

Hydrogen-Donor-Assisted Solvent Liquefaction of Lignin to Short-Chain Alkylphenols Using a Micro Reactor/Gas Chromatography System

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S Supporting Information

ABSTRACT: The benefit of using hydrogen donor solvents in lignin solvolytic conversion was studied using a micro reactor coupled to online gas chromatography/mass spectrometry with a flame ionization detector. This system is able to achieve very high heating rates of reactants and capable of analyzing the reaction products immediately after the reaction is completed, thus allowing for probing “semi” time-resolved reactions occurring during lignin conversion. These features have been impossible for the batch reactors typically employed in previous solvent liquefaction studies. The study showed that the hydrogen donor solvents tetralin and isopropanol were effective in converting lignin into short-chain alkyl phenols (SCAP) at high yield. The yield of SCAP increased with an increasing reaction temperature over the range of 300–400 °C and reaction time over the range of 5–15 min, which is attributed to stabilization of lignin-derived products by hydrogen abstraction from the hydrogen donor solvents. The molecular weight distributions of solvolysis products revealed that molecular weight significantly decreased with increasing reaction times in the presence of a hydrogen donor solvent. In contrast, in the absence of a hydrogen donor solvent, the molecular weight of products increased with increasing reaction times. Also, the peak assigned to oligomers increased and shifted to higher molecular weights at the same reaction conditions. Overall, the solvolytic conversion of lignin involves thermal cleavage of lignin macromolecules, followed by secondary reactions, including cracking and repolymerization, among the primary products. The presence of a hydrogen donor was found to suppress repolymerization reactions by stabilizing the primary products to alkyl-substituted phenols and promoting demethoxylation.

INTRODUCTION

Lignin, the second most abundant natural polymer in the biosphere, is produced in large quantities by the pulp and paper industry and is expected to become increasingly available with the commercial development of cellulosic ethanol.¹ Lignin differs chemically from carbohydrates in that it has a complex aromatic substructure. Unlike cellulose, which consists of a linear chain of repeating glucose units, lignin is a three-dimensional polymer of phenolic monomers with a variety of functional groups and chemical bonds, the structure of which varies with biomass source. This complicates chemical or biological modification and recovery of products.²

Lignin is commonly used as low-value boiler fuels, with less than 5% of the world's supply used for other purposes.³ Because of its availability and low cost, lignin has been intensely studied as a renewable feedstock for production of biofuels and biobased chemicals. Lignin macromolecules can be depolymerized into value-added monomeric phenols via thermochemical processing, including pyrolysis and solvolysis.⁴

Solvolysis of lignin has several advantages over lignin pyrolysis. Dependent upon the choice of solvent, it is possible to selectively depolymerize lignin because the solvent can strongly influence the decomposition of lignin.⁴ Whereas pyrolysis of lignin produces up to 40 wt % char as a product,^{5,6} solvolysis in appropriate solvents yields only small amounts of char.⁷ Several solvents and solvent combinations with and without catalysts have been tested for their ability to depolymerize lignin.^{8–10} Previous studies suggest that phenolic

compounds produced during solvolysis are reactive, with a strong tendency to repolymerize.^{7,11} The addition of hydrogen gas or a hydrogen donor agent is expected to reduce repolymerization by stabilizing reactive phenols. The main advantages of using hydrogen donor solvents (HDSs) instead of hydrogen gas for solvolysis is that lower operating pressures can be employed.¹² HDSs, such as tetralin and isopropanol, were first employed in coal liquefaction to stabilize free radicals that otherwise recombine to form char.¹² Several HDSs have been tested in biomass solvolysis.^{12–19} Vasilakos and Austgen¹² converted cellulose in tetralin solvent and reported that tetralin promoted the bio-oil yield while reducing the oxygen content in the bio-oil. They also used isopropanol as a HDS to obtain 75 wt % yield of bio-oil from cellulose. Rinaldi et al.^{20,21} recently investigated lignin valorization in the presence of catalyst using isopropanol. They tested to decompose lignin using isopropanol as a hydrogen-transfer initiator and found that the molecular weight of bio-oil decreased and did not undergo repolymerization.²⁰ Davoudzadeh et al.¹⁴ investigated depolymerization of lignin at a low pressure using catalyst and tetralin. They found that increasing the reaction temperature to 400 °C increased lignin liquefaction in tetralin in the presence of hydrogen gas. Dorrestijn et al.¹⁵ tested lignin solvolysis using 9,10-dihydroanthracene and 7H-benz[de]anthracene as the

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HDS and reported that the yield of phenolic compounds increased with hydrogen donor addition. Kleinert et al.¹⁶ optimized solvolysis conditions for depolymerization of lignin to produce liquid biofuel using a mixture of formic acid and alcohol solvent as hydrogen donors.

In the previous studies using lab-scale batch reactors, it took a relatively long time (up to 1 h) before the samples reach preset temperatures. After reactions, the reactors had to be completely cooled to room temperature before the post-reaction products were taken out from the reactors for subsequent analysis. Thus, it has been difficult to investigate time-resolved reactions occurring during solvolysis at a given experimental condition in these studies. The present study overcomes these limitations by conducting solvolysis experiments in a micro reactor with online gas chromatography/mass spectrometry with a flame ionization detector (GC/MS–FID), which is able to rapidly heat reactants to the preset temperature and immediately analyze the vapor-phase products before secondary reactions occur. Because very small amount of samples are used in the system, heat- and mass-transfer limitations are also greatly suppressed. When this system is employed, the benefit of using HDSs over non-HDS is investigated using two HDSs and a non-HDS.

■ EXPERIMENTAL SECTION

Materials. Cornstover-derived organosolv lignin used in this study was obtained from Archer Daniels Midland (ADM) Company. To remove any catalytic effects of inorganic impurities, the lignin was purified by washing in 0.1 N hydrochloric acid, followed by repeated washing with deionized water until a neutral pH was obtained. The proximate and ultimate analyses of organosolv lignin were conducted using thermogravimetric analysis (TGA) (Mettler Toledo, Columbus, OH) and a Vario Micro Cube elemental analyzer (Elementar, Germany), respectively. The results of proximate and ultimate analyses are shown in Table 1. Tetralin, isopropanol, and naphthalene were purchased from Sigma-Aldrich and used without further purification.

Table 1. Ultimate and Proximate Analyses of Organosolv Lignin

Proximate Analysis (wt %)	
moisture	4.92
volatile	59.64
fixed carbon	34.48
ash	0.97
Ultimate Analysis (wt %)	
C	62.80
H	5.75
O ^a	29.81
N	1.64

^aBy difference.

Solvolysis Using an Online Micro Reactor. Solvolysis of lignin was conducted in a sealed glass capsule (inner diameter, 1.6 mm; outer diameter, 2.24 mm; and height, 26 mm) and heated in a micro reactor (PY1-1050, Frontier Laboratories, Japan) attached to a micro furnace pyrolyzer (PY-3030D, Frontier Laboratories, Japan) with online product analysis, illustrated in Figure 1. Tetralin and isopropanol were used as HDSs, and naphthalene was used as a non-HDS for comparison. Prior to actual test, a blank run test was performed. From this blank test, it was confirmed that isopropanol and tetralin act as hydrogen-donating agents in the given experimental conditions. For example, it was found that isopropanol converted to acetone upon donation of hydrogen and tetralin converted to naphthalene in the same manner. Approximately 500 µg of lignin samples and 5 µL of

solvent (except for naphthalene, for which 5.7 mg was added) were placed in a glass capsule. After the capsule was inserted in a heat sink, the open end was purged with nitrogen and sealed using a micro torch. The sealed glass capsule was inserted into the micro reactor, and the micro reactor was placed in the furnace of the Frontier micro pyrolyzer. Although the actual heating rate of the sample is difficult to directly measure, a computational fluid dynamics (CFD) simulation of the system indicated an approximate heating rate of 6 °C/s (in comparison to only less than 0.5 °C/s for autoclave experiments). Experiments were conducted at 300, 350, and 400 °C for 5, 10, or 15 min. The pressure within the glass capsule was calculated for each reaction temperature using the van der Waals equation of state. The calculated pressure ranged from 1.5 to 1.9 MPa for tetralin and from 3.1 to 3.8 MPa for isopropanol in the temperature range of 300–400 °C. After the desired reaction time was reached, the screw on the top of the micro reactor was turned, which crushed the glass capsule, releasing volatiles to the gas stream, which were directly swept to a GC system for analysis. Identification and quantification of solvolysis products of lignin were performed using GC (Varian CP-3800, Palo Alto, CA) equipped with MS (Saturn 2200 MS, Palo Alto, CA) and a FID. The capillary column used was a Phenomenex ZB-1701 (60 m × 0.25 mm × 0.25 µm). The injection temperature was 275 °C, and the split ratio used was 1:100. The GC oven temperature was programmed to hold at 35 °C for 3 min, ramp up to 280 °C with 3 °C/min, and then hold for an additional 4 min. In this work, 21 lignin-derived monomeric phenols were identified and quantified using a GC/MS–FID system after calibrating with authentic compounds purchased from Sigma-Aldrich.

Separate solvolysis experiments were conducted to investigate the molecular weight distribution of products, including non-volatile products that cannot be detected by GC. Instead of crushing the glass capsule after the desired reaction time, it was removed from the furnace chamber and immediately cooled in an ice bath to prevent further reaction. The glass capsule was cracked open, and the liquid products were dissolved in 1 mL of tetrahydrofuran (THF). All samples were filtered with a Whatman 0.45 µm glass microfiber (GMF) syringe filter before analysis. Gel permeation chromatography (GPC) analysis was performed using a high-performance liquid chromatography system (Ultimate 3000, Dionex, Sunnyvale, CA) equipped with a Shodex refractive index (RI) and diode array detector (DAD). GPC standards, which contained polystyrene ranging from 162 to 38 640 g/mol, were purchased from Agilent and used for calibration.

■ RESULTS AND DISCUSSION

Lignin Solvolysis with Tetralin. Typical GC/MS chromatograms of lignin solvolysis with tetralin or isopropanol are given in Figure S1 of the Supporting Information. Table 2 lists the compounds identified and quantified by GC analysis. Among the 21 phenolic compounds investigated in this study, alkylated (methyl, ethyl, and propyl) phenolic monomers as well as phenol, guaiacol, and syringol are referred to as short-chain alkyl phenols (SCAP). Similarly, 4-vinylphenol, 2-methoxy-4-vinylphenol, and 2,6-dimethoxy-4-vinylphenol are categorized as vinylphenols (VP). Because the peaks of 4-vinylphenol and 2-methoxy-4-vinylphenol on the chromatogram slightly overlapped each other, the peaks were treated as one and quantified using the response factor of 4-vinylphenol.

The yields of monomeric phenols from the solvolysis of lignin with tetralin are presented in Figure 2. It should be noted that the GC retention times of 2-methoxyphenol and 4-methylphenol coincided with that of tetralin, precluding their quantitative analysis. As shown in this figure, the yield of total monomeric phenols (TMP) slightly increased with increasing reaction time over the range investigated. However, the influence of the reaction time was relatively small in the overall range tested. Increasing reaction times from 5 to 15 min at 300

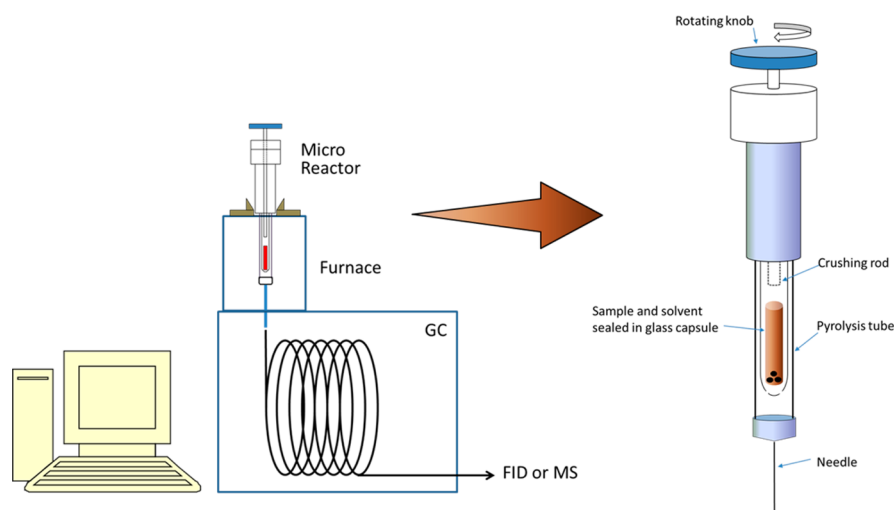


Figure 1. Schematic diagram of the online micro reactor system.

Table 2. List of Monomeric Phenols Identified and Quantified

compound	molecular formula	carbon distribution ^a
phenol ^b	C ₆ H ₆ O	C6
2-methoxyphenol ^b	C ₇ H ₈ O ₂	C6
2-methoxy-4-methylphenol ^b	C ₈ H ₁₀ O ₂	C1C6
4-ethylphenol ^b	C ₈ H ₁₀ O	C2C6
4-ethyl-2-methoxyphenol ^b	C ₉ H ₁₂ O ₂	C2C6
4-vinylphenol ^c	C ₈ H ₈ O	
2-methoxy-4-vinylphenol ^c	C ₉ H ₁₀ O ₂	
2-methoxy-4-propylphenol ^b	C ₁₀ H ₁₄ O ₂	C3C6
2,6-dimethoxyphenol ^b	C ₈ H ₁₀ O ₃	C6
isoeugenol (<i>trans</i>)	C ₁₀ H ₁₂ O ₂	
2,6-dimethoxy-4-methylphenol ^b	C ₉ H ₁₂ O ₃	C1C6
vanillin	C ₈ H ₈ O ₃	
2,6-dimethoxy-4-ethylphenol ^b	C ₁₀ H ₁₄ O ₃	C2C6
1-(4-hydroxy-3-methoxyphenyl)-ethanone	C ₉ H ₁₀ O ₃	
2,6-dimethoxy-4-vinylphenol ^c	C ₁₀ H ₁₂ O ₃	
1-(4-hydroxy-3-methoxyphenyl)-2-propanone	C ₁₀ H ₁₂ O ₃	
2,6-dimethoxy-4-propylphenol ^b	C ₁₁ H ₁₆ O ₃	C3C6
4-hydroxybenzenepropanoic acid, methyl ester	C ₁₀ H ₁₂ O ₃	
2,6-dimethoxy-4-(1-propenyl)-phenol (<i>trans</i>)	C ₁₁ H ₁₄ O ₃	
1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone	C ₁₀ H ₁₂ O ₄	
1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone	C ₁₁ H ₁₄ O ₄	

^aCarbon distribution was determined by the number of carbons in the side chain for the alkylphenols. ^bShort-chain alkylphenols. ^cVinylphenols.

°C increased the yield of TMP from 5.5 to 5.9 wt %, increased the yield of SCAP from 1.9 to 2.8 wt %, and decreased the yield of VP from 2.8 to 2.3 wt %. Although the same trend was observed at higher temperatures (350 and 400 °C), the effect was small.

The reaction temperature, different from the influence of the reaction time, had a larger influence on product yields for lignin decomposition in tetralin. For the shortest reaction time tested (5 min), as the reaction temperature increased from 300 to 400 °C, the yield of TMP increased from 5.5 to 10.9 wt %, the yield of SCAP increased from 1.9 to 7.7 wt %, and the yield of VP decreased from 2.8 to 2.2 wt %. The highest yields of TMP and SCAP were observed at 400 °C. For the longest reaction time (15 min), the yield of TMP increased from 5.9 to 11.4 wt % and the yield of SCAP increased from 2.8 to 8.7 wt % as the reaction temperature increased from 300 to 400 °C. Using a HDS resulted in a decrease in the yield of vinyl (styrene

derivatives) group containing phenols with increasing the time and temperature, possibly because of further hydrogenation.¹⁵ The increase in the yield of SCAP and decrease in the yield of VP in the overall reaction conditions investigated resulted in increasing selectivity toward SCAP. As shown in Table S1 of the Supporting Information, the selectivity of SCAP increased from 34.4% (300 °C and 5 min) to 76.4% (400 °C and 15 min) over the entire reaction temperature and time tested.

Distribution into the different product groups (C6, C1C6, C2C6, and C3C6; see Table 2 for descriptions) was determined by the number of carbons in the side chain of the products (see Table S1 of the Supporting Information). For tetralin, the yield of each group increased with both increasing the reaction temperature and time. After 15 min at 400 °C, the yield of C6 units was 3.5 wt %, followed by C2C6 (3.2 wt %), C1C6 (1.7 wt %), and C3C6 (0.3 wt %) units. This suggests that the high yield of C6 units is attributed to enhanced cracking of side

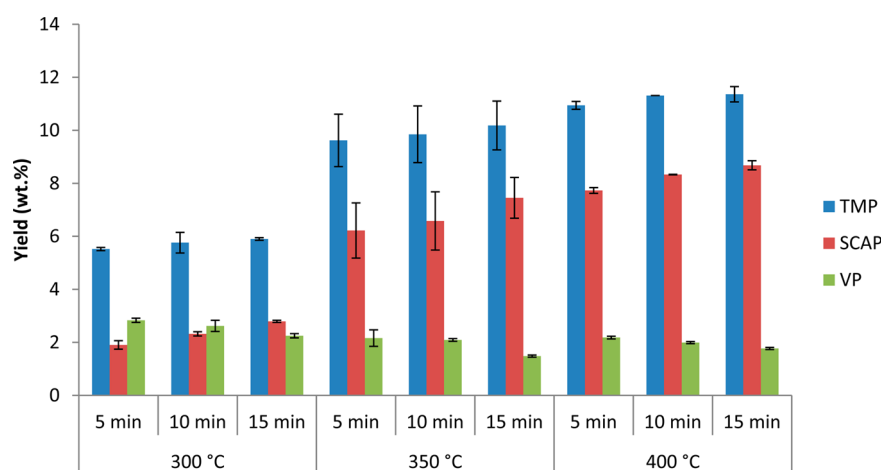


Figure 2. Product distribution obtained from the lignin/tetralin system at various reaction conditions (TMP, total monomeric phenols; SCAP, short-chain alkylphenols; and VP, vinylphenols).

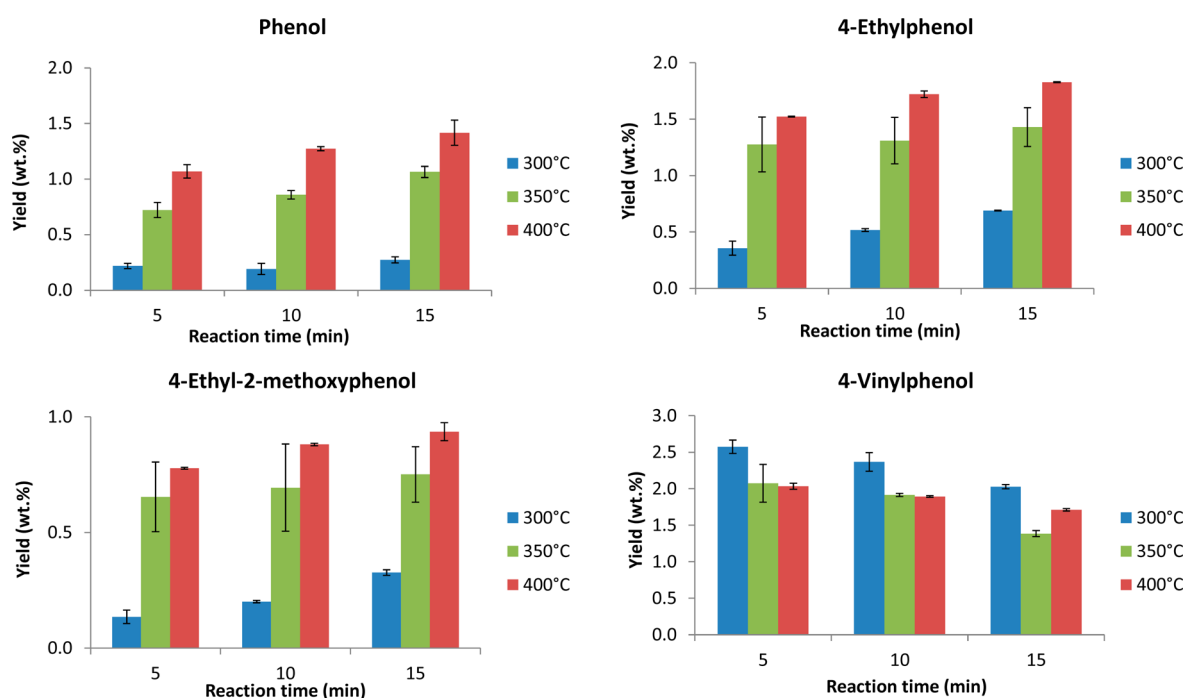


Figure 3. Products from solvent liquefaction of lignin in tetralin.

chains with increasing the reaction time.²² Furthermore, the increase in the yield of C2C6 units can be explained by HDS-induced stabilization. In previous work with the same lignin, phenol (C6), syringol (C6), 4-vinylphenol (C2C6), and 2-methoxy-4-vinylphenol (C2C6) were found to be the major products from lignin pyrolysis.⁶ Generally, VP are the major phenolic compounds in the pyrolysates of lignocellulosic materials, resulting from the cleavage of β -O-4 linkages.²³ Because tetralin is capable of capping the highly reactive allyl- and vinyl-substituted phenols,²⁴ VP are thought to have stabilized via hydrogenation to alkyl-substituted phenols (SCAP), predominantly to 4-ethylphenol (C2C6) and 4-ethyl-2-methoxyphenol (C2C6) found in this study (see Figure 3).

At higher reaction temperatures and longer reaction times, decreases were observed in guaiacyl/*p*-hydroxyphenyl (G/H) ratios and syringyl/*p*-hydroxyphenyl (S/H) ratios, which

demonstrates that demethoxylation reactions were promoted in the presence of tetralin.¹⁵ At 400 °C, the G/H ratio and S/H ratio decreased 13 and 15% when the reaction time increased from 5 to 15 min. The conversion of G- or S-unit phenols to H-unit phenols because of demethoxylation is expected.

Lignin Solvolysis with Isopropanol. The influences of the reaction temperature and time on product yields for lignin decomposition in an isopropanol solvent are shown in Figure 4. In general, the influence of the reaction time was relatively small in the range investigated. At the lowest temperature tested (300 °C), as the reaction time was increased from 5 to 15 min, the yield of TMP increased from 3.9 to 4.3 wt %, SCAP increased from 1.6 to 2.4 wt %, and VP showed a relatively modest decrease from 1.7 to 1.2 wt %. Similarly small effects of reaction time were also observed at higher reaction temperatures.

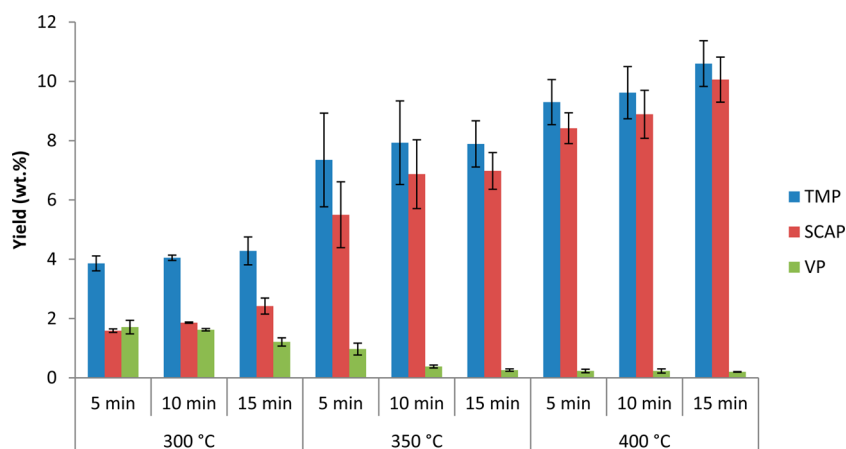


Figure 4. Product distribution obtained from the lignin/isopropanol system at various reaction conditions (TMP, total monomeric phenols; SCAP, short-chain alkylphenols; and VP, vinylphenols).

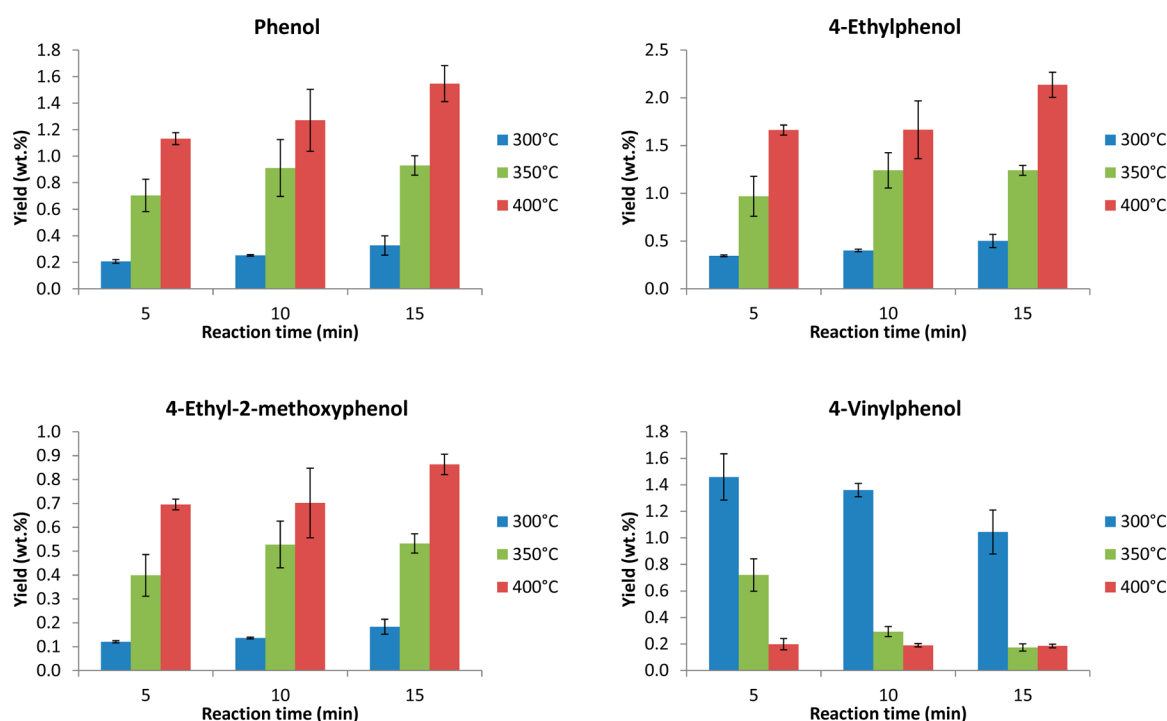


Figure 5. Products from solvent liquefaction of lignin in isopropanol.

The temperature had a much larger influence on product composition. For the shortest reaction time tested (5 min), as the reaction temperature increased from 300 to 400 °C, the yield of TMP increased from 3.9 to 9.3 wt % and the yield of SCAP increased from 1.6 to 8.4 wt %, while the yield of VP decreased from 1.7 to 0.2 wt %. Similarly, large changes with the temperature were observed for longer reaction times.

Selectivity toward SCAP was strongly influenced by both the reaction time and temperature (see Table S2 of the Supporting Information). The selectivity toward SCAP increased from 41.2% (at 300 °C and 5 min run) to 94.9% (at 400 °C and 15 min run) over the entire reaction temperature and reaction time tested. Examination of the product distribution compared to the lignin/tetralin system (34.4–76.4%) showed higher selectivity of SCAP. This might be attributed to the high hydrogen donor capability of isopropanol because the yield of

VP from lignin/isopropanol was significantly lower than that from lignin/tetralin at all reaction conditions.

Table S2 of the Supporting Information shows the distribution of products into the different groups. The yield of each group increased as the reaction time increased at all temperatures tested. At 400 °C, the highest yield was observed from C6 units (4.9 wt %), followed by C2C6 (3.3 wt %), C1C6 (1.5 wt %), and C3C6 (0.3 wt %), which are in the same order as found from the lignin/tetralin system. Figure 5 shows the yield of major products from lignin decomposition in isopropanol solvent at each reaction condition. As discussed, the yields of phenol (C6), 4-ethylphenol (C2C6), and 4-ethyl-2-methoxyphenol (C2C6) increased with a prolonged reaction time, while the yield of 4-vinylphenol (including 2-methoxy-4-vinylphenol) decreased at the same reaction conditions. Other vinylphenols showed similar trends at this condition. This result supports the hypothesis that secondary reactions, including

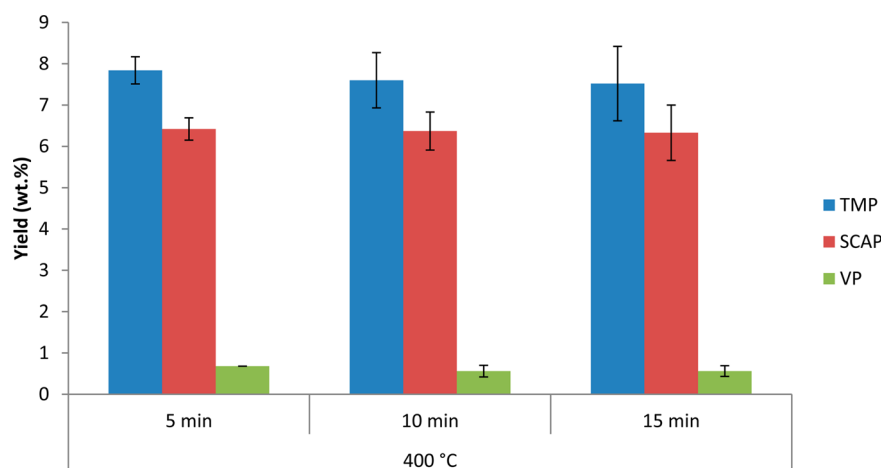


Figure 6. Product distribution obtained from the lignin/naphthalene system at various reaction conditions (TMP, total monomeric phenols; SCAP, short-chain alkylphenols; and VP, vinylphenols).

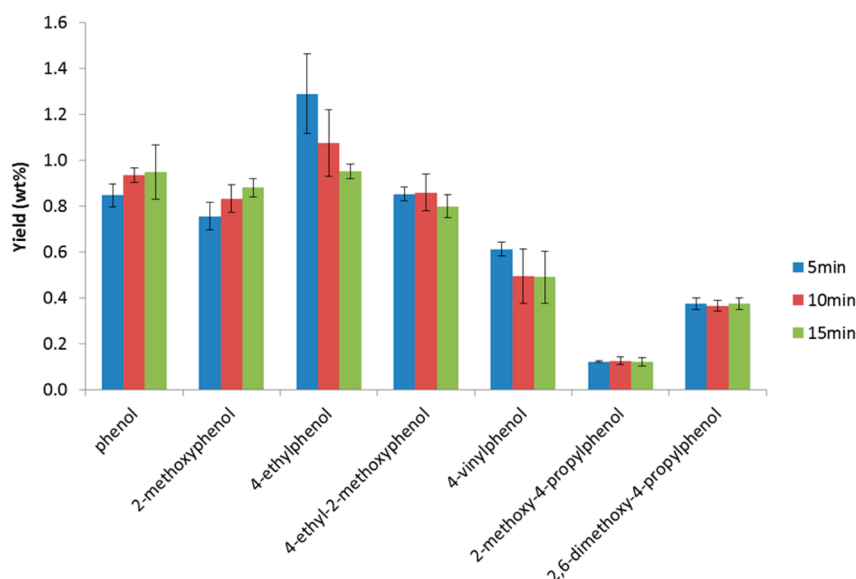


Figure 7. Products from solvent liquefaction of lignin in naphthalene at 400 °C.

side-chain cleavage and stabilization of reactive functional groups through hydrogenation, take place in the presence of a HDS.

Also, a conversion from S and G unit to H unit was observed at a higher reaction temperature and a longer reaction time. As found in the lignin/tetralin system, a demethoxylation was promoted in the presence of HDS. G/H and S/H ratios decreased 5.2 and 26.4%, respectively, after 15 min at 400 °C compared to the ratios after reacting for 5 min at the same temperature.

Lignin Solvolysis with Naphthalene. Lignin was reacted in naphthalene, which is not a hydrogen donor, to further test the hypothesis that the HDSs increase selectivity toward SCAP.^{25,26} The results of these tests are presented in Figure 6. The solvolytic conversion of lignin in naphthalene at 400 °C for 5 min resulted in TMP yields of 7.8 wt %. The yield of SCAP in this reaction condition was 6.4 wt %, which was lower than that for tetralin (7.7 wt %) and isopropanol (8.4 wt %). In contrast to the cases with tetralin and isopropanol, increasing the reaction time to 15 min increased the yield of TMP to 7.5 wt % and decreased the yield of SCAP to 6.3 wt %. While the yield of

SCAP increased with time when the solvent was tetralin or isopropanol, the yield decreased with time when naphthalene was the solvent. The decrease in yields of TMP and SCAP with the reaction time when naphthalene was the solvent is likely the result of secondary reactions, with primary products likely converted into higher molecular weight substances. This suggests that a prolonged reaction time in the absence of hydrogen is deleterious to yields of TMP and SCAP.²⁶ Although the selectivity toward SCAP slightly increased from 81.9 to 84.4% with increasing the reaction time from 5 to 15 min at 400 °C, this is because the yield of TMP (which includes both reactive phenols and SCAP) was reduced more significantly compared to the yield of SCAP. Table S3 of the Supporting Information shows the distribution of SCAP into the different product groups. As shown, the yield of C6 compounds increased, while the yield of other groups decreased or remained constant with increasing the reaction time. The increase in the yield of C6 units can be explained by secondary reactions that crack side chains of phenolic compounds,^{22,27} which occurred regardless of the solvent type. The yields of phenol and 2-methoxyphenol, as shown in

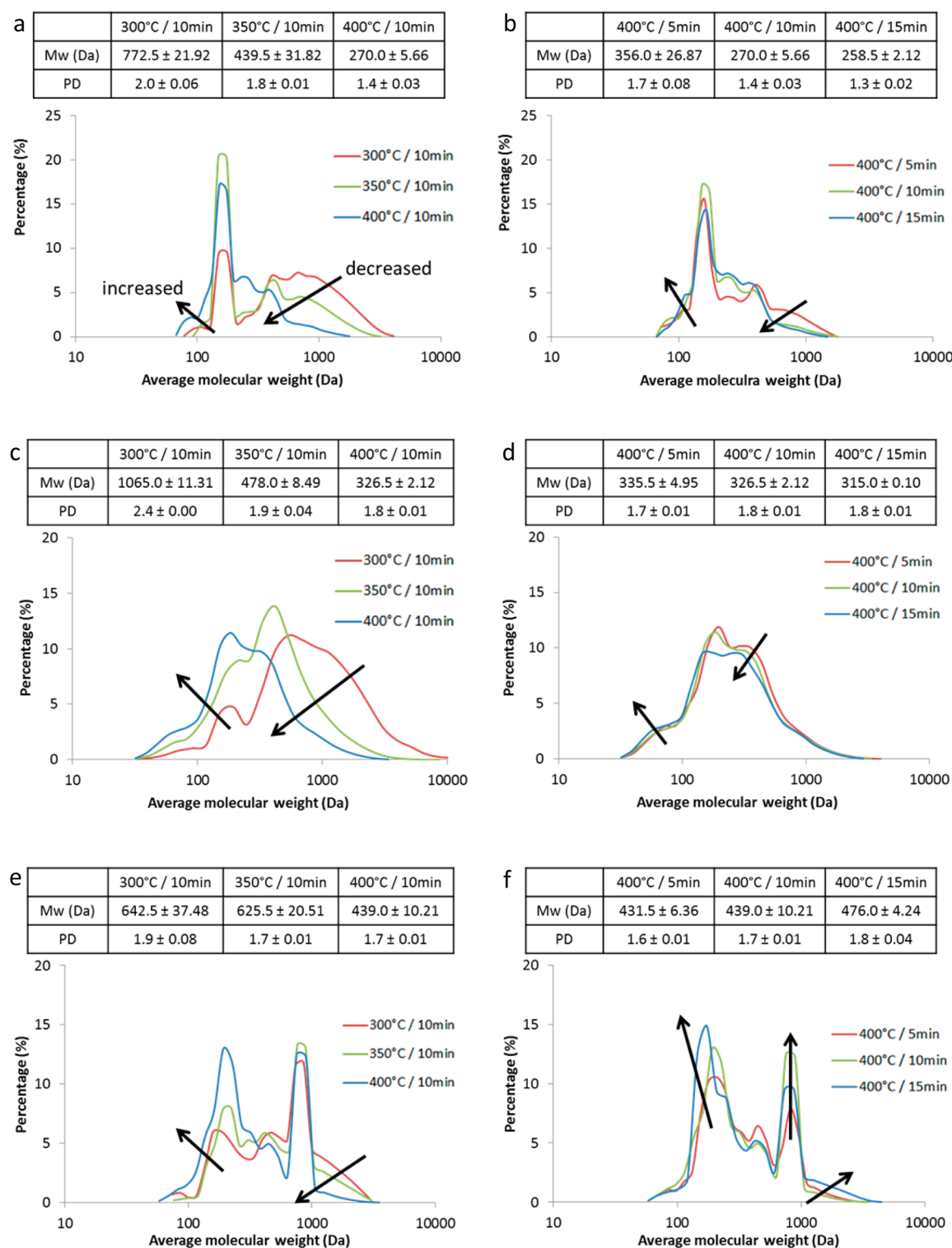


Figure 8. Average molecular weight and molecular weight distribution of solvolysis products from each solvent system: (a and b) lignin/tetralin, (c and d) lignin/isopropanol, and (e and f) lignin/naphthalene.

Figure 7, support this explanation. As the reaction time was prolonged to 15 min, the yield of C2C6 units, including 4-ethylphenol, decreased from 3.1 to 2.8 wt %. In the absence of a hydrogen donor, the primary products are able to repolymerize to high-molecular-weight compounds or char.²⁴

The demethoxylation reaction observed from the lignin/HDS system did not occur in the absence of a hydrogen donor. At 400 °C, the yield of the H unit decreased 11% with

increasing the reaction time from 5 to 15 min and the yield of G and S units was marginally affected over this reaction condition, which led to an increase in G/H and S/H ratios (see Table S3 of the Supporting Information).

Molecular Weight Distributions by GPC. The molecular weight distributions of the reaction products of lignin in tetralin, isopropanol, or naphthalene, determined by GPC analysis, are shown in Figure 8. As described in our previous

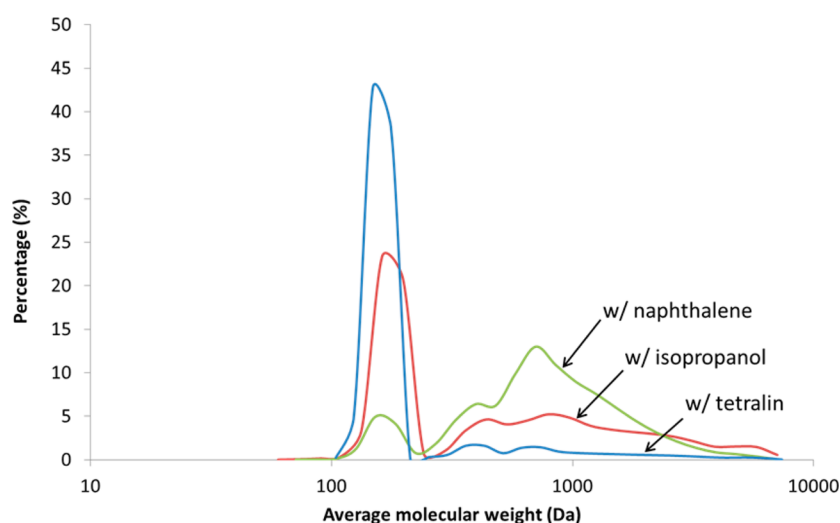


Figure 9. Molecular weight distribution of products obtained from 2-methoxy-4-vinylphenol with each solvent.

work, the unreacted lignin had a molecular weight of 1640 Da and polydispersity of 1.9.²⁸ At 300 °C and 10 min (Figure 8a), the molecular weight of reaction products obtained for tetralin as the solvent ranged from 78 and 4000 Da. The average molecular weight and polydispersity at this reaction condition were 773 Da and 2.0, respectively. As shown in panels a and b of Figure 8, the broad peak at 400–4000 Da decreased or shifted to a lower molecular weight region with an elevated reaction temperature (300–400 °C) and increased reaction time (5–15 min). The peak around 100 Da slightly increased over the entire reaction conditions tested. The average molecular weight of reaction products considerably decreased to 259 Da at 400 °C and 15 min with a reduced polydispersity value of 1.3. These results indicate that thermal decomposition of lignin in the presence of a HDS encouraged the production of low-molecular-weight bio-oil with relatively uniform molecular size distribution.

Lignin depolymerization in isopropanol showed a similar trend in molecular weight distributions, as shown in panels c and d of Figure 8. When lignin was thermally decomposed in isopropanol, the average molecular weight of the reaction products significantly decreased from 1065 to 326 Da and the polydispersity value decreased from 2.4 to 1.8 with increasing reaction temperatures (300–400 °C) at a fixed reaction time (Figure 8c). Also, it was found that the broad peak, which appeared around 200–1000 Da, decreased with increasing reaction times (5–15 min), as shown in Figure 8d. In this figure, a shoulder below 100 Da increased with prolonged reaction times, corresponding with the GC results of increased C6 phenolic units.

The molecular weight distributions of solvolysis products obtained for naphthalene as the solvent are shown in panels e and f of Figure 8. In comparison to the reaction at 300 °C, a shoulder in the spectra above 1000 Da decreased and the peak below 200 Da increased when the reaction temperature was increased to 400 °C (Figure 8e). Because of the incomplete lignin conversion at low temperature, the decrease in the molecular weight of products with increasing the reaction temperature can be explained by thermally induced bond rupture, regardless of the solvent type. It has been observed that the cleavage of the OH functional group linked to the aliphatic side chain as well as the breaking of the alkyl side chain and aryl ethers occurs when the temperature increases.⁴

However, it appeared that HDSs were more effective in reducing the formation of oligomers with molecular weight around 1000 Da than when naphthalene was the solvent.

Figure 8f shows that the molecular weight of products from the thermal conversion of lignin in naphthalene increased with increasing reaction times (5–15 min). The peaks below 130 Da shifted to a lower molecular weight region possibly because of cracking reactions. The overall molecular weight of the reaction products, however, increased as the reaction further progresses in the absence of a hydrogen donor. This could be attributed to the increase in oligomers with a molecular weight of 1000 Da or higher, as shown in Figure 8f, as a result of primary products repolymerizing. Inspection of this figure confirms that secondary cracking and secondary repolymerization reactions take place simultaneously during thermal decomposition of lignin. In the presence of a HDS, however, the secondary repolymerization reactions are mitigated. The low volatility and high viscosity of high-molecular-weight phenolic oligomers are undesirable constituents in bio-oil whether the bio-oil is directly used for fuel or upgraded to gasoline and diesel. Preventing the formation of phenolic oligomers in favor of low-molecular-weight compounds would improve the utilization of bio-oil.

Repolymerization is likely caused by the high reactivity of lower molecular weight phenolic products. While the solvolytic conversion of lignin produced a significant amount of VP as primary products, they are known to be very reactive toward repolymerization because of the highly reactive unsaturated C=C group on the side chain.^{22,28} It was observed that SCAP increased at the expense of VPs when hydrogen donors were used as solvents. Therefore, this repolymerization could potentially be suppressed through the reaction of hydrogen donors with vinyl functionalities to form saturated alkyl groups. In the case of naphthalene, VPs cannot be stabilized against repolymerization because of the absence of hydrogen donors. To test this hypothesis, 2-methoxy-4-vinylphenol was reacted with both HDSs and non-HDSs. The products obtained from each solvent system were analyzed by GPC to determine molecular weight distributions (Figure 9). As shown, two peaks appeared around 150 and 700 Da from the thermal reaction of 2-methoxy-4-vinylphenol with naphthalene (non-HDS), which could be assigned to monomers and oligomers, respectively. When reacted with HDS, however, the peak around 150 Da significantly increased, while the broad peak of the oligomeric

region noticeably decreased. This result indicates that secondary repolymerization reactions involving vinyl functionalities can be suppressed with the assistance of HDSs.

It was previously reported that methoxy groups promote repolymerization, which could cause char formation.²⁹ Thus, demethoxylation of lignin products occurred by the reaction with HDSs could also contribute this suppression of repolymerization.

It should be noted that, because of the amount of samples (500 μg) and solvents ($\sim 5\ \mu\text{L}$) used for the present study, unreacted solvents were not able to be separated from the reaction products at post-reactions. Thus, the GPC chromatograms reported above may also include the solvent peaks. However, this does not affect usefulness of the discussion above because only the differences in decreasing or increasing trends of the compounds at varied molecular weight ranges with different reaction conditions are important in the present study.

CONCLUSION

The benefit of using HDSs for lignin solvolysis over non-HDS was explored using a micro reactor system coupled with online GC/MS–FID. It was found that HDSs were effective in converting lignin to SCAP. The yield of SCAP was over 10 wt % lignin, although no catalysts were used. When a hydrogen-donating solvent was employed, hydrogen abstraction from the solvents stabilized the primary products of lignin decomposition and resulted in the formation of an increasing amount of alkyl-substituted phenols. In comparison, lignin does not only yield relatively smaller amounts of TMP and SCAP, but the yield of SCAP also decreased with increasing the reaction time when non-HDS was employed. This is because highly reactive phenols, including VPs and possibly free radicals, produced as primary products of lignin decomposition, repolymerized to high-molecular-weight compounds. The conversion of G- or S-unit to H-unit phenolic monomers was also observed with HDSs, suggesting that HDSs also facilitate demethoxylation.

Analysis of molecular weight distributions of the reaction products indicated that the solvolytic conversion of lignin involved thermally induced decomposition of lignin macromolecules, followed by secondary reactions, including side-chain cracking and repolymerization reactions among the primary products. It was found that the presence of a hydrogen donor significantly reduced oligomer formation and stabilized products to alkyl-substituted phenols. Further, the present results will help to provide a basis for developing solvolysis models that can predict specific chemical compounds.

ASSOCIATED CONTENT

Supporting Information

Gas chromatogram of lignin solvolysis with tetralin and isopropanol (Figure S1) and list of monomeric phenols identified and quantified for tetralin (Table S1), isopropanol (Table S2), and naphthalene (Table S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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