

## Research Article

# Influence of RANEY Nickel on the Formation of Intermediates in the Degradation of Lignin

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Lignin forms an important part of lignocellulosic biomass and is an abundantly available residue. It is a potential renewable source of phenol. Liquefaction of enzymatic hydrolysis lignin as well as catalytical hydrodeoxygenation of the main intermediates in the degradation of lignin, that is, catechol and guaiacol, was studied. The cleavage of the ether bonds, which are abundant in the molecular structure of lignin, can be realised in near-critical water (573 to 673 K, 20 to 30 MPa). Hydrothermal treatment in this context provides high selectivity in respect to hydroxybenzenes, especially catechol. RANEY Nickel was found to be an adequate catalyst for hydrodeoxygenation. Although it does not influence the cleavage of ether bonds, RANEY Nickel favours the production of phenol from both lignin and catechol. The main product from hydrodeoxygenation of guaiacol with RANEY Nickel was cyclohexanol. Reaction mechanism and kinetics of the degradation of guaiacol were explored.

## 1. Introduction

Earth's resources of crude oil are limited [1]. An important challenge for scientists and engineers is to develop technologies that are largely independent from fossil crude oils. Biomass, especially organic waste material, has a high potential to replace crude oil as a basic input material for the production of many organic chemicals. Lignocellulosic biomass is one of the most abundant renewable organic materials in the world. Lignin, a major component of lignocellulosic biomass, is mostly available as waste material. The paper industry produces more than 50 million tons of dry lignin every year worldwide [2]. It is mainly burned to recover its energetic value. Lignin has a structure similar to brown coal, being an aromatic heteropolymer. The three basic building blocks, *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, are interlinked by C–C or ether bonds. The latter is the weaker one of the two bonds mentioned and thus of high interest for lignin degradation. As lignin is relatively resistant to chemical or enzymatic degradation, harsh reaction conditions are required to break down this polymer [3]. By cleavage of the ether bonds, aromatic monomers are formed.

Thus lignin provides high potential to serve as a renewable source for phenol or benzene [4]. Phenol is extremely interesting as building block for synthetic polymers, resins, and epoxy- or polyurethane [3]. It is however a challenge to gain a high-value product from a chemically complicated and inhomogeneous component as lignin. In order to do so, char formation is to be avoided. Char formation can be “caused by hydrogen shuttling from the lignin matrix before the actual process temperature is reached, which implies that the structure of lignin under liquefaction conditions is irreversibly changed” as postulated by Dorrestijn et al. [5] or by repolymerisation of (di-) hydroxybenzene as it occurs during liquefaction of coal [6]. Furthermore a broad product spectrum is observed in many lignin liquefaction approaches thus requiring a cost-intensive separation.

Fast pyrolysis or solvolysis processes are so far one of the most promising advances to liquefaction of lignin [7, 8]. Choosing the right solvent for solvolysis is one of the key challenges. Water is a promising solvent for lignin liquefaction. Although the yield of monoaromatic components is not as high as in organic solvents, it shows a narrower product spectrum and a high selectivity in respect to phenol and

catechol [9, 10]. The yield of catechol and phenol can be even increased by applying an acidic or a basic environment [11]. Wahyudiono et al. [10] pointed out the significance of the water density on the product composition for hydrothermal lignin degradation. High water density led to higher phenol and cresol yields between 623 K and 673 K. Yokoyama et al. [12] found that char formation from lignin in aqueous media was promoted by low temperatures, high pressures, and long reaction times. Saisu et al. [13] suggested that the addition of phenol could prevent the char formation in supercritical water. However, complete suppression of char formation could not be achieved. A further advantage of water is its abundance at rather low prices and its chemical stability at the required temperatures and pressures.

Literature provides some data for kinetic investigation of the degradation of lignin [14]. The reaction kinetics of the degradation of intermediate components, that is, guaiacol, was studied by Wahyudiono et al. [15]. Whether radical-induced reactions or hydrolysis plays the most important role for the degradation of guaiacol is one of the issues discussed in this paper.

It was shown in the past that heterogeneous catalysts have a high potential to promote hydrodeoxygenation of methoxyphenols which are present in biooils [16, 17]. In this work the benefits of a heterogeneous catalyst, that is, RANEY Nickel, in respect to the liquefaction of lignin will be discussed.

Gasification is one of the challenges when dealing with a catalyst for hydrothermal biomass treatment. A part of the biomass will always be gasified, as the application of a heterogeneous catalyst commonly promotes gasification processes [18, 19]. Possible reaction pathways of the lignin liquefaction are shown in Figure 1. A better understanding of the reaction mechanisms of the catalysed hydrothermal degradation of lignin is essential for maximizing selectivity and yield of valuable products, for example, phenol, by optimizing the reaction parameters.

## 2. Experimental

Experiments were carried out in microbatch reactors of 5 and 10 mL volume. The experimental setup for experiments carried out with enzymatic hydrolysis lignin was the following. 3 mL water, 0.4 g lignin, and optionally 110 mg RANEY Nickel (dry matter) were placed in a 5 mL autoclave. The autoclave was purged with nitrogen. It was heated at different temperatures for different reaction times.

The experimental setup for experiments carried out with intermediates was the following. 5 mL of a 10 g/L aqueous solution of the intermediate (Catechol or Guaiacol) as well as 55 mg of RANEY Nickel catalyst (dry matter) was placed in a 10 mL autoclave. The autoclave was purged with nitrogen and hydrogen and thereafter pressurized with 1 MPa H<sub>2</sub>. It was heated at different temperatures for 1 h.

The oven used for heating was a HP-5890. The heating rate was 30 K/min. After the predefined reaction time, the reactor was cooled down to 298 K in the oven by air cooling. The gas was removed from the reactor through the high-pressure capillary tubes. The product gas mixture passed a gas sample tube first and then entered a gasometer where

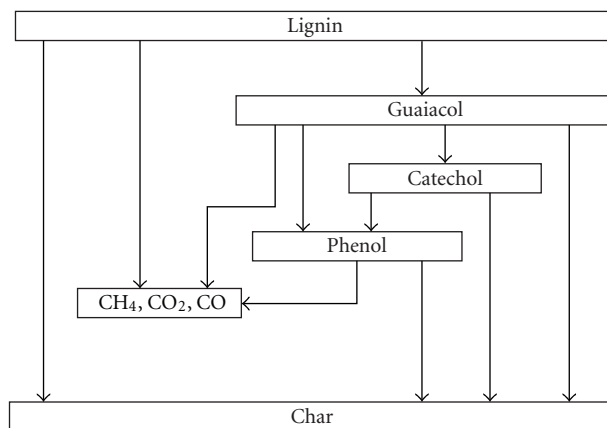


FIGURE 1: Possible reaction pathways for hydrothermal lignin degradation.

the volume of the gas was determined. The reactor was opened in order to remove liquid and solid products which were thereafter separated from each other by filtration. The solids were dried, and the mass of liquid and solid phase was determined.

GC analysis of the gaseous phase was performed on a HP 7890A equipped with a 30 m Porapak Q Molsieve column, a FID front detector, and a TDC back detector, which was controlled by a HP-Chem laboratory data system. The heating program was as follows. The initial temperature of 323 K was maintained for 22.2 min after which the temperature was raised at a rate of 20 K/min up to 423 K. 15 min after reaching this temperature, it was further raised at a rate of 50 K/min up to 493 K. This temperature was held for 5 min. The whole run had a duration of 48.6 min. The temperature of the injection port was maintained throughout the whole run at 523 K, the pressure was kept constantly at 255 kPa, and the FID was at 573 K. For one measurement 100  $\mu$ L of the sample was injected.

Extraction was performed on the liquid samples. The pH of the aqueous phase was adjusted to a value between 3 and 4 by optionally adding HCl. Aqueous sample and the extraction agent, ethyl acetate with 1000 mg/L pentadecane added, were mixed in a separation funnel in the ratio aqueous phase/organic phase = 2.5. The phases were left to settle for one hour and thereafter were separated. Pentadecane was used as extraction standard in order to determine the quantity of extraction agent that was diluted in the aqueous phase and vice versa. The solubility of pentadecane in water was assumed to be negligible. Around 20% of the ethyl acetate dissolved in the aqueous phase.

A sample of the organic phase was analyzed on a GC-FID (HP 5890) with a Restek XRI1-MS column of 30 m length and a capillary diameter of 0.25 mm. The initial oven temperature was 333 K. After 3 min the oven was first heated to 423 K with a heating rate of 5 K/min then to 573 K with a heating rate of 12 K/min. *n*-pentacosane was chosen to be the internal standard for GC analysis. For the identification of unknown substances GC-MS was used. GC-MS analysis was performed on a HP6890 equipped with a 30 m DP5 column

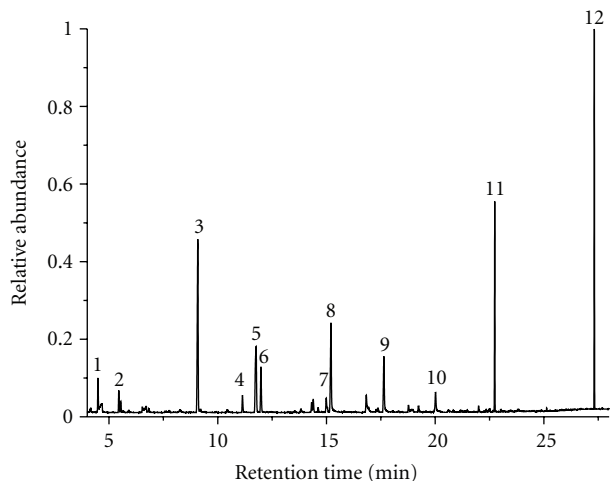


FIGURE 2: GC-FID Chromatogram of the organic fraction obtained from extraction of aqueous product after hydrothermal treatment of lignin for 30 min at 673 K with RANEY Nickel (chemical compounds are listed in Table 1).

with 0.25 mm diameter and a film thickness of 0.25  $\mu\text{m}$  as well as a MS detector (MSD5973). The sample was injected at 40°C oven temperature and 305°C injector temperature. After maintaining the oven temperature constant for 5 min, it was raised to a final temperature of 300°C with a heating rate of 20°C/min. For every substance identified by GS-MS it was proven that the retention time in GC-FID of the pure substance corresponded with the retention time of the unknown substance in the sample. A chromatogram from GC-FID of an organic sample obtained from extraction of the aqueous product after hydrothermal treatment of lignin with RANEY Nickel at 673 K for 30 min is shown in Figure 2. All chemical species that could be quantified by GC analysis are listed in Table 1.

The heterogeneous catalyst used was RANEY Nickel purchased from Merck-Schuchardt composed of 88 wt.-% Nickel and 12 wt.-% aluminum. The catalyst is conserved in water for ignition prevention. The suspension of catalyst and water contains 50 wt.-% water. The enzymatic hydrolysis lignin purchased from SEKAB (Sweden) originates from spruce. Spruce wood is treated with the so-called SSF process. This includes a pre treatment catalyzed by  $\text{SO}_2$  and filtration of the lignin after hydrolysis, fermentation, and distillation. The amount of cellulose in SEKAB-lignin is supposed to be negligible as no furfural or other typical products of hydrothermal treatment of cellulose could be detected by GC analysis of the liquid product. Results of an elemental analysis of enzymatic hydrolysis lignin are given in Table 2.

Received samples were dried for 48 h at 333 K and were ground to a maximum particle size of 200  $\mu\text{m}$ . Guaiacol with a purity >98% was purchased from Alfa Aesar, catechol with a purity >99% from Merck. The water used was deionised by a Millipore Direct Q3 with a minimum volume resistivity of 18.4 M $\Omega\text{cm}$ . Ethyl acetate (>99.5%) from Merck, pentadecane (>99%), and pentacosane (>99%) were used for extraction and analysis.

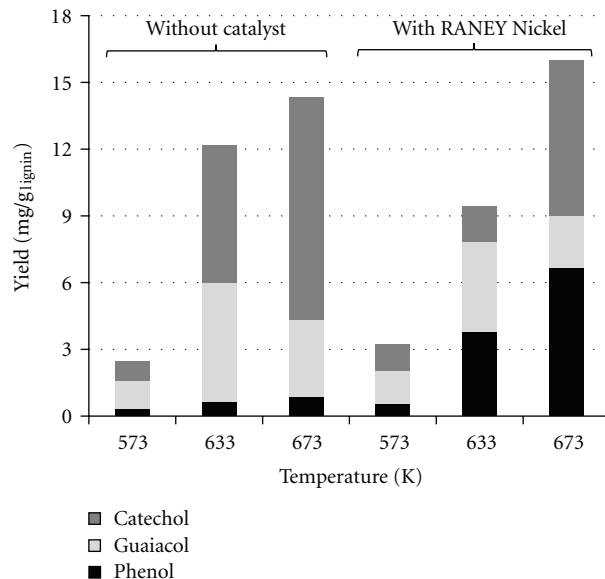


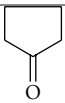
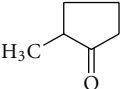
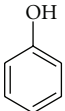
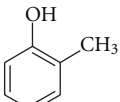
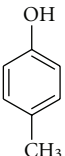
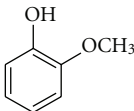
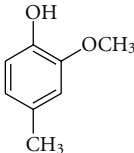
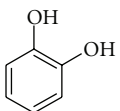
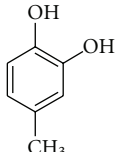
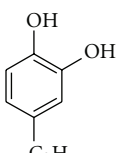
FIGURE 3: Yield of monoaromatic substances after hydrothermal treatment of lignin with and without catalyst at 30 min reaction time.

### 3. Results and Discussion

**3.1. Experimental Results.** The yield of monoaromatic components as well as gaseous components and solid residue from enzymatic hydrolysis lignin in near critical water with and without addition of RANEY Nickel was studied. The yield is defined as output mass of the observed component divided by the input mass of lignin. The sum of all yields will not necessarily be 100%, since water might also be involved in a number of reactions going on in the reactor, for example, water gas shift reaction [19, 20] and methanation [21]. However, for easy comparison, all results are displayed as yield. Solid residue was not divided into unconverted lignin and coke or char, since it was gravimetrically not possible around 633 K the yield of methoxylated phenols reaches a maximum (see Figure 3). Above 633 K the yield of all methoxylated phenols (e.g., guaiacol) decreases while the yields of hydroxybenzenes (e.g., phenol) and dihydroxybenzenes (e.g., catechol) still increase up to temperatures of 673 K. At temperatures around 573 K the yields of all monoaromatic substances are low, independent of an added catalyst.

However, the RANEY Nickel catalyst shows an effect on the selectivity with respect to phenol. At temperatures above 633 K the yield of phenol can be increased while the yield of guaiacol and catechol is kept rather low. Longer reaction times and higher temperatures lead to even lower yields of guaiacol and catechol as well as higher yields of phenol and *p*-cresol. The formation of *p*-cresol is especially favoured by high temperatures (see Table 4). The yield of solid residue decreases towards longer reaction times. The higher the temperature the faster the yield of solid residue decreases. At very long reaction times (1200 min) no solid residue is left. This result shows a basic difference to other research efforts where no catalyst was applied. Wahyudiono et al. [10] found

TABLE 1: Chemical compounds detected by GC-FID (see Figure 2).

| #Chemical compound | Name                    | Retention time<br>min | Molecular weight<br>g/mol | Formula                                       | Chemical<br>structure   |
|--------------------|-------------------------|-----------------------|---------------------------|---|---|
| 1                  | Cyclopentanone          | 4.49                  | 84.12                     | C <sub>5</sub> H <sub>8</sub> O               |    |
| 2                  | 2-Methyl-cyclopentanone | 5.45                  | 98.14                     | C <sub>6</sub> H <sub>10</sub> O              |    |
| 3                  | Phenol                  | 9.08                  | 94.11                     | C <sub>6</sub> H <sub>6</sub> O               |    |
| 4                  | <i>o</i> -Cresol        | 11.14                 | 108.14                    | C <sub>7</sub> H <sub>8</sub> O               |    |
| 5                  | <i>p</i> -Cresol        | 11.76                 | 108.13                    | C <sub>7</sub> H <sub>8</sub> O               |    |
| 6                  | Guaiacol                | 11.99                 | 124.14                    | C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>  |   |
| 7                  | 4-Methyl-guaiacol       | 15.00                 | 138.16                    | C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> |  |
| 8                  | Catechol                | 15.21                 | 110.10                    | C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>  |  |
| 9                  | 4-Methyl-catechol       | 17.64                 | 124.14                    | C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>  |  |
| 10                 | 4-Ethyl-catechol        | 20.02                 | 138.16                    | C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> |  |
| 11                 | <i>n</i> -Pentadecane   | 22.74                 | 212.41                    | C <sub>15</sub> H <sub>32</sub>               |   |
| 12                 | <i>n</i> -Pentacosane   | 27.32                 | 352.68                    | C <sub>25</sub> H <sub>52</sub>               |   |

that the solid residue even increased towards longer reaction times.

At high temperatures an increased gas production can be observed. The gas yield is higher if a RANEY Nickel catalyst

is present in the reactor (see Figure 4). Most of the produced gas is carbon dioxide. Less than 20% is methane and less than 2.5% are other hydrocarbon gases (C<sub>2</sub>–C<sub>4</sub>). The total gas yield tends to increase towards long reaction times. The yield

TABLE 2: Elemental analysis of enzymatic hydrolysis lignin from SEKAB (Sweden).

|                  | C    | H   | N   | S   | O    | Ash |
|------------------|------|-----|-----|-----|------|-----|
| Percentage/(g/g) | 60.5 | 6.7 | 0.6 | 0.1 | 30.1 | 2.0 |

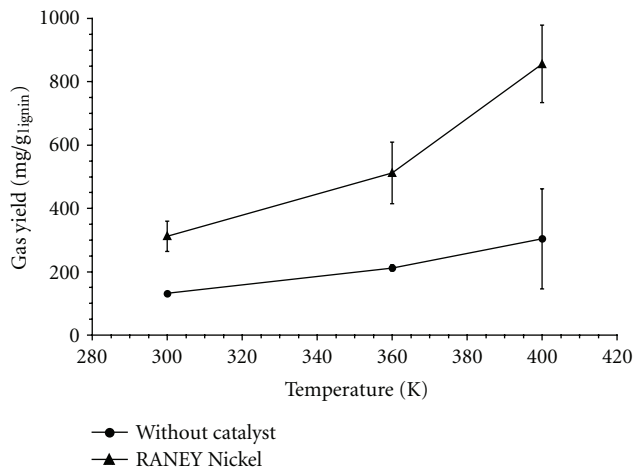


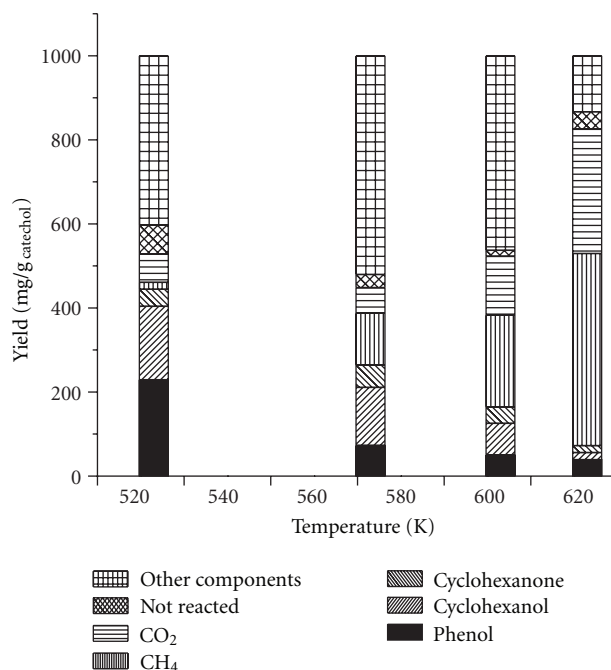
FIGURE 4: Gas yield with and without catalyst at different temperatures and 30 min reaction time.

of all hydrocarbon gases increases towards high temperatures and long reaction times. This tendency is visible in Tables 3 and 4.

The effect of a RANEY Nickel catalyst on intermediate components formed within liquefaction of lignin was investigated. Experiments with catechol and guaiacol showed that RANEY Nickel helps convert catechol into phenol (see Figure 5) in the presence of H<sub>2</sub>. Guaiacol reacts mostly to yield cyclohexanol (see Figure 6). However, cyclohexanol was not found in the product mixture of experiments carried out with lignin and RANEY Nickel.

However, at temperatures above 573 K the main product of the hydrothermal treatment of the intermediate compounds was gas, mostly methane and carbon dioxide (see Figures 5 and 6). According to literature hydrothermal degradation of guaiacol without catalyst [22] yields mostly catechol, phenol, and cresol.

At temperatures up to 573 K the formation of monoaromatic substances is rather slow. After 30 min reaction time only about 20% of the maximum yield, observed at 673 K, is reached. Also a heterogeneous catalyst like RANEY Nickel is not able to increase the formation of monoaromatic substances. It is hence not involved in breaking the lignin structure by, for example, the cleavage of ether bonds. However, the catalyst promotes the hydrogenation of intermediate products of lignin degradation, that is, guaiacol and catechol. Phenol is a secondary or even tertiary product derived from guaiacol or catechol [23, 24]. At 603 K long reaction times (1200 min) are necessary to maximize the phenol yield, which implies that the formation of phenol is rather slow. At higher temperatures (673 K) the reaction rate of the

FIGURE 5: Yield of main products from hydrogenation of 10 g/L catechol in water with RANEY Nickel and H<sub>2</sub> (1 MPa).

formation of phenol increases but also the gasification of phenol is favored. This is probably the reason for decreasing phenol yields towards long reaction times (see Table 4). Experimental efforts with intermediate compounds showed that catechol can be transformed into phenol and guaiacol into cyclohexanol with RANEY Nickel at relative low temperatures (523 K). Although guaiacol is also an intermediate product of lignin liquefaction, cyclohexanol was not found in product mixtures obtained from experiments with lignin. A possible explanation is to be found in the temperature which is of critical importance for lignin liquefaction and in the abundance of hydrogen present in experiments carried out with intermediate compounds. The product spectrum varies a lot when the temperature is increased. At higher temperatures and with RANEY Nickel present the gasification of guaiacol, and catechol is promoted. The gas yield surmounts the yield of aromatic components at temperatures above 573 K. Experiments with lignin showed, that the formation of solid residue in near critical water is restrained by RANEY Nickel. Whether solid residues are low in this context because RANEY Nickel suppresses the formation of intermediates (e.g., radicals) that are likely to polymerize or since it promotes the gasification and liquefaction of char that had already been formed could not yet be answered.

**3.2. Studies of Reaction Kinetics.** The decomposition of guaiacol seems to be a key reaction within the chain of reactions taking place when lignin is exposed to high temperatures. Therefore it is worth having a closer look on the decomposition of guaiacol. Dorrestijn and Mulder [25] showed that guaiacol degradation during pyrolysis of lignin is a radical-induced reaction. Toor et al. [11] postulate

TABLE 3: Results of hydrothermal lignin degradation experiments, input: 0.4 g lignin, 3 g H<sub>2</sub>O.

| <i>t</i><br>Min | <i>T</i><br>K | Solid residue | Phenol | <i>o</i> -Cresol | <i>p</i> -Cresol | Guaiacol               | 4-Methyl-guaiacol | Catechol | 4-Methyl-catechol      | CH <sub>4</sub> | C2-C4 | CO <sub>2</sub> |
|-----------------|---------------|---------------|--------|------------------|------------------|------------------------|-------------------|----------|------------------------|-----------------|-------|-----------------|
|                 |               |               |        |                  |                  | mg/g <sub>Lignin</sub> |                   |          | mg/g <sub>Lignin</sub> |                 |       |                 |
| 30              | 573           | 599,4         | 0,3    | 0,0              | 0,1              | 1,2                    | 0,3               | 0,9      | 0,0                    | 0,2             | 0,2   | 106,3           |
| 30              | 633           | 432,1         | 0,7    | 0,0              | 0,0              | 5,3                    | 1,5               | 6,2      | 2,0                    | 3,7             | 2,8   | 195,3           |
| 30              | 673           | 374,6         | 0,9    | 0,3              | 0,5              | 3,4                    | 1,2               | 10,0     | 4,1                    | 8,9             | 4,8   | 263,5           |

TABLE 4: Results of hydrothermal lignin degradation experiments, input: 0.4 g lignin, 0.1 g RANEY Nickel, 3 g H<sub>2</sub>O.

| <i>t</i><br>Min | <i>T</i><br>K | Solid residue | Phenol | <i>o</i> -Cresol | <i>p</i> -Cresol | Guaiacol               | 4-Methyl-guaiacol | Catechol | 4-Methyl-catechol      | CH <sub>4</sub> | C2-C4 | CO <sub>2</sub> |
|-----------------|---------------|---------------|--------|------------------|------------------|------------------------|-------------------|----------|------------------------|-----------------|-------|-----------------|
|                 |               |               |        |                  |                  | mg/g <sub>Lignin</sub> |                   |          | mg/g <sub>Lignin</sub> |                 |       |                 |
| 30              | 573           | 361,3         | 0,6    | 0,0              | 0,0              | 1,5                    | 0,4               | 1,2      | 0,0                    | 15,3            | 3,1   | 245,7           |
| 30              | 603           | 268,4         | 2,1    | 0,2              | 0,6              | 4,0                    | 1,0               | 1,7      | 1,0                    | 32,4            | 7,6   | 322,8           |
| 270             | 603           | 98,1          | 9,1    | 0,6              | 2,8              | 2,2                    | 0,8               | 3,4      | 1,8                    | 31,7            | 7,3   | 584,4           |
| 1200            | 603           | 1,7           | 12,5   | 0,8              | 7,5              | 0,0                    | 0,3               | n.q.*    | 0,0                    | 34,3            | 11,5  | 533,4           |
| 30              | 633           | 193,3         | 3,8    | 0,3              | 1,3              | 4,0                    | 2,0               | 1,6      | 1,3                    | 39,8            | 9,0   | 510,9           |
| 120             | 633           | 131,9         | 8,8    | 0,7              | 4,4              | 1,1                    | 2,6               | 0,5      | 1,6                    | 48,6            | 9,4   | 389,7           |
| 270             | 633           | 90,6          | 9,6    | 0,7              | 6,2              | 0,1                    | 0,9               | n.q.*    | 0,3                    | 40,1            | 9,1   | 751,2           |
| 30              | 673           | 101,7         | 6,7    | 0,6              | 3,4              | 2,3                    | 1,0               | 7,0      | 3,9                    | 41,0            | 8,1   | 684,7           |
| 270             | 673           | 34,0          | 12,2   | 1,1              | 8,6              | 0,0                    | 0,5               | 0,4      | 0,3                    | 46,1            | 15,8  | 212,5           |
| 1200            | 673           | 0,0           | 8,5    | 0,4              | 10,6             | 0,0                    | 0,8               | n.q.*    | 0,0                    | 67,9            | 19,7  | 773,1           |

\* Not quantified, concentration <100 mg/L.

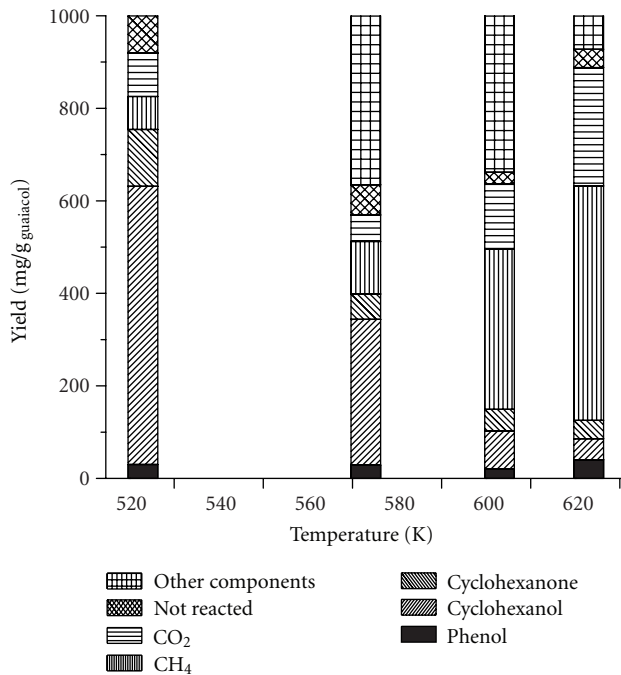
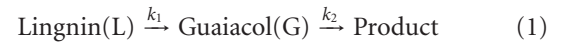


FIGURE 6: Yield of main products from hydrogenation of 10 g/L guaiacol in water with RANEY Nickel and H<sub>2</sub> (1 MPa).

that guaiacol decomposes in water via hydrolysis to form catechol, phenol, and cresol.

The yield of guaiacol within the liquefaction of lignin will depend not only on its degradation to catechol, in principle, but also on the formation of guaiacol from lignin, that is,

the degradation of lignin including the cleavage of C–C and C–O bonds. Kinetics of lignin degradation has been studied by Zhang et al. [14] who proposed that the lignin degradation between 573 and 643 K is terminated after only a few minutes. The following series of reactions is assumed:



The yield of guaiacol ( $C_G/C_{L,0}$ ) is thus calculated using the following equation:

$$\frac{C_G}{C_{L,0}} = \frac{k_1}{k_2 - k_1} (e^{-k_1\tau} - e^{-k_2\tau}). \quad (2)$$

Assuming that  $k_2 \ll k_1$  at the realized reaction conditions, the yield of guaiacol will be independent from  $k_1$  for a large range of temperatures and can be described by the following equation:

$$\frac{C_G}{C_{L,0}} = e^{-k_2\tau}, \quad k_2 \approx k_2. \quad (3)$$

The experimentally determined yield of guaiacol can thus be fitted by assuming a first-order reaction that is, the logarithm of the yield displayed in Figure 7 decreases proportionally with increasing reaction times. The values of the reaction rate  $k_2'$  for temperatures between 603 K and 633 K the activation energy ( $EA'$ ), and values for  $k_0'$  were calculated from the guaiacol yields obtained from experiments with lignin. The apparent activation energy  $EA'$  was found to be around 170 kJ/mol, which is slightly below the values that can be found in the literature (236 kJ/mol  $\pm$  19 kJ/mol [26]) for the pyrolytic degradation of guaiacol as well as for the

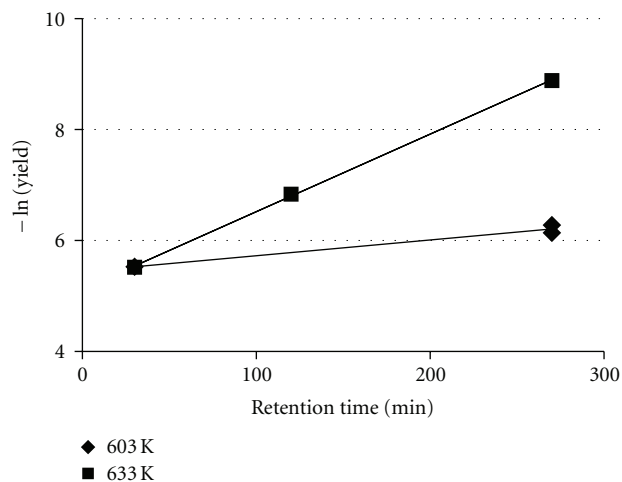


FIGURE 7: Guaiacol yield after hydrothermal treatment of lignin with RANEY Nickel.

TABLE 5: Apparent Arrhenius parameters of a first order degradation of guaiacol by pyrolysis and hydrothermal treatment in subcritical, near critical and supercritical water.

|                          | EA<br>kJ/mol | EA'<br>kJ/mol | Log<br>( $k_0/\text{min}^{-1}$ ) | Log<br>( $k'_0/\text{min}^{-1}$ ) |
|--------------------------|--------------|---------------|----------------------------------|-----------------------------------|
| Pyrolysis [26]           | 236 ± 19     |               | 17.4 ± 0.4                       |                                   |
| Near critical water      |              | 170 ± 12      |                                  | 12.2 ± 0.8                        |
| Subcritical water [15]   | 33.4         |               | 0.07                             |                                   |
| Supercritical water [15] | 39.35        |               | 1.5                              |                                   |

bond energy of the C–O bond in a monomeric guaiacyl structure ( $268 \pm 8$  kJ/mol [27]). The values of activation energy found in literature for hydrolytic degradation of guaiacol are significantly lower (see Table 5). However, the determined values of the reaction rates complement those determined by Wahyudiono et al. [15]. The development of the reaction rate (see Figure 8) reveals that in the range of the critical temperature of water a change of the reaction mechanism occurs. In the same range of temperatures the relative permittivity of water changes dramatically.

The apparent kinetic data of guaiacol degradation in near critical water is comparable with that of pyrolysis (see Figure 8). That implies a change of the reaction mechanism from hydrolysis at subcritical temperatures to radical-induced degradation at near and supercritical temperatures. A similar change of reaction mechanisms was already found for the degradation of glycerol in near and supercritical water [28].

#### 4. Conclusions

Conversion of lignin and intermediate compounds (guaiacol, catechol) in near critical water at the presence of a RANEY Nickel catalyst and the yields of monoaromatic and gaseous components as well as the yield of solid residues were experimentally determined. RANEY Nickel promotes the

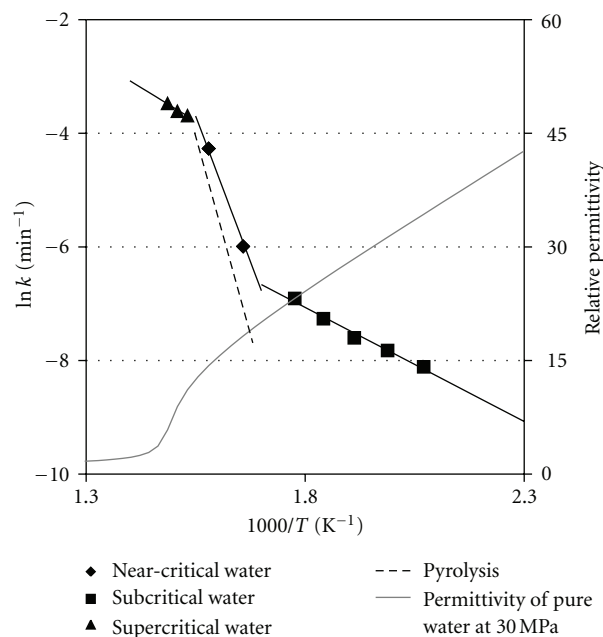


FIGURE 8: Arrhenius plot of guaiacol degradation in near critical water compared with experimental values from experiments in sub- and supercritical water and via pyrolysis.

gasification of the studied substances at high temperatures and catalyses the hydrodeoxygenation of catechol and guaiacol at low temperatures. Furthermore, it suppresses the char formation. It has no direct influence on the breaking of the molecular structure of lignin. The latter requires high temperatures. It is possible to increase the yield of phenol from lignin in near-critical water by adding a RANEY Nickel catalyst. However, most of the lignin is then gasified, also a part of the phenolic components.

Hence, concerning the recovery of phenol from lignin, a two step process should be taken into consideration for further research. The first step would be a high-temperature reaction ( $\geq 673$  K) at relative short reaction times ( $< 30$  min) which enables the depolymerisation and the formation of catechol, but suppresses the formation of char and partially that of gaseous components. The kinetic studies showed that especially in the near-critical region of water the kinetic factor of guaiacol degradation increases significantly. In order to avoid methoxylated phenols, for example, guaiacol, and promote the production of dihydroxybenzenes, for example, catechol, the first step should therefore be conducted in near or supercritical water. The second reactor should be a fixed-bed reactor that works at around 523 K where intermediate products from the first reactor, that is, catechol, are transformed into higher-value aromatics, for example, phenol, on a RANEY Nickel catalyst. The experimental results showed that at 523 K catechol can be transformed into phenol with relatively high selectivity. At these mild conditions the formation of char and gas can be restrained.

The kinetics of the degradation of guaiacol within the hydrothermal liquefaction of lignin followed a model for a first-order reaction. Within the assumed model kinetics

of the formation of guaiacol could be neglected. Hence the kinetics of the cleavage of ether bonds present in the molecular structure of lignin is not of critical importance if the recovery of phenol from lignin is the focus of the research. It is proposed that the mechanism for the hydrothermal degradation of guaiacol switches from hydrolysis to radical induced in the near-critical region.

## Disclosure

It is disclosed that none of the authors has a direct financial relation to commercial identities mentioned in the paper.

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