 | 1.9 |
| RL-2 | 720 | 410 | 1.8 |
| RL-3 | 680 | 390 | 1.7 |
| Alcell Lignin | 3300 | 900 | 3.7 |

Table 3.Molecular weight averages and polydispersities of acetylated ALCELL® lignin and hydrocracked oligomers (polystyrene weight equivalent).