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1 Influence of reaction conditions on solvolysis of organosolv lignin using water
2 and green organic co-solvents as reaction medium

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23 Abstract

24 This study investigated the non-catalysed solvolysis of sulphur free organosolv lignin using
25 mixtures of organic solvents (methanol, ethanol and 2- methyltetrahydrofuran) and water with
26 emphasis on the novel biphasic 2- methyltetrahydrofuran (2-MTHF) / water reaction medium.
27 The effect of co-solvents, co-solvent-to-water ratio and temperature were studied. 2-MTHF
28 proved to be effective co-solvent with water that significantly suppressed char formation and
29 also demonstrated promising protection effect on monoaromatic compounds. The yield of
30 solvolyzed lignin (SL) and char were in the range of 40.0 – 88.6 % and 10.4 – 0.1 %
31 respectively, based on initial amount of dried lignin. The yield of monoaromatics maximized
32 to 67.2 mg g⁻¹ of lignin at 310 °C and 60 min with syringol, syringaldehyde, 4-methylsyringol,
33 1,2,3- trimethoxy-5-methyl benzene and guaiacol as the main compounds.

34 Keywords

35 Lignin, Solvolysis, Monoaromatics, Green solvents, 2- methyltetrahydrofuran

36 1. Introduction

37 From the perspective of green chemistry, it is recommended to utilize non-toxic renewable
38 materials such as lignocellulosic biomass compared to fossil materials wherever possible for
39 the production of fuels and chemicals [1]. The key to sustainability and certainly helpful in
40 lowering the carbon foot print is the replacement of oil-based raw materials with lignocellulosic
41 materials [2]. Complete valorisation of all the constituents is required to take the full advantage
42 of the lignocellulosic materials. Cellulose and hemicelluloses are already utilized in
43 industrially established processes, for example in paper and board making. However, lignin is
44 mostly incinerated in recovery boilers as a low value fuel for generating energy and heat.
45 According to estimates, 50 million tons per annum of lignin is produced worldwide in waste
46 streams of wood pulping industry [3]. Additionally, large amount of lignin as a by-product is
47 expected to be available in coming years due to fast developments in cellulosic ethanol industry
48 [4]. Out of the currently available lignin quantity, only 1 – 2 % is separated and utilized for
49 producing flocculating agents, dispersing agents and some commercial products such as
50 vanillin from sulphite lignin and liginosulfonate from kraft lignin with, DMSO, a niche product
51 also from kraft lignin [5–7].

Lignin is considered as an abundant source of low cost, renewable phenolics due to the presence of aromatic rings in its structure. The key challenge in unlocking lignin's potential is the complicated network structure consisting of a wide range of chemical bonds, namely ether (α -O-4, β -O-4 and 5-O-4) bonds and condensed (5-5, β - β , β -5, β -1) carbon – carbon bonds [8]. Ether linkages are more prone to degradation than the condensed C-C bonds due to their lower dissociation energy [9–11]. Upon cleavage of these ether bonds, reactive intermediates are formed which can either degrade to smaller molecules through dealkylation, demethoxylation and hydrolysis reactions or repolymerize with each other to form condensed molecules of very high molecular weights [10–12].

Irrespective of the challenges posed by the complicated structure of lignin, the interest for converting lignin to fuels and chemicals has maintained over few decades. Among the conversion techniques, solvolysis has gained researchers' attention [9,13–17]. In solvolysis, organic solvents including alcohols [13,16,18–21], phenols [17], ketones [13] are utilized under subcritical and supercritical conditions with and without water for degrading lignin. The physical properties of solvents, such as polarity and dielectric constant, play an important role in the dissolution of reaction products. It has been reported that the depolymerization of organosolv lignin with supercritical acetone (dielectric constant = 20.7) gave 5% and 8% higher yields of bio-oil than supercritical ethanol (dielectric constant = 24.3) and supercritical methanol (dielectric constant = 33), respectively, manifesting the effect of difference in the dielectric constants of solvents [13]. Pure water under subcritical conditions can contribute in enhancing the reactions due to a higher ion product ($10^{-12} \text{ mol}^2 \text{ kg}^{-2}$, ca. 350 °C) compared to water at room temperature ($10^{-14} \text{ mol}^2 \text{ kg}^{-2}$, ca. 25 °C), which favours acid and base catalyzed reactions due to higher concentration of H^+ and OH^- ions [22,23]. The increase in water content of the ethanol and water reaction medium demonstrated positive influence on the yield of phenolics. As an example, the maximum amount of phenolics was achieved at 25 % ethanol in ethanol-water reaction medium at 310 °C and 30 min for the degradation of alkali lignin compared to pure ethanol [15].

The use of green solvents in chemical processing is encouraged considering solvents as a prominent source of waste [24]. Ionic liquids [25,26] and deep eutectic solvents [27,28] along with some organic solvents such as ethanol and 2-MTHF are mentioned as green solvents for the solvolysis of lignin and lignocellulosic materials. Ionic liquids are molten salts with some advantages over conventional solvents such as low vapour pressure, non-explosive, non-

oxidizing and thermally stable. However, the high price of ionic liquids is still the challenge for industrial applications and demand effective recovery process of ionic liquid. Deep eutectic solvents are eutectic mixtures of hydrogen bonding donors and hydrogen bonding acceptors. They possess physical and chemical properties comparable to ionic liquids. Advantages of deep eutectic solvents include easy synthesis, stable nature, low cost and most importantly environmental-friendly [29]. Among organic solvents, ethanol and 2-methyltetrahydrofuran (2-MTHF) are considered as green solvents and can be produced from lignocellulosic materials [24,30]. In a bioethanol production facility, the biomass is first pre-treated to hydrolyze hemicelluloses. Ethanol is then produced by reacting the pre-treated biomass, rich in cellulose, with cellulase enzymes to produce glucose, which is subsequently fermented to ethanol [4]. The typical way of producing 2-MTHF is from pentoses via 2-methylfuran and then hydrogenated to 2-MTHF. In addition, hexoses are dehydrated under acidic conditions to levulinic acid and then hydrogenated to 2-MTHF [31].

In our earlier work, we tested the role of sub-critical water as a reaction medium for the production of bio-oil rich in monoaromatic compounds from the same lignin used in this study [32]. Results demonstrated that water could depolymerize lignin through hydrolysis reactions to monoaromatic phenols such as syringol, guaiacol and 3-methoxycatechol. However, 25% of the feed lignin was transformed into char even under the conditions for an optimum yield of monoaromatic phenolic compounds. Therefore, the objective of this research was to investigate the performance of 2-MTHF-water mixture as a green and novel reaction medium for lignin solvolysis. Special emphasis was on suppressing the char formation and preventing the degradation of monoaromatic phenolic compounds. Material balances were comprehensively calculated with special attention given to separating char and residual lignin. 2-MTHF has a lower value of dielectric constant (6.97) than methanol (33), ethanol (24.3) and acetone (20.7), which should improve the solubility of lignin in the reaction mixture. Additionally, the obtained results were compared with a set of lignin solvolysis trials utilising conventional green co-solvents, namely ethanol and methanol. Moreover, solvolyzed lignin was analysed with GC-MS (gas chromatography and mass spectroscopy), elemental analysis, and GPC (gel permeation chromatography) for shedding light on the changes in the composition and molecular weight distribution. The principles of green chemistry were the motivating factor behind this study, and encouraged us to study sulphur-free lignin, hence preventing the formation of hazardous sulphur-containing waste.

2. Materials and methods

2.1. Materials

Organosolv lignin, extracted from beech wood by ethanol/water pulping, was kindly supplied by Fraunhofer Institute, Germany. The lignin used in this study has been extensively characterized in our research group and some characterization data is presented in Table 1. Lignin model compounds, including phenol (99.5 %) guaiacol (98 %), catechol (99.0 %), 4-methylcatechol (95.0 %), syringaldehyde (98.0 %), 4-methylsyringol (97.0 %), 3-methoxycatechol (99.0 %), 4-methylguaiacol (98.0 %), and syringol (99.0 %) were purchased from Sigma Aldrich and used as standard compounds in the GC analysis. Anisole (purity 99.0 %) purchased from Sigma Aldrich was used as an internal standard. Methanol (99.9 %) and 2-methyltetrahydrofuran (2-MTHF; 99.9 %), purchased from Sigma Aldrich, and ethanol (99.5 %) purchased from Altia Oyj were used as co-solvents in the solvolysis reactions. Tetrahydrofuran (THF; 99.9 %), ethylacetate (99.7 %) were also purchased from Sigma Aldrich and utilised for extraction or dissolving solvolyzed lignin samples for analysis. Sodium hydroxide (99.2 %, VWR chemicals BDH Prolabo) was used for separating residual lignin from char. Sulphuric acid (95.0 – 97.0 %, Sigma Aldrich) was used for acidification. All chemicals were used as received except sodium hydroxide and sulphuric acid, which were diluted to required concentrations in distilled water.

Table 1. Properties of feed organosolv lignin [32,33].

Ash	Sugars	Mw ^a	Mn ^a	PD ^b	C	H	N	O	S	S / G Ratio ^c
wt. %	wt. %	g mol ⁻¹	g mol ⁻¹		% of Dry lignin					
0.05	2.4	3428	606	5.66	62.5	5.9	0.3	30.9	0.0	1.29

a. Number-average (Mn) and Weight-average (Mw) molecular weights b. Polydispersity (PD) c. Syringyl to guaiacyl units.

2.2. Solvolysis reactions

Solvolysis reactions were conducted in a SS-316T Parr reactor with a 500 mL capacity. In a typical experiment, the reactor vessel was charged with 5g of air dried organosolv lignin and 200 mL of water and co-solvent mixture. The volume ratio of water and co-solvents (methanol, ethanol and 2-MTHF) was adjusted as required. After sealing, the reactor was purged and filled with nitrogen (2 MPa) and heated to required temperature and maintained for 60 min under

constant stirring at 500 rpm. At the end of the reaction time, the reactor was cooled to room temperature by circulating cold water in the cooling tube inside of the reactor vessel. Gases were vented through the relief valve after collecting gas samples in a SS-316 vessel, after which the reactor was opened.

2.3. Products separation

Figure 1a illustrates the products separation scheme followed when 2-MTHF was used as the co-solvent and Figure 1b represents the separation scheme followed when either methanol or ethanol was used as the co-solvent. The portion of lignin which was solubilized in the reaction medium (co-solvent/water) is named as solvolyzed lignin (SL) and the portion of lignin insoluble in reaction medium but soluble in sodium hydroxide and was recovered after acidification is named as residual lignin (RL).

The reaction mixture was filtered to remove insoluble solids (IS). The filtered reaction mixture containing 2-MTHF and water was allowed to phase separate in a separation funnel. The organic phase was collected and water phase was discarded to waste. 2-MTHF was evaporated under vacuum leaving behind SL. SL was further vacuum dried at 40 °C overnight to remove residual solvent.

In case of alcohols, i.e. methanol and ethanol, as co-solvents, the filtered reaction mixture after IS separation was evaporated under vacuum to remove alcohols leaving behind SL in water. Ethylacetate was added to extract SL from water and allowed to phase separate in a separation funnel. The organic phase was collected and water phase was discarded to waste. Rest of the procedure was the same as mentioned earlier.

The reactor was washed by adding 200 mL of 1 M NaOH to remove solids from reactor wall and stirred at 700 rpm for 30 min. The NaOH solution from the reactor washing was mixed with IS. In the next step, NaOH solution was filtered again to separate sodium hydroxide insoluble solids named as char. The filtered solution was acidified to a pH < 2 by the addition of 5 M H₂SO₄. Consequently, dissolved residual lignin (RL) was precipitated, filtered, washed with water and left for drying at room temperature.

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Figure 1a – b. Procedures for products separation and recovery.

2.4. Analytical methods

Volatile compounds present in the SL samples were analysed using a Shimadzu GC-MS with an HP-MS column (30 m x 0.25 mm x 0.25 μ m). The SL sample was dissolved in ethyl acetate to a pre-determined concentration along with 10 ppm of anisole as internal standard and 1 μ L of the solution was injected at an inlet temperature of 280 $^{\circ}$ C with a split ratio of 10. Temperature of the column was kept at 40 $^{\circ}$ C for 2 min, then increased at a rate of 6 $^{\circ}$ C min $^{-1}$ to 300 $^{\circ}$ C, and kept for 10 min. Electron impact ionization was used at 70 eV. NIST database and model compounds were used for the interpretation of the peaks. Guaiacol was used as calibration standard for calculating the response factor (RF) in order to quantify the amount of monoaromatic compound in the injected sample. Further details on monoaromatics calculations are given in Appendix A.

The molecular weight averages of the SL and RL samples were determined with Agilent HPLC-system by means of Phenogel columns (5 μ m – 5 nm and 100 nm) and UV detector at 280 and 260 nm was used for samples and polystyrene standards. THF was used as an eluent

at a rate of 1.0 mL min⁻¹ and the analysis was carried out with an injection of 50 µL of sample at room temperature. Calibration was performed using syringol and biphenyl together with polystyrene standards ranging from 76600 g mol⁻¹ to 208 g mol⁻¹. Prior to the analysis, RL samples and feed lignin were acetylated according to the method mentioned in our earlier publication [32].

Elemental analyses were carried out by Perkin Elmer model 2400 series II CHNS elemental analyzer (230 V). The amount of oxygen in the samples was calculated by subtracting the sum of other elements from 100 %.

IR spectra for the SL and RL samples were recorded using unicam Mattson 3000 with PIKE technologies Gladi ATR. Absorbance mode was used with 16 scans per spectrum and resolution of 16. The range of the spectrum is selected from 0 – 4000 cm⁻¹. Air spectrum was used as background.

Gaseous products were analysed with Agilent 6890 GC system consisting of 25 µl gas sampling loop and two analysis lines for permanent gases and hydrocarbons. HP-PLOT-Q (30 m x 0.53 mm x 40 mm) and Molesieve 0.5 nm (30m x 0.53mm x 25 µm) columns with TCD were used for permanent gases analysis and Al₂O₃/KCl (50m x 0.32mm x 8 µm) column with flame ionization detector (FID) was used for hydrocarbons analysis.

2.5. Calculation for products yield and lignin conversion

The yield of products are mentioned as weight percentage (%) of dried feed lignin mass and were calculated according to the equations 1 to 4. The conversion of dried lignin was calculated by equation 5.

$$Yield\ of\ RL\ (\%) = \frac{Mass\ of\ RL\ (g)}{Mass\ of\ dried\ lignin\ (g)} * 100 \quad (1)$$

$$Yield\ of\ SL\ (\%) = \frac{Mass\ of\ SL\ (g)}{Mass\ of\ dried\ lignin\ (g)} * 100 \quad (2)$$

$$Yield\ of\ Char\ (\%) = \frac{Mass\ of\ char\ (g)}{Mass\ of\ dried\ lignin\ (g)} * 100 \quad (3)$$

$$Yield\ of\ Gas\ (\%) = \frac{Mass\ of\ gas\ (g)}{Mass\ of\ dried\ lignin\ (g)} * 100 \quad (4)$$

$$Conversion\ (\%) = Yield\ of\ SL + Yield\ of\ Char + Yield\ of\ Gas \quad (5)$$

3. Results and discussion

3.1. Mass balance

The effects of the reaction medium on the solubilization of lignin and the products distribution were investigated at 270 °C and presented in Figure 2a. It is evident that the solvolysis process was significantly influenced by the reaction medium. The degree of lignin conversion to products was higher in all cases compared to pure water at 270 °C [32]. According to the solvent's ability of solvolyzing lignin, the best result of lignin conversion into products was 88.9 % obtained using 2-MTHF/water, followed by 59.1 % and 42.9 %, respectively, for ethanol/water and methanol/water. Methanol/water proved to be the least lignin solvolyzing reaction medium. The lower lignin solvolyzing effect of methanol compared to ethanol has been reported earlier [13]. The amount of gases formed was less than 1 % in all cases. The yield of SL generally increased with decrease in the value of dielectric constant of the used organic co-solvent. The highest yield of SL was 86.8 % achieved when 2-MTHF/water was used as the reaction medium whereas the minimum yield of SL was 40.0 %, achieved for methanol/water as the reaction medium.

The presence of an organic solvent in an aqueous reaction medium suppressed the formation of char, which was observed in higher amounts in an earlier study with pure water as reaction medium [32]. According to the solvents, the highest char content of 2.4 % was observed in the case of methanol/water whereas the lowest char content of 1.2 % was obtained in the case of ethanol/water. An intermediate char content of 1.8 % was produced in a 2-MTHF/water reaction mixture. This could be explained by a higher solubility of lignin in organic solvents compared to water, which prevented the condensation reactions of the intermediates.

Due to the highest yield of SL in the reaction mixture of 2-MTHF/water, this solvent mixture was subsequently used for further optimization. To understand the effect of solvent volumes on the solvolysis of lignin, a series of experiments was performed at 150/50, 100/100 and 50/150 (mL/mL) of 2-MTHF/water. Figure 2b represents the effects of changing volumes of 2-MTHF/water on the product distribution from lignin solvolysis. At a (150/50) mL/mL of 2-MTHF and water, 10.4 % of char was obtained. When the volume of water in the reaction medium was increased from 50 mL to 100 mL the yield of SL increased from 75.8 % to 86.8 % together with a decrease in char yield to 1.8 %. A further increase in the volume of water in

the reaction medium to 150 mL led to a drop in the yield of SL to 57.7 %. RL and char obtained at this solvents ratio was 23.7 % and 2.3 %, respectively.

These results demonstrate the synergistic effect of 2-MTHF and water on char suppression. This could have been caused by an increased ion product of water that catalysed the hydrolysis of intermediates to lower molecular weight compounds together with efficient protection of reactive lignin fragments by 2-MTHF. However, the lower SL yield without any significant increase in the char yield when water was increased from 100 mL to 150 mL suggested that the contribution of 2-MTHF towards SL yield was more prominent than that of water. A higher char yield with higher 2-MTHF ratio in the reaction medium could possibly result from the cross-linking of SL intermediates, similar to the lignin reactions in pure solvents [16,17].

Increasing the reaction temperature had a minor impact on the product distribution. The yield of char was negligible at temperatures of 290 °C and 310 °C with 2-MTHF/water of volumes 100/100 (mL/mL), as shown in Figure 2c. The yield of gases increased slightly from 0.3 % at 270 °C to 1 % at 310 °C. The gases identified were mainly carbon dioxide and carbon monoxide. Methane was only observed in the reaction carried out at 310 °C for a reaction time of 60 min. The formation of these gases were due to the cleavage of aliphatic propane chains and conversion of methyl groups [14].

Figure 2. Solvolysis reaction material balances. **a)** Effects of different co-solvents at 270 °C and 60 min with co-solvent to water volume of 100/100 (mL/mL). **b)** Effect of changing volumes of 2-MTHF to water (mL/mL) at 270 °C and 60 min. **c)** Effect of increasing temperature at 60 min of reaction time with 2-MTHF to water volume of 100/100 (mL/mL).

The material recovered in all of the reactions contained more than 90 % of the feed lignin except for the trials carried out at 270 °C and 60 min with 50 / 150 (mL/mL) of 2-MTHF to water. The major portion of the missing amount could be attributed to the lignin products which got solubilized in the aqueous phase and was not quantified. In addition some solids could not be recovered from the reactor due to their extremely sticky nature and therefore also missing

from the mass balance. However, these solids were cleaned by excessive washing with soap and hot water together with the brush to make the reactor ready for next run.

3.2. Solvolyzed lignin (SL) characterization

3.2.1. Monoaromatic compounds quantification

SL was characterized with GC-MS for identification of the monoaromatic compounds produced during solvolysis in order to understand the effect of reaction conditions on the composition. GC-MS characterization results from all SL samples are given in Table 2 and a representative GC spectra with the list of identified compounds is given in Appendix A.

The important reactions involved in the degradation of lignin to monoaromatic compounds were the cleavage of α -O-4 and β -O-4 linkages in the lignin structure. Both of these bonds had low energy of dissociation i.e. 215 kJ mol⁻¹ and 290 – 305 kJ mol⁻¹ for α -O-4 and β -O-4, respectively [34]. Table 2 shows that syringaldehyde was produced in the highest quantity among all the identified monoaromatic compounds contained in the SL samples from methanol/water, ethanol/water and 2-MTHF/water with volume ratio of 1 at 270 °C and 60 min. The ratio of the total amount of monoaromatic compounds originating from syringyl units to the total amount of compounds originating from guaiacyl units was higher (between 3.1 – 3.5) in all solvent mixtures, indicating higher content of syringyl than guaiacyl units in the feed lignin (beech wood lignin). The amount of syringol and guaiacol were higher in the SL samples obtained from ethanol/water compared to 2-MTHF/water whereas the amount of syringaldehyde and syringylacetone were higher in 2-MTHF/water compared to ethanol/water. These results indicated that ethanol was more supportive towards hydrolysis and had lower tendency of protecting monoaromatic compounds from degradation compared to 2-MTHF when used as co-solvents with water. The reason behind the lower amounts of syringol and guaiacol compared with syringaldehyde in all the reaction mediums may be smaller number of hydrolysis reactions taking place under these experimental conditions. Vanillin, acetosyringone and syringylacetone were also observed as major compounds present in the SL samples. The formation of syringaldehyde, acetosyringone and syringylacetone can result from syringyl intermediates whereas vanillin could result from guaiacyl intermediates formed during degradation of the lignin macrostructure. Apart from the mentioned components, the composition of the other analysed degradation products in the SLs obtained from

methanol/water, ethanol/water and 2-MTHF/water were nearly indistinguishable with each other, pointing towards similar reaction pathways.

An increase in the formation of syringol and guaiacol can be observed with increasing volume of water from 50 mL to 150 mL in the reaction medium. The amount of guaiacol increased from 1.3 to 2.4 mg g⁻¹; for syringol the respective increase was from 4.2 to 6.1 mg g⁻¹. On the other hand, a decreasing trend in the amount of other compounds including syringaldehyde, vanillin, acetosyringone and syringylacetone was observed along with the increase of water ratio in the reaction medium. This showed that the increase in the water ratio supported the hydrolysis reactions of lignin and intermediate compounds. It was reported that the presence of an organic co-solvent with water above 25 % volume had a negative impact on the production of monomers from lignin by stabilizing the reaction intermediates [15].

An increase in the reaction temperature had a significant effect on the composition of reaction products present in the SL samples. The formation of syringol and guaiacol increased when the temperature was increased from 270 to 310 °C; the formation of creosol, 4-ethylguaiacol and 4-propenylsyringol was observed above 270 °C, pointing towards new reaction pathways. Moreover, the amount of creosol, p-ethylguaiacol, 4-methylsyringol, 1,2,3-trimethoxy-5-methyl-benzene, methoxyeugenol increased gradually with the increase in the reaction temperature from 270 to 310 °C. The amount of syringaldehyde decreased from 12.2 to 9.3 mg g⁻¹, while other major reaction products, such as vanillin, acetosyringone and syringylacetone, remained stable along with the increase in the reaction temperature from 270 to 310 °C. This indicated that in addition to the hydrolysis of lignin, some demethoxylation and demethylation reactions were also taking place at higher temperatures, giving rise to further degradation of the reaction products to smaller molecules. Presence of syringaldehyde, vanillin, acetosyringone and syringylacetone in SL samples obtained at 310 °C and 60 min was further pointing towards the preventive character of 2-MTHF towards monoaromatics as co-solvent because these compounds were absent from bio-oil samples under pure hydrothermolysis at same reaction conditions [32].

Table 2. The amount of the identified monomeric compounds in the SL samples under all reaction conditions. The results are calculated from the GC-MS data. The reaction time was 60 min in all of the solvolysis experiments.

Temperature (°C)	270	270	270	270	270	270	270	290	310
Organic Solvent / Water (mL / mL)	100 / 100	100 / 100	100 / 100	150 / 50	100 / 100	50 / 150	100 / 100	100 / 100	100 / 100

Reaction Medium	Methanol / Water	Ethanol / Water	2-MTHF / Water	2-MTHF / Water	2-MTHF / Water	2-MTHF / Water	2-MTHF / Water	2-MTHF / Water	2-MTHF / Water
mg g ⁻¹ of feed lignin									
Name of Compound	Effect of co-solvent			Effect of co-solvent ratio			Effect of Temperature		
Anisole	Internal Standard								
Guaicol	1.4	2.0	1.6	1.3	1.6	2.4	1.6	3.6	6.5
Creosol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.9	1.4
4-Ethylguaiaicol	0.0	0.0	0.0	0.0	0.0	0.4	0.0	1.4	2.0
Syringol	4.7	6.5	4.4	4.2	4.4	6.1	4.4	10.0	20.3
Vanillin	3.0	3.5	4.1	3.2	4.1	2.8	4.1	3.8	4.1
4-Methylsyringol	0.7	0.6	0.7	0.8	0.7	0.6	0.7	2.1	7.4
Acetovanillone	0.6	0.7	0.8	0.0	0.8	0.6	0.8	1.1	0.7
Benzene, 1,2,3-trimethoxy-5-methyl-	0.4	0.7	0.7	0.0	0.7	0.8	0.7	2.8	7.1
Guaiaicylacetone	0.0	0.4	0.6	0.0	0.6	0.5	0.6	0.0	0.0
Syringaldehyde	9.3	9.9	12.2	11.2	12.2	7.3	12.2	10.5	9.3
4-Propenylsyringol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.8
Methoxyeugenol	0.0	0.2	0.2	0.0	0.2	0.2	0.2	1.1	1.4
Homosyringaldehyde	0.0	0.2	0.3	0.0	0.3	0.2	0.3	0.0	0.0
Acetosyringone	2.1	2.5	2.3	2.9	2.3	1.5	2.3	2.8	3.4
Syringylacetone	1.1	2.1	2.5	3.0	2.5	1.7	2.5	2.7	2.8
Sum	23.5	29.4	30.5	26.5	30.5	25.2	30.5	42.9	67.2

3.2.2. Average molecular weight distributions

Figure 3 a – c represent the GPC chromatograms of the SL samples obtained at different reaction conditions, and Table 3 shows the average molecular weight distributions of the SL samples obtained at all reaction conditions. Based on our earlier experience and other published results the chromatograms were divided into three regions, namely A (monomers), B (dimers) and C (higher average molecular weight compounds) [32,35]. The average molecular weight (Mw) and polydispersity (PD) of the feed lignin were 3428 g mol⁻¹ and 5.66, respectively. The Mw and PD values obtained for all tested SL samples were significantly lower in contrast to the feed lignin.

The solvolysis of lignin was reportedly improved in a reaction medium which had higher hydrogen bonding capability [36], solubility parameter close to 11 (cal/cc)^{1/2} [37] and lower dielectric constant [9]. Table 3 shows that the average molecular weight (Mw) of the SL samples increased when the solvent was changed in the order methanol/water < ethanol/water < 2-MTHF/water. Figure 3a illustrates a clear change in the average molecular weight distribution in region C. The variation in the average molecular weight distribution could be attributed to the difference in the dielectric constant of the co-solvents: 2-MTHF (6.97) <

ethanol (24.3) < methanol (33). Moreover, the results suggested that the hydrogen bonding interaction of 2-MTHF / water with lignin was probably stronger than that of alcohol / water, leading to a higher average molecular weight of the obtained SL. In addition, the increased ion product of water under subcritical condition increased the acidic character of the reaction medium containing alcohols which resulted in lower average molecular weight of SL samples. The peaks in region B shifted toward region A for all co-solvents. In contrast, the feed lignin peaks in region A overlapped with SL peaks suggesting lower degradation in this region.

The average molecular weight of SL samples steadily increased when the volume of water in the reaction mixture was increased from 50 mL ($M_w = 814 \text{ g mol}^{-1}$) to 150 mL ($M_w = 1147 \text{ g mol}^{-1}$). The higher yield of char and lower average molecular weight of SL sample was obtained in the reaction with higher 2-MTHF volume fraction. In comparison, a lower char yield and higher average molecular weight of SL was obtained in the reaction with lower 2-MTHF volume fraction. This indicated that the condensation of the larger lignin intermediates occurred at higher 2-MTHF volume fraction. The condensed fraction was removed as char during filtration leaving behind relatively lower average molecular weight SL. On the contrary, the excess of water increased the ionic product of the mixture, leading to increased depolymerization of larger lignin fragments, which in turn decreased the char yield. However, condensation of smaller lignin fragments such as dimers and trimers increased, thus increased the M_w of SL. As illustrated in Figure 3b, Using 50 mL of water yielded one peak in region A and two in region B, while the situation was reversed when the solvent contained 150 mL of water. This phenomenon indicated the advantage of water as a co-solvent for effective lignin degradation to smaller molecules such as monomers, dimers and trimers. This finding was also supported by the GC-MS results which showed an increased formation of guaiacol, syringol and ethyl guaiacol at higher amount of water in the reaction medium. The intensities of peaks obtained in the region of 2.9 – 3.5 log M_w in region C of Figure 3b decreased in the order 50 / 150 > 100 / 100 > 150 / 50 mL of 2-MTHF / mL of water. Since GPC analysis was based on UV detection, the increased intensity at lower water ratio suggested the formation of stronger UV chromophores instead of the increased yield of these chromophores in SL.

The increase in the reaction temperature had only minor effect on the average molecular weight distribution of the SL samples. The M_w of SL decreased from 956 g mol^{-1} at 270°C to 756 g mol^{-1} at 310°C . In addition, an increase in the reaction temperature favored the formation of

381 monoaromatic compounds compared to region B as indicated by the peak formation patterns
 382 in Figure 3c due to higher lignin degradation.

383 **Table 3.** Weight-average (Mw), number-average (Mn) molecular weight and polydispersity
 384 (PD) of SL samples obtained under various reaction conditions.

Reaction Medium	Volume	Temperature	Mn	Mw	PD
	mL / mL	°C	g mol ⁻¹	g mol ⁻¹	
Feed lignin			606	3428	5.5
Methanol / Water	100 / 100	270	332	490	1.5
Ethanol / Water	100 / 100	270	403	695	1.7
2-MTHF / Water	100 / 100	270	456	956	2.1
2-MTHF / Water	150 / 50	270	413	814	2.0
2-MTHF / Water	100 / 100	270	456	956	2.1
2-MTHF / Water	50 / 150	270	495	1147	2.3
2-MTHF / Water	100 / 100	270	456	956	2.1
2-MTHF / Water	100 / 100	290	428	886	2.1
2-MTHF / Water	100 / 100	310	392	756	1.9

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Figure 3. Average molecular weight distribution of SL samples **a)** From different co-solvents at 270 °C and 60 min with co-solvent to water volume of 100/100 (mL/mL). **b)** From changing volumes of 2-MTHF to water (mL/mL) at 270° C and 60 min. **c)** At different reaction temperatures after 60 min with 2-MTHF to water volume of 100/100 (mL/mL). The direction of arrow points from higher molecular weight towards lower molecular weight fractions. The UV response of the detector was measured at 280 nm wave length.

3.2.3. Elemental Analysis

Elemental compositions of the SL samples obtained under all tested reaction conditions after vacuum drying at 60 °C are presented in Table 4. A gradual increase in the carbon content of the SL samples occurred with increasing reaction temperature, increasing volume of water in the reaction medium and changing co-solvent from methanol to ethanol and to 2-MTHF. It is known that the carbon content in SL increases due to the formation of volatiles through decarbonylation, decarboxylation and dehydration reactions along with increasing time and temperature. However, the low formation of gases in all the reactions indicated that this increase in carbon content of the SL samples was not only because of the above mentioned reactions. The high carbon content could also be pointing towards condensed compounds, which were extracted into the SL fractions due to increment in the non-polar character of co-solvents. Another cause could be the association of furan compounds in SL fraction as a residue which may have formed during the reactions from 2-MTHF degradation under tested reaction conditions.

Table 4. Elemental Analysis of SL samples obtained after treatment with different co-solvents, different solvent compositions and different temperatures on dry basis.

Reaction Medium	Ratio	Temperature	C	H	N	O	Heating Value
	mL / mL	°C	Wt %				(MJ / kg)
Feed lignin			62.5	5.9	0.3	30.9	24.1
Methanol / Water	100/100	270	63.7	5.8	0.4	30.0	24.5
Ethanol / Water	100/100	270	65.6	5.6	0.2	28.6	25.1
2-MTHF / Water	100/100	270	66.9	6.2	0.4	26.5	26.8
2-MTHF / Water	150/50	270	65.8	6.3	0.4	27.5	26.4
2-MTHF / Water	100/100	270	66.9	6.2	0.4	26.5	26.8
2-MTHF / Water	50/150	270	67.7	5.6	0.5	26.2	26.2
2-MTHF / Water	100/100	270	66.9	6.2	0.4	26.5	26.8
2-MTHF / Water	100/100	290	67.5	6.1	0.4	26.0	26.9
2-MTHF / Water	100/100	310	68.2	5.7	0.4	25.8	26.5

3.2.4. FTIR

FTIR is a good method for understanding the structure of lignin and was used for lignin characterization in several studies [10,38,39]. In this study, the structural changes occurred in SL in comparison to feed lignin were analysed. Figure 4 a – c shows the finger print regions of the collected FTIR spectrums from feed lignin and SL samples obtained at different solvolysis conditions. In order to compare the differences in the spectra, the intensity of the peak at 1120 cm^{-1} was normalized to 1 in all spectra. This peak was indicative of the syringyl type aromatic ring vibration with highest intensity in all samples. Table 5 presents the characteristic peaks in the FTIR spectra based on the literature [38,40]. Detailed observations on FTIR peaks of SL samples are presented in Appendix B.

Some clear changes were observed in the samples obtained after the solvolysis treatment compared to the feed lignin. C=O stretching bands were observed at (1727, 1670 cm^{-1}) in the SL samples. The band observed at 1727 cm^{-1} was assigned to non-conjugated ketone and carboxyl group whereas the band observed at 1670 cm^{-1} was assigned to C=O stretching conjugated to aromatic ring. The band around 1727 cm^{-1} was intensified in methanol/water, weakened in ethanol/water, diminished in 2-MTHF/water and cannot be seen as a separate band but as a broad peak centring at about 1670 cm^{-1} after the treatment. The band at 1670 cm^{-1} became shoulder in methanol/water and did not change in ethanol/water. The absorbance bands representative of aromatic ring vibrations were observed at 1600, 1511, 1425 cm^{-1} . The

intensities of bands at 1600 and 1511 cm^{-1} decreased to some extent whereas absorption band at 1425 cm^{-1} weakened drastically after solvent treatments and gradually diminished only to a slight shoulder as the reaction temperature was increased from 270 to 310 $^{\circ}\text{C}$ with 2-MTHF as co-solvent, indicating some degree of breakdown in propyl chains attached to the aromatic rings. The band at 1670 cm^{-1} has broaden in the SL sample obtained after the treatment at 310 $^{\circ}\text{C}$ with 2-MTHF as co-solvent, strengthening the claim of depolymerization with increment in the reaction temperature. The peak at 1329 cm^{-1} , representative of syringyl ring, was more intense with separate absorption band than the peak at 1271 cm^{-1} representing guaiacyl ring indicating more syringyl based compounds such as syringol and syringaldehyde in SL as indicated in the GC-MS results of SL. Increase in the intensity of peak 836 cm^{-1} indicated the formation of alkyl substituted G and S rings in monoaromatics. An increase in the relative intensity owing to the condensed G rings at 1226 cm^{-1} along with increase in reaction temperature suggested the coupling reactions of compounds having G rings. The SL, contained very different sizes of lignin-derived molecules, was completely soluble in the organic co-solvents with water. Thus, the solid SL samples recovered through solvent evaporation contained both the monoaromatic, as well as the condensed structures. Therefore, both patterns of degradation to monoaromatic units and formation of condensed phenolic structures are visible in the FTIR spectra.

Table 5. List of the characteristic bands assigned to the feed lignin and the SL samples [31, 32].

Observed Band in Lignin	literature	Origin
cm^{-1}	cm^{-1}	
1727	1709 - 1738	C=O stretching in non conjugated ketone and carboxyl group
1670	1655 - 1675	C=O stretching in conjugated to the aromatic ring
1600	1593 - 1605	Aromatic ring vibrations
1511	1505 - 1515	Aromatic ring vibrations
1463	1460 - 1470	C-H deformations (asymmetric)
1425	1422 -1430	Aromatic ring vibrations with C-H in plane deformation
1365	1365 - 1370	C-H deformations (symmetric)
1329	1325 - 1330	Syringyl ring breathing with C-O stretching
1271	1266 - 1270	Guaiacyl ring breathing with C-O stretching
1226	1221 - 1230	C-C, C-O and C=O stretch; G condensed > G etherified
1124	1120	Aromatic C-H in plane deformation, syringyl type
1035	1030 - 1035	Aromatic C-H in plane deformation, guaiacyl type
918	915 - 925	C-H out of plane; aromatic
836	834	Para-substituted aromatic group

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Figure 4. FTIR spectra of SL samples **a)** From different co-solvents at 270 °C and 60 min with co-solvent to water volume of 100/100 (mL/mL). **b)** From changing volumes of 2-MTHF to water (mL/mL) at 270° C and 60 min. **c)** At different reaction temperatures after 60 min with 2-MTHF to water volume of 100/100 (mL/mL).

3.3 Residual lignin (RL) characterization

FTIR analysis, average molecular weight distributions and elemental analysis of selected RL samples were performed to follow the changes in lignin structure after solvolysis treatments in different reaction mediums.

Figure 5 presents the molecular weight distribution of feed lignin and RL samples obtained after the solvolysis treatments with water and various co-solvents. All the RLs were lower in average molecular weight compared to feed lignin. The degradation phenomenon was more visible in the form of strong peak formation around 3500 g mol^{-1} in region C present in all RL samples. On the contrary, the peaks presented in monomeric region A and dimeric region B of feed lignin significantly diminished. This phenomena suggested the agglomeration of lignin degradation products in monomeric, dimeric and oligomeric region. The lowest average molecular weight of 1653 g mol^{-1} was observed for RL sample obtained from 2-MTHF and water system while the highest average molecular weight was observed in ethanol. Table 6 summarizes the number average (M_n) and weight average (M_w) molecular weight and polydispersity of RLs.

Figure 5. Average molecular weight distribution of RL samples from different co-solvents at 270 °C and 60 min with co-solvent to water volume of 100 / 100 (mL / mL).

Table 6. Weight-average (Mw), number-average (Mn) molecular weight and polydispersity (PD) of RL samples obtained from different co-solvent and water reaction systems.

Sample	Volume	Temperature	Mw	Mn	PD
	mL / mL	°C	g mol ⁻¹	g mol ⁻¹	
Feed Lignin	-	-	3492	626	5.6
Methanol / Water	100 / 100	270	2051	862	2.4
Ethanol/Water	100 / 100	270	2442	928	2.6
2-MTHF/Water	100 / 100	270	1653	714	2.3

The FTIR analysis of RLs showed some differences compared to the feed lignin as illustrated in Figure 6. The peak observed at 1425 cm⁻¹, representative of aromatic ring vibration in feed lignin significantly decreased and became shoulder in RL samples. The strong decrease in absorption band at 1271 cm⁻¹, representative of guaiacyl units compared to the separate syringyl band at 1329 cm⁻¹, indicated higher loss of guaiacyl units than syringyl units of feed lignin. It was also noted that intensity of band 1226 cm⁻¹, representing condensed guaiacyl structures, was higher in RL sample obtained after 2-MTHF / water treatment, which indicated the higher occurrence of these structures in RL compared to feed lignin.

Figure 6. FTIR spectra of RL samples from different co-solvents at 270 °C and 60 min with co-solvent to water volume of 100/100 (mL/mL).

Table 7 presents the elemental composition of RL samples. An increase in the carbon content of RL obtained from 2-MTHF / water treatment indicated higher removal of oxygen probably by demethoxylation reactions to produce methanol and other decarboxylation reactions. The carbon content of RL slightly decreased after ethanol / water treatment while the effect was more pronounce when the solvent was methanol / water.

Table 7. Elemental Analysis of RL samples from different co-solvents at 270 °C and 60 min with co-solvent to water volume of 100/100 (mL/mL).

Reaction Medium	Ratio	Temperature	C	H	N	O	Heating Value
	mL / mL	°C	Wt %				(MJ / kg)
Feed lignin			62.5	5.9	0.3	30.9	24.1
Methanol / Water	100/100	270	56.7	4.8	0.3	38.2	19.2
Ethanol / Water	100/100	270	61.7	4.9	0.4	33.0	22.0
2-MTHF / Water	100/100	270	65.8	5.6	0.4	28.2	25.2

4. Reaction Pathways

The proposal of a precise reaction mechanism for lignin degradation under the applied reaction conditions is challenging due to the high number of side reactions occurring during the treatment. The key reactions in the solvolysis of lignin under high temperatures are the cleavage of ether bonds such as α -O-4 and β -O-4 bonds and also some C-C bonds depending on severity

of reaction. Based upon the results obtained in the current study, an overall view of reaction pathways is presented in Figure 7.

The reaction medium can be divided into two systems based on the miscibility of co-solvents (methanol, ethanol and 2-MTHF) with water. Methanol or ethanol as co-solvent with water formed a homogeneous reaction medium whereas 2-MTHF as co-solvent with water formed a bi-phasic reaction medium. The yield of SL in bi-phasic system was significantly higher than homogeneous reaction medium. The molecular mass distribution results indicated higher average molecular weight of SL from bi-phasic system compared to homogeneous system. However, there was no drastic change in the GC-MS results of SL samples obtained from both reaction systems. These findings suggested that the physical properties of solvents such as dielectric constant, solubility parameter and hydrogen bonding capability of the reaction medium affected the solubility of feed lignin during the reaction. The feed lignin is more soluble in more hydrophobic co-solvent rather than hydrophilic co-solvent. The average molecular weight distribution of RL samples revealed that RL obtained from bi-phasic reaction medium had lower average molecular weight compared to homogeneous reaction medium which confirmed that a larger part of lignin was solubilized in bi-phasic system rather than homogeneous reaction medium. The significantly lower char formation in the reactions using organic co-solvent with water could be attributed to the increased solubility of lignin and reaction intermediates in the reaction medium which lowered the reaction hindrance and stabilized the reaction intermediates.

The dominance of either 2-MTHF or water in the reaction medium promoted the condensation of solubilized lignin fragments. However, 2-MTHF produced comparatively more char than water when used in excess in the reaction medium resulting in SL of lower average molecular weight. Higher amount of 2-MTHF in the reaction medium seemed to promote cross-linking of larger lignin fragments resulting in higher yield of char. Similar effect was observed in earlier studies where alkaline lignin [41] and pine saw dust [9] were solvolyzed in ethanol/water mixture. On the other side, cross-linking occur in smaller lignin fragments when water was in excess in the reaction medium. However, these cross-linked fragments were still soluble in the reaction medium and did not contribute to the yield of char. This phenomenon produced SL with increased average molecular weight and slightly decreased monoaromatics yield from the reaction with 50 mL 2-MTHF / 150 mL water. Minimum char yield was obtained by the treatment in equivolume mixture of 2-MTHF / Water. Increase in temperature positively

535 affected the formation of monoaromatics through increased hydrolysis and thermal cracking of
536 SL. In addition to ether bond cleavage, the nature of some monoaromatic compounds such as
537 methyl syringol and ethyl guaiacol found in GCMS results indicated the cleavage of C-C bonds
538 such as C $_{\alpha}$ -C $_{\beta}$ and C $_{\beta}$ -C $_{\delta}$ present in aliphatic carbon chains.

541 Figure 7. Tentative reaction pathways for lignin solvolysis using water and co-solvents.

5. Conclusion

Technical lignin (3428 g mol⁻¹) derived from an ethanol-water organosolv process was successfully solvolyzed using water/organic co-solvents under non-catalyzed reactions at temperatures, 270 – 310 °C. The novel 2-MTHF/water biphasic reaction medium demonstrated great potential in preserving the monoaromatic compounds from degradation during the reaction. 2-MTHF as a co-solvent was proved extremely successful in char suppression, which was not the case in our earlier work on pure hydrothermolysis of the same lignin and reaction conditions. The best yield of 88.6% SL with less than 1% char was achieved with 2-MTHF/water at 310 °C. The resulting SL of the best yield had significantly lower molecular weight of 756 g mol⁻¹ and contained 67.2 mg of monoaromatics per gram of feed lignin equivalent to 7.8 % monoaromatics. The significantly lower molecular weight and increased amount of monoaromatic phenolic compounds in SL suggest its potential application in metal coatings to inhibit corrosion and in polyolefins to enhance their antioxidant activity. In a next step we will investigate the relationship between monoaromatic yield and amount of β -O-4 linkages in the initial lignin.

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