



# Effect of Process Variables on the Solvolysis Depolymerization of Pine Kraft Lignin

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## Abstract

Lignin modification opens the possibility of using it in polyol bio-based polymers, such as phenol–formaldehyde resins, polyurethanes, composites, and binders. Pine kraft lignin Indulin AT was partially depolymerized and the resulting products analyzed to determine their degree of valorization. Depolymerized lignin products were analyzed by GPC-SEC (molar mass),  $\Delta\epsilon$ -IDUS (phenolic hydroxyls), HACL (formaldehyde uptake), <sup>13</sup>C-NMR (hydroxyl and methoxyl groups), and <sup>1</sup>H-DOSY (molar mass distribution). The dominant parameter in lignin depolymerization by solvolysis was reaction temperature. According to the results, a higher reaction temperature decreases the average molar masses and PDI of lignin as well as the primary and secondary aliphatic hydroxyls, while simultaneously increasing the phenolic hydroxyls and formaldehyde uptake of lignin. Other variables (time, formic acid wt %, ethanol wt %, lignin load) had lesser effects. Partial depolymerization by solvolysis in mild conditions without catalyst is a viable valorization route for lignin, by which lignin properties can be significantly improved.

**Keywords** Lignin · Solvolysis · Depolymerization · Formic acid

## Statement of Novelty

This work was undertaken to determine the most critical process variables which influence the activation of lignin by solvolysis. With this knowledge, the critical variables can be optimized.

## Introduction

The increasing environmental and political stress related to the valorization of fossil-derived feedstocks opens up an opportunity to use bio-derived resources for the production of value-added chemicals. Lignocellulosic or woody biomass has the potential to be used as a renewable and alternative bioresource for the production of fuels and

chemicals, which have conventionally been produced from fossil-derived feedstocks [1]. Biorefineries rely on lignocellulosic biomass and utilize the easily convertible fractions of lignocellulose: cellulose and hemicellulose [2]. Lignin is the second most abundant polymer in nature and accounts for up to 10–25% of lignocellulosic biomass. Lignin is available in the market mainly as a byproduct from pulp and paper production, as well as a waste stream from second-generation bioethanol production. Lignin is remarkably underutilized in biorefineries, despite the fact that the lignin molecules could be broken into numerous valuable chemicals through bio- and chemo-catalytic treatment [3, 4]. The main reason for lignin underutilization is its recalcitrance, i.e. its resistance to physical and chemical treatments. Lignin can be theoretically depolymerized to monophenols; however, this is a very energy-intensive process with high temperatures and pressures. Even without taking into account the energy requirements, the formation of recondensation products (such as char) would need to be minimized. Therefore, in order to improve lignin utilization, a techno-economically viable process needs to be developed to valorize lignin. Lignin is an amorphous polyphenolic material with a complex and heterogeneous polymeric structure. Lignin molecules are

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comprised of three phenylpropanoid monomers, namely coniferyl, sinapyl, and *p*-coumaryl alcohol [5].

The reactivity of lignin can be increased by chemical and thermal modification techniques such as demethylation, methylation, and phenolation [6]. Additionally, alkaline depolymerization of lignin has been tested with NaOH/Urea solutions, yielding a product with increased phenolic hydroxyls [7]. Metal-catalyzed (heterogeneous) oxidative solvolysis of lignin was studied by Ouyang et al. [8] using H<sub>2</sub>O<sub>2</sub> as oxidant, where they achieved an 18% yield of monophenols when using methanol and water as co-solvents.

Lignins can repolymerize (recondense) during depolymerization by depletion of ether bonds and increase in carbon–carbon bonds [9]. In the presence of hydrogen, these repolymerization reactions could be capped. Formic acid can be used as an in-situ hydrogen-donor source since its thermal decomposition yields molecular hydrogen [9, 10]. Formic acid has been used together with alcohols in lignin solvolysis to obtain low-oxygen “bio-oils” [11, 12].

Partial depolymerization by solvolysis of lignin in sub- and supercritical conditions in the presence of hydrogen-donor solvents (to cap recombination reactions) has also been employed to reduce the steric hindrance associated with the lignin molecules [13, 14]. An ethanol–water mixture can be utilized as the solvolysis nucleophilic solvent [13]. Instead of aiming for monophenols, a milder (partial) depolymerization can be pursued, where the targets are mostly the  $\beta$ -ethers (mostly  $\beta$ -O-4 linkages) [15].

Valorized lignin can be used in a variety of applications. Lignin can be used as a phenol replacement in phenol–formaldehyde resins (PFRs) [16]. PFRs are widely used in various applications including industrial coatings, insulation, lamination, wood bonding, and most importantly plywood adhesives [5, 17]. In polyurethanes, lignin can be used as a polyol precursor for cross-linking due to its polyphenolic structure and abundance of aliphatic hydroxyl groups [18]. Polyurethanes have a myriad of applications, including foams, coats, membranes [19], and even medical applications like bone repair [20]. Additionally, lignin can also be used in composites [21], binders [22], and as a carbon fiber precursor [23].

Nuclear magnetic resonance (NMR) spectroscopy is a versatile method to characterize complex materials. It is also commonly used to analyze different types of hydroxyl groups (phenolic, aliphatic, carboxylic) in lignins. With NMR, it is possible to quantify the amount of both aliphatic ( $\alpha$ -OH,  $\beta$ -OH) and phenolic (OH<sub>ph</sub>) hydroxyl groups. The NMR methods usually require preparation and derivatization of the lignin samples, like acetylation and phosphorylation [24–26]. There has also been attempts to analyze lignin without modifications using plain DMSO-*d*<sub>6</sub> solvent [27]. NMR is also one of very few methods for measuring diffusion of molecules without tracers. The diffusion coefficients

of molecules are related to hydrodynamic radius and molecular weights [28–30]. Two-dimensional diffusion ordered spectroscopy (DOSY) has been utilized to study solution state structures and organization of small organic molecules, organometallic aggregates, and macro-molecules [31–33]. Johnson et al. [34] determined the weight distribution of polymers by DOSY. Furthermore, DOSY makes it possible to measure the polydispersity index (PDI) of linear polymers [35], and it has been exploited in the analysis of molecular weights of natural organic matter [36, 37] as well as lignin and its model compounds [38].

The purpose of this investigation was to determine the effects of process variables on partial depolymerization of kraft lignin (Indulin AT) under solvolysis conditions, particularly on its molar mass, phenolic hydroxyl (OH<sub>ph</sub>) content, and formaldehyde uptake capabilities. The effects were detected using various advanced analysis techniques, including NMR and ultraviolet spectrophotometry, as well as size–exclusion chromatography. By depolymerizing lignin, a decrease in molar mass can be obtained, as well as an increase in the OH<sub>ph</sub> content [39], which could be favorable for the production of bio-based polymers.

## Materials and Methods

### Lignin Solvolysis

Indulin AT pine kraft lignin was procured from Meadwestvaco Specialty Chemicals, ethanol absolute and acetone from VWR Chemicals, and formic acid 98–100% from Merck. Ultrapure water was produced using a Type 1 Milli-Q water system from Millipore Corporation.

Depolymerization of Indulin AT by solvolysis was carried out in semi-micro autoclave steel reactors with maximum volume capacity of 10 mL. Each reactor was closed with a screw cap equipped with a thermowell. Spiral wound gaskets (stainless steel/graphite) were utilized to provide the seal between the reactor body and the reactor cap. The caps were tightened first finger-tight and then slightly tighter with a wrench to provide a good seal.

For the depolymerization by solvolysis, 0.25 g of Indulin AT lignin were fed to the reactor, after which 4.81 mL of 50 wt% ethanol were added (2.69 mL of absolute ethanol and 2.12 mL of ultrapure water). Following the addition of aqueous ethanol, 0.183 mL of formic acid were added. The final solvent volume was approximately 5 mL with 5 wt% formic acid. The final solid-to-liquid ratio was 50  $\frac{\text{g}_{\text{Lignin}}}{\text{L}_{\text{solvent}}}$ .

The reactors were preheated in an electric ceramic block heater with wall temperature of about 400–450 °C until the required temperature was reached. The reactors were then carefully moved to a constant-temperature fluidized sand-bath (Techne fluidized sand bath SBL 2D). The reactors

were placed in the sandbath inside a stainless-steel meshed cage (to allow the fluidized sand to be contact with the reactors). The reactor caps were kept above the sand and the thermocouple electric connections outside the dome of the sandbath. The reaction time was measured from the moment the reactor reached the desired temperature, i.e. when it was moved from the preheater to the sandbath. Preliminary experimentation on a 500 mL batch autoclave reactor had revealed the maximum reactor pressure to be between 80 Bar (at 250 °C) and 150 Bar (at 315 °C), thus the liquid volume in the semi-micro reactors was fixed to 5 mL to reduce the risk of leaks and explosion.

After the reaction time, the reactors were quenched in a chilled water container. When the reactors had reached an inner temperature of less than 40 °C, they were carefully opened inside a fumehood. About 10 mL of acetone were fed to each reactor and the contents stirred with a spatula, after which the contents of the reactor were poured into a 50 mL beaker. In order to decrease mass loss, an additional 10 mL of acetone were added to the reactor, stirred, and moved to the beaker. This procedure was done for each reactor and its corresponding beaker. The beakers were dried overnight (about 18 h) at 65 °C for total solvent evaporation and were subsequently moved into desiccators to cool down. After drying and cooling, the solid product was scraped off with a metal spatula and transferred to glass vials for analysis.

### Formaldehyde Uptake and Hydroxylamine Hydrochloride Method

The formaldehyde reactivity of lignin was determined by an alkaline formaldehyde-lignin reaction followed by a free-formaldehyde determination, based on the methods described by Wooten et al. [40] and El Mansouri et al. [41]. The final titration was based on the hydroxylamine hydrochloride (HACL) method ISO 9197 [42]. Formaldehyde 36% (with 10% methanol), NaOH, and isopropanol were procured from VWR Chemicals. Methanol absolute and HCl were obtained from Merck, and hydroxylamine hydrochloride 100 g/L from HACH. Ultrapure water from a Type 1 Milli-Q water system from Millipore Corporation was used for the aqueous mixtures.

For each analysis, a sample of 100 mg of lignin was placed in a 35 mL cylindrical vial with a PTFE screw cap, after which 2.5 mL of 40 vol % methanol were added. Following the methanol, 100 µL of 36% formaldehyde (equivalent to 38 mg of formaldehyde) and 50 µL of 10 M NaOH (equivalent to 20 mg of NaOH) were added. A magnetic stirrer was added to the vial. The vial was closed and placed in a Labnet 1550 Vortemp incubator and the lignin reaction with formaldehyde was carried out for 4 h at 50 °C and 60 RPM. After the 4 h were completed, the vial was removed from the incubator and allowed to cool for 5 min,

after which 5 mL of 75 vol % isopropanol were added to the vial. The vial was slightly agitated by hand and allowed to cool to room temperature. The pH of the mixture at this point (measured with a VWR pHenomenal PC 5000 H pH meter) was around 12.1–12.5.

The pH of each solution was adjusted to 3.5 with 0.1 M HCl. About 4.1–4.8 mL of 0.1 M HCl were utilized in every case. For each free-formaldehyde determination, 2.5 mL of 100 g/l HACL were added to the vial under magnetic stirring. After 10 min of reaction at room temperature, the solution was titrated with 0.1 M NaOH until the pH of 3.5 was obtained again. The titration was carried out with the help of a Metrohm 776 Dosimat equipped with a Metrohm 728 Stirrer. The same procedure was repeated for the blank solution (without lignin). The amounts of 0.1 M NaOH in the analyses varied between 10.5 and 12.8 mL (the highest amounts corresponding to the blanks).

The HACL method ISO 9397 [42] is based on the reaction of formaldehyde and hydroxylamine hydrochloride at room temperature in acidic conditions, where HCl is released as one of the products (Eq. 1). The released HCl is determined by titration and thus the free formaldehyde can be indirectly determined by the sodium hydroxide equivalents used in the titration.



To determine the formaldehyde uptake, the amount of free formaldehyde can be calculated from the NaOH milliequivalents (in mmol) as depicted in Eqs. 2–5.

$$\begin{aligned} n[\text{mmol}] &= V_{\text{NaOH}}[\text{mL}] \cdot M[\text{mmol/mL}] \\ &= meq_{\text{NaOH}}[\text{mmol}] = meq_{\text{HCl}}[\text{mmol}] \end{aligned} \quad (2)$$

$$m_{\text{sample}}[\text{mg}] = n_{\text{sample}}[\text{mmol}] \cdot 30.031[\text{mg/mmol}] \quad (3)$$

$$m_{\text{blank}}[\text{mg}] = n_{\text{blank}}[\text{mmol}] \cdot 30.031[\text{mg/mmol}] \quad (4)$$

$$F[\text{mg/g}_{\text{Lignin}}] = (m_{\text{blank}}[\text{mg}] - m_{\text{sample}}[\text{mg}]) / m_{\text{Lig}}[\text{g}] \quad (5)$$

where  $n$  is the free formaldehyde obtained through the milliequivalents  $meq$  of the titration volume of NaOH  $V_{\text{NaOH}}$  for the *sample* or *blank*,  $m$  is the mass of free formaldehyde  $m_{\text{sample}}$  and  $m_{\text{blank}}$  in the sample and blank respectively,  $m_{\text{Lig}}$  is the mass of lignin (0.1 g),  $F$  is the formaldehyde uptake of lignin, and  $M$  is the molarity of the titration solution (0.1 M). The molar mass of formaldehyde is 30.031.

### GPC Analysis

The molecular weight distributions of the depolymerized lignin samples were measured by size exclusion chromatography (SEC), namely gel permeation chromatography (GPC). An Agilent 1260 series chromatograph equipped

with Phenogel 5  $\mu\text{m}$   $10^3$  Å and Phenogel 5  $\mu\text{m}$  50 Å columns (Phenomenex) was used. Dimethylformamide (DMF) with 0.5 wt% LiBr was used as the mobile phase with a flow rate of 0.05 ml/min. The columns were operated at 35 °C. Detection was carried out using a variable wavelength detector (UV) at a wavelength of 280 nm. The calibration was done with polyethylene oxide (polyethylene glycol) standards (EasyVials PEO/PEG, Agilent Technologies) which were analyzed using the refractive index detector RID. For the sample preparation, lignin was dissolved at a concentration of 1 g/L in the mobile phase solvent (DMF with 0.5 wt% LiBr). After dissolution, the samples were filtered through 0.45  $\mu\text{m}$  PTFE syringe filters. DMF dissolves several polymer types, thus the filtering time (residence time in the syringe) had to be minimized to avoid dissolution of the syringes, which would cause interference in the chromatograms. The filtration was carried out under a fumehood and each syringe was used only once. The used syringes were disposed of according to laboratory safety procedures.

The chromatograms were normalized to 100 relative absorption units (RAU) using the maximum value of absorption as per Eq 6.

$$RAU_i = (100/AU_{\max}) \cdot AU_i \quad (6)$$

where  $RAU_i$  is the relative absorption value at molar mass  $i$ ,  $AU_{\max}$  is the maximum value of absorption in the sample, and  $AU_i$  is the absorption value at molar mass  $i$ .

Molar masses and polydispersity were calculated as follows (Eqs. 7–9).

$$M_n = \sum AU_i / \sum (AU_i/M_i) \quad (7)$$

$$M_w = \sum (AU_i M_i) / \sum AU_i \quad (8)$$

$$PDI = M_w/M_n \quad (9)$$

where  $M_n$  and  $M_w$  are the number- and mass average molar masses respectively,  $AU_i$  is the value of absorption units at a corresponding molar mass  $M_i$  for a specific data point  $i$ , and  $PDI$  is the polydispersity.

## $\Delta\epsilon$ -IDUS Analysis

Analysis of phenolic hydroxyl groups was carried out by Ultraviolet (UV) Spectrophotometry using a revised version of the previously reported  $\Delta\epsilon$ -IDUS method [43]. The samples were analyzed using quartz cuvettes with a 1 cm path-length in a Shimadzu 1800 double-beam spectrophotometer at wavelengths 300 and 360 nm. For each measurement, the reference cuvette contained the sample in a neutral (pH 6) solution and the sample cuvette contained the sample in the alkaline (pH 12 or 13.3) solution. The absorbance of

each sample is the so-called *difference absorbance* ( $\Delta A$ ), making it four  $\Delta A$ s in total for each sample, two per alkalinity level (pH 12 and 13.3) and two per each wavelength (300 and 360 nm). The measurements were done with three lignin concentrations for each sample: 20, 40, and 60 mg/L, for a total of 12 measurements (12  $\Delta A$  values) per sample. The *difference mass absorptivities*  $\Delta a$  (L/g-cm) were calculated as the slope of a plot of concentration versus  $\Delta A$  with zero intercept for each combination of pH level, wavelength, and lignin concentration, yielding a total of four  $\Delta a$  values per sample. The  $\Delta a$  values were used to calculate the phenolic hydroxyl group content with the equations previously reported.

## Upscaling

The procedure to depolymerize lignin by solvolysis was upscaled to a 1 L stainless steel Autoclave Engineers Inc. reactor. The temperature was set to 250 °C, the time to 2 h, the lignin load to 50 g/L, and the total solvent to 700 mL. The reactor was equipped with an impeller mixer, heating jacket, water-cooling coil, pressure indicator, and temperature controller. No leaks were detected under these conditions during the experiments. After the reaction, the reactor was quenched using the water-cooling coil. The reactor was then opened and the liquid product was poured into a drying tray. The tray was placed inside an oven at 65 °C overnight for total solvent evaporation. The dried products were carefully scraped off the tray and the resulting powder was thoroughly mixed in a container.

Normally, it is expected that an upscaled process will be less efficient than a micro or semi-micro process due to mass transfer limitations and dead zones. However, in this case, the upscaled reactor had a mixing impeller, which was expected to bring the performance of the reactor closer to the performance of semi-micro experiments. The upscaled process conditions for the macro (1 L) reactor compared to its semi-micro (10 mL) counterpart can be seen in Table 1.

## Acetylation of Upscaled Reactor Samples

Prior to the  $^{13}\text{C}$ -NMR analysis, samples were acetylated with a mixture of pyridine and acetic anhydride ( $\text{Ac}_2\text{O}$ ) catalyzed with perchloric acid ( $\text{HClO}_4$ ).  $\text{Ac}_2\text{O}$ ,  $\text{HClO}_4$  (60 wt%) and pyridine were procured from VWR Chemicals. The acetylating solution was prepared with 1:1 (vol:vol) acetic anhydride and pyridine. A volume of 10 mL of acetylating solution was used for each lignin sample of 1 g. The acetylation solution was prepared by adding first the  $\text{HClO}_4$  to the pyridine and then adding the  $\text{Ac}_2\text{O}$  to the mixture. A volume of 100  $\mu\text{L}$  of 60% perchloric acid were added per 10 mL of solution (5 mL  $\text{Ac}_2\text{O}$ , 5 mL pyridine). The reaction was carried out in Erlenmeyer flasks with stoppers under stirring at room

**Table 1** Parameters of the macro and semi-micro reactors

Parameters	Semi-micro	Macro
Temperature (°C)	250	250
Heating time (min)	15	30
Reaction time (h)	2	2
Cooling time (min)	15	30
Ethanol (wt%)	50	50
Formic acid (wt%)	5	5
Lignin load (g/L)	50	50
Reactor volume (mL)	10	1000
Lignin mass (g)	0.25	35
Solvent volume (mL)	5	700
Mixing (RPM)	–	300

temperature for 4 days under darkness. After acetylation, the acetylated solutions were precipitated with 100 mL of a pH 2 precipitation solution. The precipitation solution was made with 83.5  $\mu$ L of 12 M HCl per 100 mL of solution. An ice bath was set up for the precipitation beaker and a magnetic stirrer was added. The precipitation solution was at about 1–3 °C before adding the lignin solution. The acetylated lignin solution was added dropwise into the precipitation solution under constant stirring. The solution was then filtered through a 1.2  $\mu$ m fiberglass filter in a Büchner funnel and the precipitate was allowed to dry at room temperature for 24 h under a fume hood. The samples were subsequently freeze-dried under vacuum overnight.

### <sup>13</sup>C-NMR Analysis of Upscaled Lignin Samples

To prepare samples for NMR measurements the freeze-dried lignin was accurately weighed out into a 2 ml vial (~90–120 mg). A standard solution of trioxane in DMSO-d<sub>6</sub> was prepared by carefully weighing out the trioxane (126.2 mg) and adding 4.0 mL of DMSO-d<sub>6</sub>. From the standard, 600  $\mu$ L were added to the lignin vial yielding ca. 200 mg/mL of lignin solution. The prepared solution was dark brown, without insoluble fractions.

NMR measurements were carried out on 14.1 T Bruker Avance III 600 spectrometer equipped with a 5-mm broadband (BB) probe operating at 150.9 MHz for carbon. Experiments were conducted at room temperature. Quantitative <sup>13</sup>C spectra were recorded using inverted gate proton decoupling sequence (Bruker standard sequence “zgig30”). The number of scans was 9000, relaxation delay was 36 s (at least five times T<sub>1</sub>) and the excitation pulse angle was 30°. The positions of the peaks were referenced to the residual solvent peak (DMSO-d<sub>6</sub> at 39.5 ppm for <sup>13</sup>C).

<sup>1</sup>H DOSY spectra were collected from 4096 scans using bipolar gradients and longitudinal eddy current delay. The gradient length and diffusion time were varied for each

**Table 2** Value of constant process conditions for each variable in semi-micro reactors

Variable	T (°C)	t (h)	EtOH (wt%)	HCOOH (wt%)	Lig (g/L)
Temperature	200–300	4	50	5	50
Time	250	2–6	50	5	50
Ethanol	250	4	40–70	5	50
Formic acid	250	4	50	3–9	50
Lignin load	250	4	50	5	50–150

sample in order to achieve 98% signal suppression at the maximum gradient strength. The length of the sine-shaped gradient pulses was set to 1.5 ms for M250C sample and 1.7 ms for I2C sample, and the gradient amplitude ranged from 1.05 to 55.6 G/cm in 32 increments. The diffusion time was 90 ms for M250C and 125 ms for I2C. CONTIN analysis was carried out using the Topspin 3.5 version with 8192 data points in the <sup>1</sup>H dimension and 32 data points in the diffusion dimension. PC (noise sensitivity factor) was set to 1 for each sample to ensure that all signals were included in the calculations.

## Results and Discussion

### Lignin Solvolysis in Semi-Micro Reactors

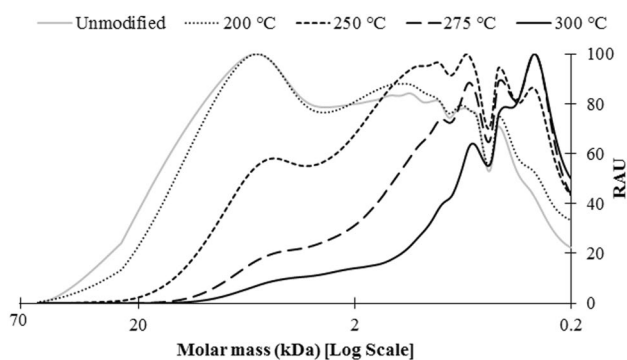
In order to assess the effect of process conditions, each variable was studied while keeping all other variables constant according to Table 2. The mass recovery of the reactors was an average of 63 wt% (50 wt% min, 81 wt% max). There was no clear pattern between process variables and mass loss, thus the mass loss was likely caused by material handling while transferring the products from the reactors to the drying beakers and subsequently to the sample vials.

The main indicators of the quality of the partially depolymerized lignin were molar mass distribution, phenolic hydroxyl group content, and formaldehyde uptake of lignin.

### Effect of Process Variables

Four different solvolysis temperatures were tested: 200, 250, 275 and 300 °C. Figure 1 shows the molar mass distribution of depolymerized lignin products at different temperatures, as reported by GPC analysis. The trend indicates a clear shift toward lower molar mass molecules as the temperature increases. It is apparent that process temperature had a significant influence on the extent of depolymerization of Indulin AT.

Average molar masses were lower at all temperatures in comparison to the original Indulin AT (Fig. 2a, b), with



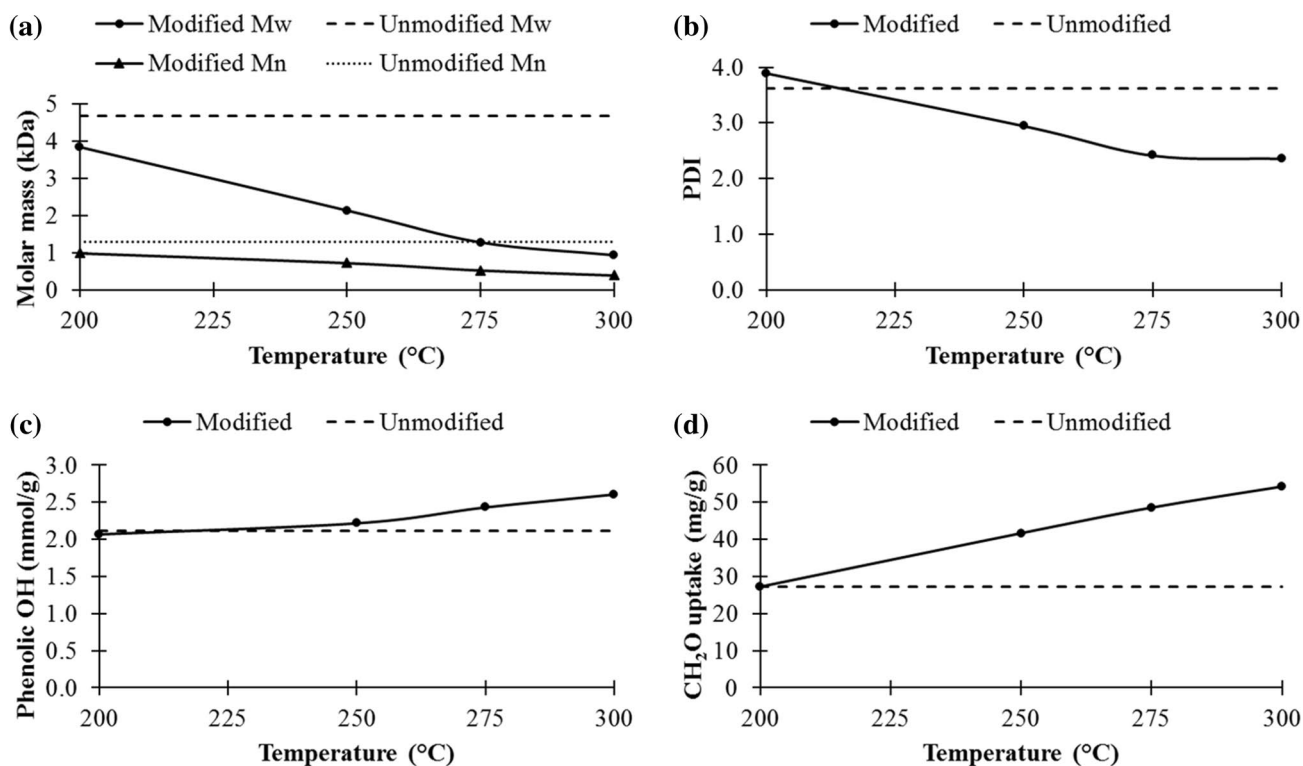
**Fig. 1** Temperature effect on molar mass distribution of lignin (see Table 2 for conditions)

the lowest average molar masses achieved at the maximum temperature of 300 °C. However, at 200 °C, the distribution and the polydispersity were nearly identical to the original lignin. At 250, 275, and 300 °C there was a clear decrease in all average molar mass indicators, including polydispersity. This suggests that not only was the lignin being depolymerized into smaller molecules, but also the distribution was becoming narrower.

The phenolic hydroxyl group content in the lignin was determined by  $\Delta\epsilon$ -IDUS, explained in Sect. " $\Delta\epsilon$ -IDUS

Analysis". It can be seen in Fig. 2c that the phenolic hydroxyls increased with increasing temperature. A higher content of phenolic hydroxyl groups would allow the lignin to better bond with formaldehyde in the production of LPF resins. This was evidenced by the marked increase in the formaldehyde uptake capability of depolymerized lignin at the temperatures higher than 200 °C (Fig. 2d). At 200 °C, however, the formaldehyde uptake showed no significant improvement. The experimental variation in the results was estimated to be approximately 10% for molar mass, 17% for PDI, 6% for phenolic OH, and 9% for  $\text{CH}_2\text{O}$  uptake (C.I. 95%).

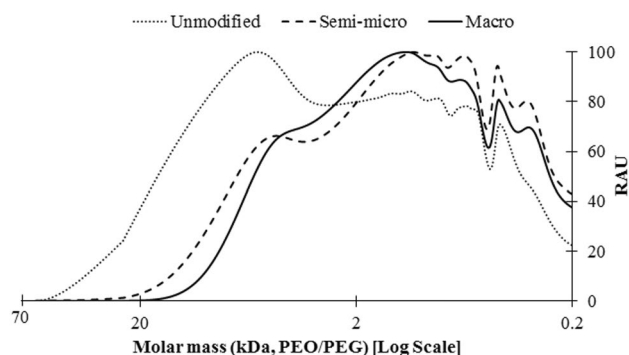
The effects of time, lignin load, ethanol concentration, and formic acid concentration on lignin solvolysis were not substantial according to the results. It appeared that a higher concentration of ethanol increased the formaldehyde uptake; however, this could be attributed to experimental variation. Although there was a decrease in average molar mass in all cases when compared to the unmodified lignin, there was no significant difference in molar mass distribution between the modified samples. Additionally, within the tested ranges, there were no significant differences in average molar mass, polydispersity, phenolic hydroxyl groups, or formaldehyde uptake. Detailed results can be seen in Table 3.



**Fig. 2** Effect of solvolysis temperature on **a** average molar mass, **b** PDI, **c** phenolic OH content, **d** formaldehyde uptake. *M<sub>w</sub>* mass average molar mass. *M<sub>n</sub>* number average molar mass

**Table 3** Detailed results from semi-micro solvolysis experiments

Temp (°C)	Time (h)	Lig. load (g/L)	Ethanol (wt%)	Formic ac. (wt%)	M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI	OH <sub>ph</sub> (mmol/g)	Formaldehyde (mg/g)
200	4	50	50	5	3836	986	3.89	2.07	27.2
250	2	50	50	5	2260	767	2.95	2.39	43.4
250	4	50	40	5	2058	694	2.97	2.15	44.4
250	4	50	50	3	2092	718	2.91	2.26	38.1
250	4	50	50	5	2132	724	2.95	2.22	41.7
250	4	50	50	7	2185	728	3.00	1.98	38.2
250	4	50	50	9	2204	698	3.16	1.96	41.8
250	4	50	60	5	2207	724	3.05	2.00	59.3
250	4	50	70	5	2090	723	2.89	2.03	53.5
250	4	100	50	5	2174	719	3.03	2.57	53.1
250	4	150	50	5	2425	767	3.16	2.29	42.8
250	6	50	50	5	2023	681	2.97	2.11	34.5
275	4	50	50	5	1274	527	2.42	2.43	48.6
300	4	50	50	5	929	393	2.36	2.60	54.3

**Fig. 3** Upscaling effect on molar mass distribution of lignin (see Table 1 for conditions)

### Lignin Solvolysis in 1 L Reactor

It was desired to upscale a promising set of process conditions from semi-micro reactor level (10 mL) to a macro reactor (1 L) level. The temperature of 250 °C was chosen due to it being an easily reachable temperature with our experimental setup. Additionally, even at 250 °C, there was not

only a significant decrease in the average molar masses and PDI, but also an increase in phenolic hydroxyl groups and formaldehyde uptake capability. Given that there had been no significant improvement in the lignin properties between 2 and 4 h in the semi-micro setup, the time was set to 2 h.

As can be seen from Fig. 3, the distribution appeared to be narrower in the macro experiment than in the semi-micro experiment at the same conditions. The macro reactor solvolysis lignin had virtually no molecules over 20 kDa, while the semi-micro contained molecules between 20 and 70 kDa. The number average molar masses  $M_n$  of both macro and semi-micro modified lignins was about 0.8 kDa compared to the about 1.3 kDa from the unmodified Indulin AT. However, the mass average molar masses  $M_w$  were dissimilar. The unmodified lignin had an  $M_w$  of 4.67, the semi-micro reactor lignin had an  $M_w$  of 2.62, and the macro reactor lignin had an  $M_w$  of 1.95. This is due to the *mass average molar mass* being significantly more sensitive to larger molecules than the *number average molar mass* (see Eqs. 6 and 7 in Sect. "GPC Analysis"). Detailed results can be seen in Table 4.

**Table 4** Comparison between solvolysis at semi-micro and macro scales (conditions in Table 1)

	Unmodified	Semi-micro	Macro
M <sub>w</sub> (kDa)	4.67	2.62	1.95
M <sub>n</sub> (kDa)	1.29	0.80	0.77
PDI	3.63	3.26	2.49
OH <sub>ph</sub> IDUS (mmol/g)	2.12 ± 0.12 (95%)	2.40 ± 0.15 (95%)	2.59 ± 0.16 (95%)
OH <sub>ph</sub> NMR (mmol/g)	4.1 ± 0.3 (95%)	–	4.8 ± 0.5 (95%)
CH <sub>2</sub> O (mg/g)	26.9 ± 2.4 (95%)	44.1 ± 3.9 (95%)	31.8 ± 2.7 (95%)

There was a marked increase in  $\text{OH}_{\text{ph}}$  between the unmodified Indulin AT and the semi-micro reactor lignin, a 13% increase. The macro reactor solvolysis lignin had a 22% increase in  $\text{OH}_{\text{ph}}$  when compared to the unmodified Indulin AT lignin. However, this discrepancy could be attributed to the experimental error, given that the semi-micro reactor lignin had a  $\text{OH}_{\text{ph}}$  range of 2.25–2.50 mmol/g, and the macro reactor lignin 2.43–2.75 mmol/g.

The formaldehyde uptake was greater in both semi-micro and macro reactors when compared to the unmodified lignin. Surprisingly, the macro reactor lignin had a lower formaldehyde uptake capability than the semi-micro reactor lignin. This suggests that despite the macro solvolysis lignin having about the same amount of  $\text{OH}_{\text{ph}}$  as the semi-micro solvolysis lignin, the upscaled solvolysis lignin had less active sites available for formaldehyde to react. Formaldehyde is able to react with phenolic structures in neighboring sites to the phenolic hydroxyl ( $-\text{OH}$ ) [44]. In lignin, those neighboring sites can be occupied by methoxyl groups ( $-\text{OMe}$  or  $-\text{OCH}_3$ ) as previously reported [43]. Thus, there were likely more of these aromatic methoxyl groups in the macro reactor lignin than in the semi-micro reactor lignin.

### NMR Analysis of Upscaled Reactor Samples

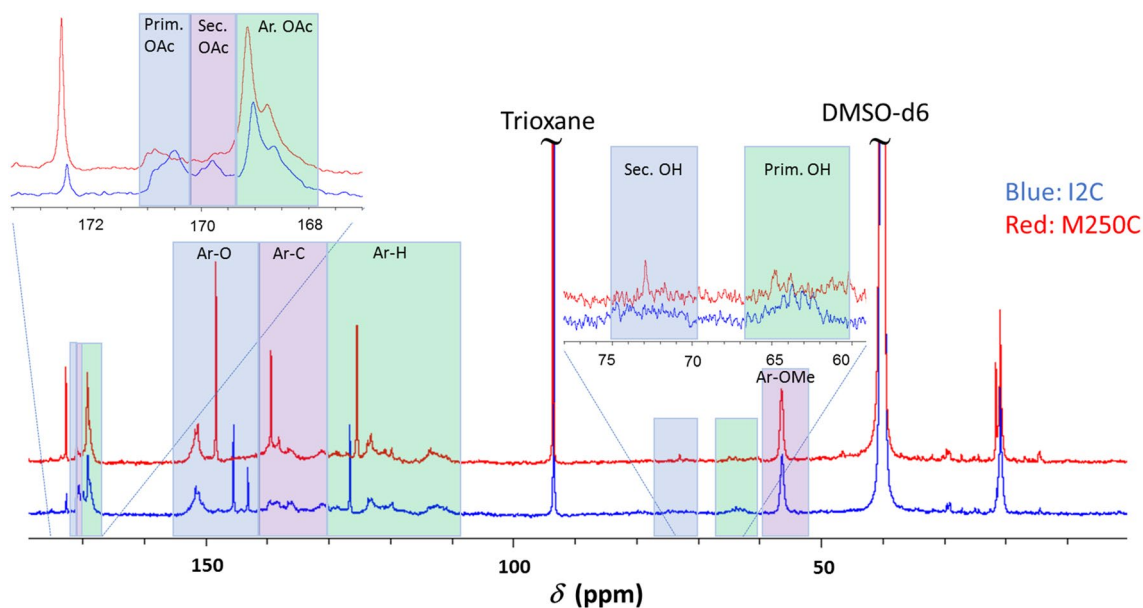
Two unmodified Indulin AT samples (denoted I1, I2) as well as two corresponding samples after the modification in a 1 L reactor at 250 °C (denoted by M250) were acetylated with and without perchloric acid catalyst (use of catalyst is denoted by C). The quantitative  $^{13}\text{C}$  spectra of I2C and

M250C samples are shown in Fig. 4. A sharp signal for the trioxane internal reference was visible at 94 ppm.

The signals of acetylated hydroxyl groups (OAc) were observed between 168–171 ppm. The signals were assigned to phenolic (ph) OAc (168–169 ppm), secondary ( $\beta$ ) OAc (169–170 ppm) and primary ( $\alpha$ ) OAc (170–171 ppm) groups [45] and they were used for the determination of hydroxyl content in acetylated samples. The deconvolution of the spectra in the acetylated hydroxyl group region required altogether 10–12 components and the positions of the peaks corresponded well with previously reported regions.

The minor, residual signals of unacetylated primary and secondary hydroxyl groups at 60–65 and 70–75 ppm showed that, for the unmodified Indulin AT samples the acetylation of aliphatic OH groups was not completed, even when the catalyst was used. These signals were included in the determination of the amount of both primary and secondary hydroxyl groups (for the secondary groups the intensities were minor).

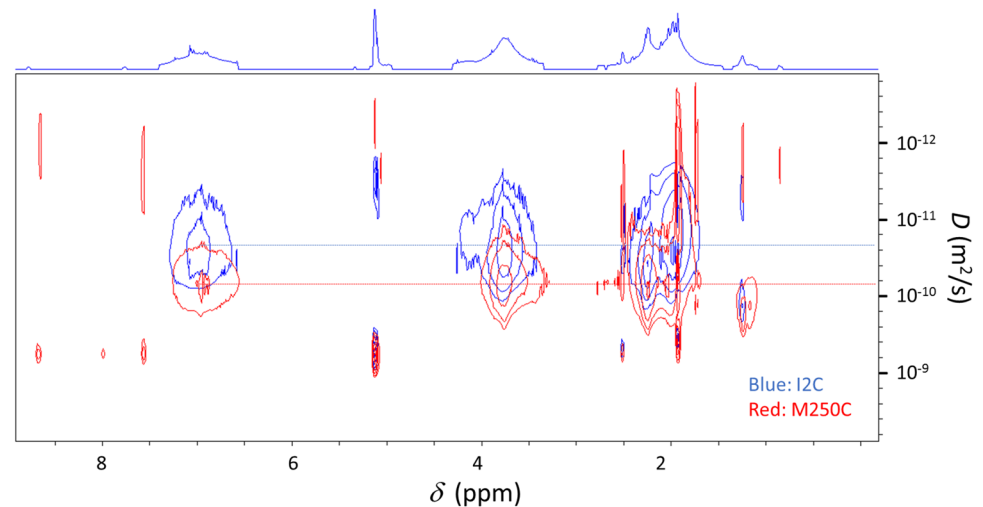
Due to the very complex nature of lignins, it is challenging to unambiguously identify the exact origin of all the signals in the  $^{13}\text{C}$  spectra [46]. Generally, signals around 140–155 ppm arise from aromatic  $\text{C}_{\text{Ar}}-\text{O}$  carbons and those around 120–139 ppm from  $\text{C}_{\text{Ar}}-\text{C}$  [47, 48]. In Fig. 4 and Fig. 5, the spectra of each sample contained sharp intense signals around 140–150 ppm. Because the presence and the amplitude of these signals was dependent on the acetylation, we interpreted that they arise from non-acetylated hydroxyl groups, because the acetylation should not affect the methoxyl signals. Therefore, the amplitudes of those signals were



**Fig. 4** Quantitative  $^{13}\text{C}$  spectra of unmodified Indulin AT lignin (I2C) and its depolymerized product (M250C) after solvolysis in the macro reactor



**Fig. 5** DOSY measurements of unmodified Indulin AT and the depolymerized (Macro 250) samples



**Table 5** Hydroxyl group content of Indulin AT and its depolymerized product in mmol/g determined by quantitative  $^{13}\text{C}$ -NMR

Lignin <sup>a</sup>	Primary ( $\alpha$ -OH) <sup>b</sup>	Secondary ( $\beta$ -OH) <sup>c</sup>	Phenolic ( $\text{OH}_{\text{ph}}$ ) <sup>d</sup>	Total OH
I1	1.8	1.4	4.4	7.6
I2	2	1	3.9	6.9
I1C	1.8	1.1	4.4	7.3
I2C	1.6	0.9	3.8	6.3
MOD250	0.7	0.6	4.4	5.7
MOD250C	0.8	0.6	5.3	6.7
$I_{\text{avg}}$	$1.8 \pm 0.2$ (95%)	$1.1 \pm 0.3$ (95%)	$4.1 \pm 0.3$ (95%)	$7.0 \pm 0.7$ (95%)
$M250_{\text{avg}}$	$0.8 \pm 0.1$ (95%)	$0.6 \pm 0.1$ (95%)	$4.8 \pm 0.5$ (95%)	$6.2 \pm 0.5$ (95%)

<sup>a</sup>All the samples were acetylated for NMR analysis. Two different unmodified samples I1, I2: taken from the same batch of Indulin AT. C: Perchloric acid used as catalyst in acetylation. M250: Sample after solvolysis at 250°C in the upscaled reactor

<sup>b</sup>Based on the integrals of the signals at 170–171 ppm and 60–65 ppm

<sup>c</sup>Based on the integrals of the signals at 169–170 ppm and 70–75 ppm

<sup>d</sup>Based on the integrals of the signals at 168–169 ppm and 140–155 ppm

included in the determination of the phenolic hydroxyl content, the results of which are presented in Table 5. Overall, the obtained hydroxyl group contents for Indulin AT are in good agreement with our previous studies, where Indulin AT exhibited 1.66 mmol/g of  $\alpha$ -OH, 0.98 mmol/g of  $\beta$ -OH, and 3.84 mmol/g of  $\phi$ -OH [43].

The use of catalyst did not appear to increase the extent of acetylation. The amount of unacetylated primary and aromatic groups were roughly the same with and without the catalyst. The analysis of four different unmodified Indulin AT samples (I1, I1C, I2 and I2C) showed some variation in the hydroxyl group content (see Table 5), which reflects the error bars of the NMR analysis. The average value of the total hydroxyl content for the unmodified samples is  $(7.0 \pm 0.7)$  mmol/g, where the error accounts for the deviation between different measurements. The solvolysis seemed to slightly increase the amount of phenolic hydroxyl groups, although the increase was within the experimental

error ( $4.1 \pm 0.3$  vs.  $4.8 \pm 0.5$  mmol/g), but the total hydroxyl group content was decreased. Interestingly, the amount of primary and secondary hydroxyl groups decreased clearly in the depolymerized samples. The cleavage of aliphatic hydroxyl groups at reductive conditions has been reported earlier [49]. In our work, the depolymerization was done at acidic conditions using formic acid as a hydrogen donor. It is possible that the formic acid reacts with the primary and secondary groups with  $\text{S}_{\text{N}}2$  mechanism (those are more basic ( $\text{pK}_{\text{a}} \sim 16$ – $18$ ) than aromatic OH ( $\text{pK}_{\text{a}} \sim 10$ )).

The amounts of aromatic methoxyl groups were determined based on the signal at 57 ppm [50]. The amount was 3.8 mmol/g for Indulin AT, 3.6 mmol/g for MOD250C, and 3.9 mmol/g MOD250. This is in a reasonable agreement with the previously reported value of 4.68 mmol/g for Indulin AT [50]. The values indicate that the depolymerization of lignin did not decrease significantly the amount of aromatic

OMe groups; the groups seem to be tightly attached despite of the rough conditions.

To analyze how the depolymerization process affects the molecular weight distribution of the lignin,  $^1\text{H}$  DOSY experiments were conducted (Fig. 5). The solvolysis clearly increased the diffusion coefficients of the molecules; the center of major signals were shifted from  $2 \times 10^{-11} \text{ m}^2/\text{s}$  to  $8 \times 10^{-11} \text{ m}^2/\text{s}$ . As the diffusion coefficient is inversely proportional to the molecular size, this is an indication of lowered molecular weight distribution in the depolymerized sample, which is in agreement with the GPC results. The amount of fragments with a very high (about  $6 \cdot 10^{-10} \text{ m}^{-10} \text{ m}^2/\text{s}$ ) diffusion coefficient was also increased in the solvolysis. Whereas GPC estimates the size distribution of the sample, DOSY is able to differentiate the molecules by apparent shape. However, quantitative determination of molecular weights from the diffusion coefficients was not possible due to high viscosity of the sample. Thus, no direct comparisons could be made between DOSY and GPC results.

## Conclusions

Depolymerization of lignin can be achieved by solvolysis with an ethanol–water mixture using formic acid as an in-situ hydrogen donor. The reactions cleave the etherified phenolic hydroxyl bonds and increase the available phenolic hydroxyl groups, while decreasing the average molar mass and polydispersity. The formaldehyde uptake capability of the lignin product is also increased in this process.

The temperature was the dominant parameter in the solvolysis reaction, having the largest and most positive effect of all parameters. The results suggest that a temperature above  $300 \text{ }^\circ\text{C}$  could be beneficial to the depolymerization process. However, the limiting factor is not the temperature itself, but the pressure buildup from the formic acid decomposition products, the release of lignin-derived gaseous products, and the vapor pressure of the solvent. At  $300 \text{ }^\circ\text{C}$ , a pressure of about 100 Bar can be expected with the current setup. If a temperature of e.g.  $450 \text{ }^\circ\text{C}$  were desired, a more specialized setup would be required with additional safety features such as an automatic pressure relief valve.

Depolymerization of lignin by solvolysis in presence of a hydrogen donor without a catalyst proved to valorize Indulin AT lignin substantially compared to the original lignin. This was evidenced by the increased formaldehyde uptake capability, lower molar mass, and increased phenolic hydroxyl content. By using uncatalyzed partial depolymerization, there could be savings on catalysts. The partial depolymerization process allows to obtain suitably sized molecules for potential applications such as phenol-formaldehyde resins and polyurethanes. The next stage should be testing the application of the modified lignins for the elaboration of

products at lab-scale. Higher formaldehyde uptake would make the modified lignin useful in phenolic resins, while a higher amount of phenolic OH would make the modified lignin useful as a polyol in polyurethanes. Additionally, uncatalyzed valorization routes should be further explored such as combining solvent fractionation and solvolysis. Moreover, the economic feasibility of the proposed method for lignin valorization should be assessed. Finally, the partial depolymerization and application of other lignins from different origin such as non-wood lignins should be explored.

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