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# Pre-methylation of lignin to improve storage stability of oil produced by solvent liquefaction

## Abstract

In this study, we methylated hydroxyl groups (phenolic hydroxyl: Phe-OH and aliphatic hydroxyl: Aliph-OH) in soda lignin (SL) prior to solvent liquefaction to improve storage stability of the resulting oil. We investigated two methylating reagents, dimethyl sulfate (DMS) and dimethyl carbonate (DMC), for selective Phe-OH and total hydroxyl group (Phe-OH and Aliph-OH) blocking. Samples of SL, DMS-SL, and DMC-SL were depolymerized into oils under supercritical ethanol (350 °C). Both methylated lignins produced higher amounts of oils and smaller amounts of char compared to untreated SL due to suppressed charring reactions. Oil produced from SL had relatively higher functional group contents than other oils from methylated lignins. Simulated one-year aging of oils was carried out and this revealed Mw increase of oil was the highest in SL (11.8 %), followed by DMC-SL (6.8 %) and DMS-SL (4.6 %). Interestingly, these increases showed linear correlation with decrease in Phe-OH after accelerated aging. Meanwhile, compositional difference in monomeric phenols in the oils were observed by GC/MS analysis. For example, methoxylated aromatics such as 4-ethylveratrole, 4-vinylveratrole, methylisoeugenol, and veratryl-2-propanone were detected only in oils from DMS-SL, and DMC-SL. Interestingly, there was no significant difference in monomeric compounds yields before and after accelerated aging among the oils, which suggests that repolymerization mainly occurred between oligomeric lignin fragments.

## Keywords

Lignin, Methylation, Solvent liquefaction, Repolymerization, Hydroxyl group

## Disciplines

Mechanical Engineering | Petroleum Engineering | Polymer Chemistry

## Comments

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**Energy & Fuels****Pre-methylation of lignin hydroxyl functionality for improving  
storage stability of oil from solvent liquefaction**

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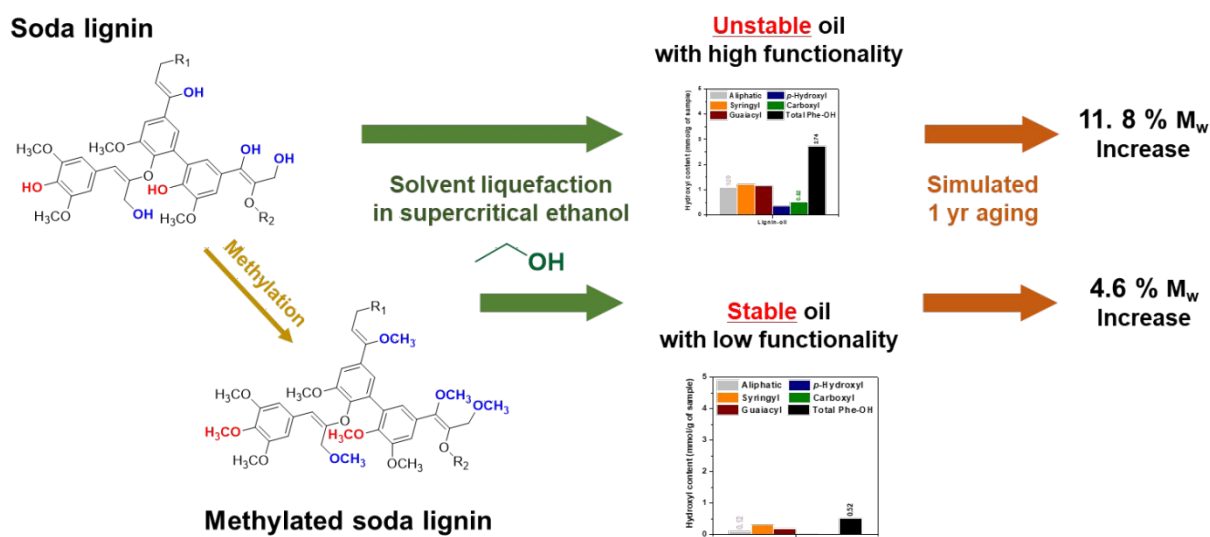
**ABSTRACT**

In this study, we methylated hydroxyl groups (phenolic hydroxyl: Phe-OH and aliphatic hydroxyl: Aliph-OH) in soda lignin (SL) prior to solvent liquefaction to improve storage stability of the resulting oil. We investigated two methylating reagents, dimethyl sulfate (DMS) and dimethyl carbonate (DMC), for selective Phe-OH and total hydroxyl group (Phe-OH and Aliph-OH) blocking. Samples of SL, DMS-SL, and DMC-SL were depolymerized into oils under supercritical ethanol (350 °C). Both methylated lignins produced higher amounts of oils and smaller amounts of char compared to untreated SL due to suppressed charring reactions. Oil produced from SL had relatively higher Phe-OH, Aliph-OH, and carboxyl content than other oils from methylated lignins. Simulated one-year aging of oils was carried out and this revealed  $M_w$  increase of oil was the highest in SL (11.8 %), followed by DMC-SL (6.8 %) and DMS-SL (4.6 %). Interestingly, these increases showed linear correlation with decrease in Phe-OH after accelerated aging. Meanwhile, compositional difference in monomeric phenols in the oils were observed by GC/MS analysis. For example, methoxylated aromatics such as 4-ethylveratrole, 4-vinylveratrole, methylisoeugenol, and veratryl-2-propanone were detected only in oils from DMS-SL, and DMC-SL. Interestingly, there was no significant difference in monomeric compounds yields before and after accelerated aging among the oils, which suggests that repolymerization mainly occurred between oligomeric lignin fragments.

**Keywords: Lignin, Methylation, Solvent liquefaction, Repolymerization, Hydroxyl group**

## Graphical abstract

- Blocking high reactive hydroxyl group in lignin improve storage stability of its derived oil from solvent liquefaction



## 1. Introduction

Lignin is the second most abundant nature polymeric material next to cellulose in earth and accounts for approximately 15 to 40 wt% of lignocellulosic biomass.<sup>1</sup> Lignin consist of methoxylated phenylpropane units with various inter-unit linkages such as  $\beta$ -O-4 (40-60%),  $\beta$ -5 (4-10%) and biphenyl (3.5-25%).<sup>2</sup> It can potentially serve as phenolic resource for producing liquid fuels and value-added chemicals.<sup>3</sup> A recent study reported that more than 1.3 billion tons of biomass was annually generated from agricultural and forestry fields in US, which suggests its use as a sustainable source of lignin-derived carbon.<sup>4</sup> In fact, approximately 50-70 million tons of lignin has been produced each year from pulp and paper industries, but less than 2 % of them were commercialized.<sup>5</sup> In addition, US Department of Energy predicts approximately 225 million tons of lignin will be additionally produced from the lignocellulosic based biorefinery by 2030.<sup>6</sup>

Solvent liquefaction is a thermochemical process performed at relatively low temperature (250 to 550 °C) compared to pyrolysis and gasification.<sup>7</sup> Solvent liquefaction is widely proposed for converting lignin into liquid fuels and chemicals including polyurethane adhesives and foams.<sup>8-11</sup> One advantage of solvent liquefaction is that products are diluted in the solvent, reducing recondensation reactions that generate undesirable products.<sup>12</sup> Oils from solvent liquefaction of lignin include phenolic monomers (alkylated phenols and oxygenated phenols) and phenolic oligomers.<sup>3, 13</sup> Previous researchers have focused on developing new catalyst/solvent systems and optimizing process condition to increase yields of oil and phenolic monomers.<sup>14-18</sup> Although many studies have been carried out there is insufficient information on the storage stability of lignin-derived oils from solvent liquefaction. During storage, changes in physicochemical properties such as viscosity, molecular weight, and chemical composition occur. In particular, variations in molecular weight can directly affect

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4 the aging of oils.<sup>19</sup> There exists only one prior study by Lyckeskog et al. who investigated  
5 storage stability of oils derived from catalytic conversion of softwood kraft lignin in  
6 subcritical water.<sup>20</sup>  
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11 It has been previously reported that phenolics in fast pyrolysis bio-oil was one of the  
12 reason for increasing molecular weight of bio-oil during storage. Diebold reported that  
13 aldehydes from carbohydrate and phenolics from lignin could combine leading to formation  
14 of resins and water.<sup>21</sup> Yang et al.<sup>19</sup> and Chen et al.<sup>22</sup> report that highly reactive functional  
15 groups including carbonyl, hydroxyl, and unsaturated carbon-carbon bonds might result in  
16 undesirable chemical reactions such as polymerization and condensation that continue during  
17 storage. Kim et al.<sup>22</sup> observed that Phe-OH content of pyrolytic lignin in bio-oil gradually  
18 decreased while molecular weight of bio-oil increased with increasing storage duration. Sen  
19 et al.<sup>23</sup> suggested blocking hydroxyl groups in lignin can prevent thermal polymerization.  
20 The results of previous studies imply that hydroxyl functionality in lignin-derived oil plays a  
21 deleterious role in storage stability.  
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36 This study explores the effect of blocking hydroxyl functionality in lignin-derived oil  
37 from solvent liquefaction on storage stability, with a special emphasis on molecular weight  
38 changes. We hypothesize that blocking hydroxyl groups in lignin prior to solvent liquefaction  
39 produces oil with reduced hydroxyl functionality resulting in improved molecular weight  
40 stability during storage. Based on this hypothesis, we prepared three lignins of different  
41 hydroxyl content via two chemoselective methylation processes. Ethanol with a relatively  
42 low critical point (243 °C, 6.39 MPa) was used as solvent in the liquefaction process because  
43 it can not only act as a hydrogen-donor solvent, but also stabilize the highly reactive phenolic  
44 intermediates.<sup>14, 24</sup> Produced oils from three lignins were further introduced to simulate one-  
45 year aging, and their change in physicochemical properties were compared using several  
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4 analytical techniques.  
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## 8 9 **2. Experimental section**

### 10 11 **2.1 Materials**

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13 Protobind 1000 soda lignin (SL, GreenValue SA, Switzerland) extracted from a mixture  
14 of sarkanda grass and wheat straw was used in this study. Before all experiments, SL was  
15 washed with 0.1 N nitric acid (HNO<sub>3</sub>) at room temperature for 5 min to remove inorganic  
16 metals, followed by rinsed with sufficient deionized water, filtered and then dried in vacuum  
17 oven at 30 °C for 24 h. Representative inorganic metals in SL determined by Inductively  
18 Coupled Plasma-Optical Emission Spectrometer (ICP-OES) (Optima 8000, PerkinElmer)  
19 were sodium (0.228 wt%), potassium (0.170 wt%), and calcium (0.014 wt%). These values  
20 decreased to 0.035 wt%, 0.024 wt%, and 0.003 wt%, respectively, after acid washing. All  
21 solvents used in this study (HPLC grade) were purchased from Fisher Scientific, and other  
22 chemicals were obtained from Sigma Aldrich.  
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### 39 **2.2 Lignin methylation**

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41 Hydroxyl groups in lignin (phenolic hydroxyl: Phe-OH and aliphatic hydroxyl: Aliph-  
42 OH) were methylated using either of two methylation reagents (dimethyl sulfate: DMS and  
43 dimethyl carbonate: DMC) as displayed in Scheme 1. According to a previous study, DMS in  
44 aqueous NaOH achieves selective methylation of Phe-OH in SL without apparent side  
45 reactions.<sup>25</sup> SL was dissolved in 0.7 M NaOH solution (50 mL/g of lignin) with DMS (5  
46 mL/g of lignin) and then heated to 80 °C for 2 h. Methylated lignin with DMS (DMS-SL)  
47 was recover after acidification with 2 M HCl followed by deionized water washing and then  
48 freeze-drying. To methylate Phe-OH and Aliph-OH functionalities using DMC, SL was  
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4 dissolved in dimethyl sulfoxide (DMSO, 20 mL/g of lignin) with DMC (2.4 mL/g of lignin)  
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6 and NaOH (0.25g/g of lignin).<sup>23</sup> This mixture was heated to 130 °C for 15 h. Methylated  
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8 lignin with DMC (DMC-SL) was recovered by same protocol as previously described for  
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10 methylation with DMS.  
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### 16 **2.3 Lignin liquefaction process**

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18 Prepared lignins were liquefied in mini-reactors (316SS, Swagelok) with total volume of  
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20 2.5 mL. Fifty milligrams of lignin and 1.25 mL of ethanol were placed in a mini-reactor.  
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22 Samples were tightly sealed in the mini-reactors and introduced into a fluidized sand bath  
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24 (Techne Industrial Bed 51) operated at 350 °C for 20 min. after which time samples were  
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26 removed and immersed in cold water.<sup>26</sup> With an estimated heating rate of 7 °C s<sup>-1</sup>, samples  
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28 required less than 1 minute to reach reaction temperature. Cooling time was similarly less  
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30 than 1 minute. Cooled reactors were opened and solid (char) and liquid product (oil and  
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32 ethanol solvent) removed. To improve mass balance, 4 mL of acetone was used to rinse the  
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34 inside of reactor, which was combined with the rest of the products. Char was separated by  
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36 centrifugation (3500 RPM for 20 min) and dried at 75 °C for 24 h. Oil was recovered from  
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38 the liquid fraction by evaporating the solvent mixture (ethanol and acetone) at 30 °C for 24 h  
39  
40 in vacuum oven. Oils were designated as SL oil, DMS-SL oil, and DMC-SL oil depending on  
41  
42 the kind of lignin. The yield of each product was calculated as following equation.  
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$$50 \text{ Oil yield (wt\%)} = \frac{\text{Weight of oil (mg)}}{\text{Weight of raw lignin (mg)}} \times 100$$

$$51 \text{ Char yield (wt\%)} = \frac{\text{Weight of solid fraction (mg)}}{\text{Weight of raw lignin (mg)}} \times 100$$

## 2.4 Accelerated aging experiment of oils

To simulate one-year aging at ambient temperature, oils were subjected to accelerated aging tests.<sup>27</sup> One hundred milligrams of oil was placed in a 20 mL glass bottle and dried in an oven at 105 °C for 4 h . Accelerated aging tests were conducted at 80 °C for 24 h.

## 2.5 Characterization of lignins and oils

An AVIII-600 NMR spectrometer with narrow bore 14.1 tesla superconducting magnet and an Avance III spectrometer console from Bruker Corporation (Billerica, MA and Karlsruhe, Germany) was used for NMR analysis. <sup>31</sup>P-NMR analysis was performed to quantify the hydroxyl group content in the lignins.<sup>28</sup> 20-25 mg of lignin was phosphitylated with 70 μl of 2-chloro-4,4,5,5,-tetramethyl-1,3,2-dioxaphospholane (TMDP) and cyclohexanol was used as an internal standard (IS). Inverse-gated decoupling pulse sequence using a 45 degree pulse angle and 5.0 s relaxation delay. Number of scans, acquisition time, and pulse lengths used in this analysis was 64, 0.557 sec, and 285 kHz pulse, respectively. The resulting <sup>31</sup>P-NMR spectra were integrated using the MestReNova v10.0 software.

The weight percentages of carbon, hydrogen, nitrogen, and sulfur of lignins were measured by Elementar elemental analyzer (vario MICRO cube). The oxygen content was calculated by difference.

Gel permeation chromatography (GPC) analysis was performed to investigate molecular weight distributions of the lignins and product oils. All lignins were acetylated with acetic anhydride/pyridine (1:1 v/v) at 70 °C for 6 h to dissolve in tetrahydrofuran (THF). Prior to GPC analyses, approximately 3 mg of sample was dissolved in 1 mL THF, with the solution filtered using a syringe filter. It was analyzed by Dionex Ultimate 3000 HPLC system equipped with two GPC columns (3 μm, 100 Å, 300 × 7.5 mm; PLgel, Agilent) connected in

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4 series. GPC column was calibrated using six polystyrene standards (Agilent EasiVial,  
5 PL2010-0400) of molecular weights ranging from 162-50,000 Da. The effluents were  
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7 detected by a Shodex refractive index detector and a diode-array detector.  
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11 Identification and quantification of chemical compounds in the oils were performed  
12 using a gas chromatograph with mass spectrometer and flame ionization detector (GC-  
13 MS/FID, Agilent HP5977A/Agilent 7890B). Oils were diluted to 5 mg/ml in acetone and 1.0  
14  $\mu\text{l}$  samples injected into Phenomenex ZB 1701 (60 m  $\times$  0.250 mm  $\times$  0.250  $\mu\text{m}$  film thickness)  
15 capillary columns with a split ratio of 1:5. In this system, the separated products were split to  
16 FID and MS system. The oven temperature program began at 50  $^{\circ}\text{C}$  for 5 min; continued at a  
17 heating rate of 10  $^{\circ}\text{C}/\text{min}$  to 180  $^{\circ}\text{C}$ ; continued at a heating rate of 5  $^{\circ}\text{C}/\text{min}$  to 290  $^{\circ}\text{C}$ ; held  
18 at that temperature for 20 min. The injector and detector temperatures were 250  $^{\circ}\text{C}$  and  
19 300  $^{\circ}\text{C}$ , respectively, and He (99.9% purity) was used as the carrier gas. The mass spectra of  
20 each compound were identified using NIST MS Search 2.0 (NIST/EPA/NIH Mass Spectral  
21 Library; NIST 02). The internal standard was 0.135 mg/ml of octadecane in acetone. The  
22 yield of compounds was quantified by application of appropriate response factors for each  
23 compound according to the following equation:<sup>29, 30</sup>  
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$$41 \text{Yield (mg/g oil)} = \text{Response factor} \times \frac{\text{Compound peak area (FID)}}{\text{Internal standard peak area (FID)}} \times \frac{\text{Internal standard mass (mg)}}{\text{Oil mass (g)}}$$

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### 46 **3. Results and discussion**

#### 47 **3.1 Methylation of SL with two different methylating reagents**

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49 Figure 1 displays (a)  $^{31}\text{P}$ -NMR spectra of methylated lignins and (b) calculated  
50 functional group contents.<sup>28</sup> As shown in Figure 1 (b), SL was enriched in both Phe-OH  
51 content (2.54 mmol/g) and Aliph-OH content (1.38 mmol/g). In contrast, DMS-SL displayed  
52 only Aliph-OH content (1.22 mmol/g) with Phe-OH being absent. Carboxyl group was still  
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4 present in DMS-SL. This result might reflect differences in reactivity of methylation reagents  
5 to carboxyl group. When DMC was used as methylating reagent, Aliph-OH content  
6 significantly decreased to 0.42 mmol/g while Phe-OH and carboxyl groups completely  
7 disappeared.  
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13  
14 Elemental composition and  $C_9$  formula for the lignins were investigated as presented in  
15 Table 1. Carbon content increased with increasing methylation in the following order: DMC-  
16 SL > DMS-SL > SL whereas oxygen content showed the opposite trend. Interestingly, DMC-  
17 SL had slightly higher sulfur content compared to the other lignin samples, which might  
18 come from the DMSO used in the DMC methylation process. According to a previous  
19 study,<sup>23</sup> DMSO anions potentially produced at higher temperatures under basic conditions  
20 could react with Aliph-OH resulting in sulfur-containing cyclic products via an intra-  
21 molecular rearrangement. Meanwhile, the  $C_9$  formula of SL showed the relative molar ratio  
22 of Phe-OH and Aliph-OH was 0.45 and 0.14, respectively, and these values decreased after  
23 both methylation processes, as anticipated.  
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37 The molecular weights of lignin samples were also examined. The resulted GPC curves  
38 and molecular weight information (the weight average molecular weight:  $M_w$ , the number  
39 average molecular weight:  $M_n$  and polydispersity index:  $M_w/M_n$ ) are shown in Figure 2 (a)  
40 and Table 2, respectively. As apparent in Figure 2 (a), the molecular weight distributions for  
41 all lignin samples were bimodal and nearly identical despite some minor changes after  
42 methylation. Although lignin samples showed similar molecular distribution, the GPC for  
43 DMC-SL showed a peak around 10000 Da, which was relatively higher than for other lignin  
44 samples, suggesting polymerization during preparation of this sample. A similar trend was  
45 observed in a previous study, which might be attributed to the presence of sulfur in DMC-SL,  
46 which might attach to unsaturated bonds in side chains of lignin to form larger molecules.<sup>21, 23</sup>  
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4 The  $M_w$  of SL and DMS-SL were similar (4010 Da) while that of DMC-SL was  
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6 approximately 10 % larger (4440 Da). Polydispersity index (PDI) of SL slightly increased for  
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8 both methylation processes.  
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### 10 11 12 13 **3.2 The yield of oils from different lignins**

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16 Figure 3 shows the yield of oil and char produced from supercritical solvent liquefaction  
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18 in ethanol (350 °C for 20 min) of the three lignin samples. The yield of oil from SL was 81.7  
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20 wt% where that of char was 18.5 wt%. The yield of oils from DMS-SL and DMC-SL were  
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22 higher (92.2 and 89.8 wt%, respectively) while char formation was significantly inhibited in  
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24 both methylated lignins. The difference in lignin depolymerized products yield between  
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26 DMS-SL and DMC-SL was negligible, which suggests that reduced Phe-OH content might  
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28 be the main reason for increased oil yield. Previous studies have noted that Phe-OH was  
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30 responsible for the formation of quinone methide intermediates and condensed carbon-carbon  
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32 bonds between lignin fragments, resulting in repolymerization.<sup>14, 31</sup> In fact, self-  
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34 repolymerization behavior of phenol (with Phe-OH) and anisole (without Phe-OH) under  
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36 supercritical ethanol over the  $\text{CuMgAlO}_x$  catalyst (at 300 °C for 1 h) was investigated by  
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38 Huang et al.<sup>32</sup> They found that repolymerization was completely suppressed when anisole  
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40 was the reactant.  
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### 48 **3.3 Evaluation of molecular weight increase in oils**

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50 Oils produced from the three lignin samples were subjected to accelerated aging tests.  
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52 During accelerated aging, approximately 6 wt% mass loss, mainly came from moisture  
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54 removal, was observed for all oils. This loss water was likely a product of condensation  
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56 reactions. Physicochemical properties of the oils before and after accelerated aging  
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4 experiment were investigated using GPC,  $^{31}\text{P}$ -NMR, and GC/MS analysis. Figure 2 (b) – (d)  
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6 show molecular weight distribution of oils before and after accelerated aging. All GPC curves  
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8 are normalized based on the weight of sample. Regardless of lignin source, the peak intensity  
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10 around 1000 Da slightly decreased whereas the peak for the higher molecular region  
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12 increased, which was similar to results obtained by Lyckeskog et al.<sup>20</sup> Meanwhile, the  
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14 change in monomeric region after accelerated aging was negligible in all samples, suggesting  
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16 that repolymerization mainly occurred between oligomeric lignin fragments during  
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18 accelerated aging. Table 2 presents the  $M_w$ , the  $M_n$ , and the PDI of oils before and after  
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20 accelerated aging. The  $M_w$  ranged from 1700 to 1760 Da, which were only 39.6 – 43.1 % of  
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22 the  $M_w$  for raw lignin. This result demonstrated that lignins were efficiently depolymerized  
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24 into smaller molecular lignin fragments during solvent liquefaction. In addition, the PDI of  
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26 lignins decreased from 3.13 – 3.49 to 2.24 – 2.79 after solvent liquefaction, indicating oil had  
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28 relatively higher homogeneity compared to raw lignin. After accelerated aging,  $M_w$  and PDI  
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30 increased for all oils, with some small variation among the oils (Table 3). Increase in both  $M_w$   
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32 and PDI after accelerated aging (%) was the highest in SL oil (11.8 % and 8.9 %) followed by  
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34 DMC-SL oil (6.8 % and 5.4 %) and DMS-SL oil (4.6 % and 3.0 %). The reason why DMC-  
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36 SL oil showed relatively greater change in  $M_w$  than DMS-SL oil might be due to the  
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38 presence of sulfur and its participation in repolymerization.<sup>21, 23</sup>  
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### 48 **3.4 Comparison of chemical properties of oils before and after accelerated aging**

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50 Understanding why oil from raw SL showed the poorest storage stability was explored  
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52 by comparing physicochemical properties of the oils before and after accelerated aging.  
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54 Changes in hydroxyl content as determined by  $^{31}\text{P}$ -NMR analysis are shown in Figure 4. Oil  
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56 from solvent liquefaction of SL had slightly decreased Aliph-OH content (1.09 mmol/g) and  
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4 carboxyl content (0.52 mmol/g) while Phe-OH content increased substantially (2.74 mmol/g)  
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6 (Figure 4 (a)). The latter increase was probably due to cleavage of aryl ether linkages to  
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8 produce Phe-OH and alkane, one of the main reactions of lignin depolymerization.<sup>33</sup> It has  
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10 been well known that supercritical ethanol is effective as a hydrogen donor via hydride  
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12 transfer of  $\alpha$ -hydrogen through a hydrogen shuttling mechanism.<sup>34, 35</sup> The decrease of Aliph-  
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14 OH results from dehydration and hydrogenation or hydrodeoxygenation in the presence of  
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16 alcohol as was found by previous researchers.<sup>36</sup> After accelerated aging of SL oil, all  
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18 functional groups decreased, indicating repolymerization. Notably, Phe-OH decreased the  
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20 most (0.45 mmol/g) among three functional groups. In the case of the DMC-SL oil, Phe-OH  
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22 decreased the most. On the other hand, DMS-SL oil showed negligible changes in functional  
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24 groups during accelerated aging. Based on these results, we investigated correlation between  
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26 the decrease in functional groups and increase in the  $M_w$  as well as PDI after accelerated  
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28 aging (Figure 5). Figure 5 (a) shows excellent linear correlations between increase in the  
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30  $M_w$ /PDI (%) and decrease in Phe-OH. Meanwhile, increase in the  $M_w$ /PDI (%) was positively  
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32 correlated with decrease in all functional groups (sum of Phe-OH, Aliph-OH, and carboxyl)  
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34 as displayed in Figure 5 (b), but it is not lineally correlated. This observation suggested Phe-  
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36 OH played a critical role in repolymerization of oils during their accelerated aging.  
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### 46 **3.5 Variation in chemical compounds in oils after accelerated aging**

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48 Previous studies reported that some compounds in fast pyrolysis bio-oil deceased after  
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50 aging, which suggests their role in repolymerization of the oil.<sup>19, 22, 37, 38</sup> In this study,  
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52 chemical composition of oils before and after accelerated aging was investigated using GC-  
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54 MS/FID instrument. GC-FID chromatogram of three oils before and after accelerated aging  
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56 are displayed in Figure S1. A total of 43 phenolic compounds were identified and are listed in  
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4 Table 4. GC-MS detectable compounds were classified into four categories on the basis of  
5 their structure to better changes after accelerated aging (Figure 6). The categories are as  
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7 follows: monomeric phenols (P), monomeric phenols with unsaturated side chain (UP),  
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9 methoxylated aromatics (MA), and methoxylated aromatics with unsaturated side chain  
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11 (UMA). As shown in Table 4, chemical composition of the oils was significantly different  
12  
13 among the oils. Oil from SL mainly consisted of P and UP type compounds such as guaiacol,  
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15 creosol, 4-ethylguaiacol, syringol, acetosyringone, 4-vinylphenol, and 4-vinylguaiacol. Oils  
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17 from DMS-SL and DMC-SL additionally contained MA and UMA such as 4-ethylveratrole,  
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19 veratraldehyde, 3,4,5-trimethoxytoluene, ethyl 3,4-dimethoxyphenyl acetate, 4-  
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21 vinylveratrole, and methylisoeugenol. The detection of MA and UMA in oils from DMS-SL  
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23 and DMC-SL indicates that significant methylation occurred in the methylated lignins. The  
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25 relative concentrations of compound in the oils before and after accelerated aging are  
26  
27 displayed in Figure 7. Although the sum of P and UP compounds slightly decreased in all the  
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29 oils after accelerated aging, overall changes were not noticeable. This indicated  
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31 repolymerization during accelerated aging of the oils mainly occurred between oligomeric  
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33 lignin fragments, which was consistent with GPC results described earlier. A slight reduction  
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35 in P and UP compounds implies that both Phe-OH in P compounds and unsaturated C=C  
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37 bonds in UP compounds could contribute toward repolymerization.<sup>39</sup>  
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#### 48 **4. Conclusions**

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50 In this study, we demonstrated that pre-methylation of lignin increases yield as well as  
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52 storage stability of oils produced by solvent liquefaction. Pre-methylation of lignin prevents  
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54 the formation of quinone methide intermediates condensation reactions that form carbon-  
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56 carbon bonds, which forms char in preference to oil during solvent liquefaction. Pre-  
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4 methylation likely inhibits molecular weight increases in oil during accelerated aging by  
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6 reducing reactive functional groups. As a result, oils from DMS-SL and DMC-SL showed  
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8 relatively lower  $M_w$  increase than oil from SL during accelerated aging. Notably, we found  
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10 positive linear correlation between decreased in Phe-OH and increase in  $M_w$  during  
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12 accelerated aging, which suggests Phe-OH were the main reactive sites for repolymerization.  
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**Table 1. Elemental composition and C<sub>9</sub> formula of lignins**

Sample	Elemental composition (wt%)					C <sub>9</sub> formula
	C	H	N	S	O	
SL	61.5	5.2	0.7	1.0	31.6	C <sub>9</sub> H <sub>8.45</sub> O <sub>2.89</sub> N <sub>0.09</sub> S <sub>0.06</sub> (OH <sub>Phe</sub> ) <sub>0.45</sub> (OH <sub>Aliph</sub> ) <sub>0.14</sub>
DMS-SL	63.2	5.3	0.7	0.8	30.0	C <sub>9</sub> H <sub>8.91</sub> O <sub>3.10</sub> N <sub>0.08</sub> S <sub>0.05</sub> (OH <sub>Aliph</sub> ) <sub>0.12</sub>
DMC-SL	64.1	4.9	0.6	2.0	28.4	C <sub>9</sub> H <sub>8.11</sub> O <sub>2.96</sub> N <sub>0.07</sub> S <sub>0.12</sub> (OH <sub>Aliph</sub> ) <sub>0.04</sub>

**Table 2. The average molecular weight of lignins and oils**

Sample	$M_w$ (Da)	$M_n$ (Da)	PDI ( $M_w/M_n$ )
SL	4010	1280	3.13
DMS-SL	4010	1150	3.49
DMC-SL	4440	1290	3.44
SL oil	1700	760	2.24
DMS-SL oil	1730	650	2.66
DMC-SL oil	1760	630	2.79
Aged SL oil	1900	780	2.44
Aged DMS-SL oil	1810	660	2.74
Aged DMC-SL oil	1880	640	2.94

**Table 3. Change in the  $M_w$  and PDI of oils after accelerated aging**

Sample	Increase in $M_w$ after accelerated aging (%) <sup>a</sup>	Increase in PDI after accelerated aging (%) <sup>b</sup>
SL oil	11.8	8.9
DMS-SL oil	4.6	3.0
DMC-SL oil	6.8	5.4

$$^a \text{ Calculated by } \frac{\{(The\ M_w\ of\ aged\ lignin - oil) - (The\ M_w\ of\ lignin - oil)\}}{The\ M_w\ of\ lignin - oil} \times 100$$

$$^b \text{ Calculated by } \frac{\{(The\ PDI\ of\ aged\ lignin - oil) - (The\ PDI\ of\ lignin - oil)\}}{The\ PDI\ of\ lignin - oil} \times 100$$

**Table 4. List of GC/MS detectable compounds in lignin-derived oils**

No.	Compound	Type	Detection <sup>a</sup>
1	4-Hydroxy-4-methyl-2-pentanone	-	A, B and C
2	1-Ethyl-4-methoxybenzene	MA	C
3	Guaiacol	P	A
4	Creosol	P	C
5	4-Ethylguaiacol	P	A, B and C
6	4-Ethylveratrole	MA	B and C
7	1,2,3-Trimethoxybenzene	MA	C
8	4-Vinylphenol	UP	A and B
9	4-Vinylguaiacol	UP	A and B
10	4-Vinylveratrole	UMA	B and C
11	Eugenol	UP	B
12	4-Propylguaiacol	MP	C
13	3,4,5-Trimethoxytoluene	MA	C
14	Syringol	P	A and B
15	<i>p</i> -Anisic acid, ethyl ester	MA	C
16	Isoeugenol	UP	A and B
17	Methylisoeugenol	UMA	B and C
18	3,4-Dimethoxybenzenepropanol	MA	C
19	Vanillin	P	A and B
20	1,2-Dimethoxy-4-(2-methoxyethenyl)benzene	MA	B and C
21	Veratraldehyde	MA	B
22	Acetovanillone	P	A
23	Ethyl <i>p</i> -methoxyhydrocinnamate	MA	C
24	Veratric acid, methyl ester	MA	C
25	4-Vinylsyringol	UP	A
26	Guaiacylacetone	P	A
27	Veratryl-2-propanone	MA	B and C
28	3,4-Dimethoxyphenethyl alcohol	MA	C
29	Asarone	UMA	C
30	2,3,4-Trimethoxyphenylacetic acid	MA	C
31	3,4,5-Trimethoxybenzaldehyde	MA	B
32	Ethyl 3,4-Dimethoxybenzoate	MA	C
33	Ethyl 3,4-dimethoxyphenyl acetate	MA	B and C
34	Methyl <i>p</i> -methoxycinnamate	MA	C
35	1,3,5-Trimethoxy-2-propenylbenzene	UMA	B and C
36	3,4,5-Trimethoxybenzoic acid, methyl ester	MA	C
37	3,4,5-Trimethoxyacetophenone	MA	B
38	Methoxyeugenol	UP	A, B and C
39	Ethyl <i>p</i> -methoxycinnamate	MA	B and C
40	Syringaldehyde	P	A and B
41	3,4,5-Trimethoxyphenylpropionic acid	MA	C
42	Acetosyringone	P	A and B
43	Methyl 3,4-dimethoxycinnamate	MA	C
44	Ethyl 3,4-dimethoxycinnamate	MA	B and C

<sup>a</sup> A, B, and C mean SL oil, DMS-SL oil and DMC-SL oil, respectively.



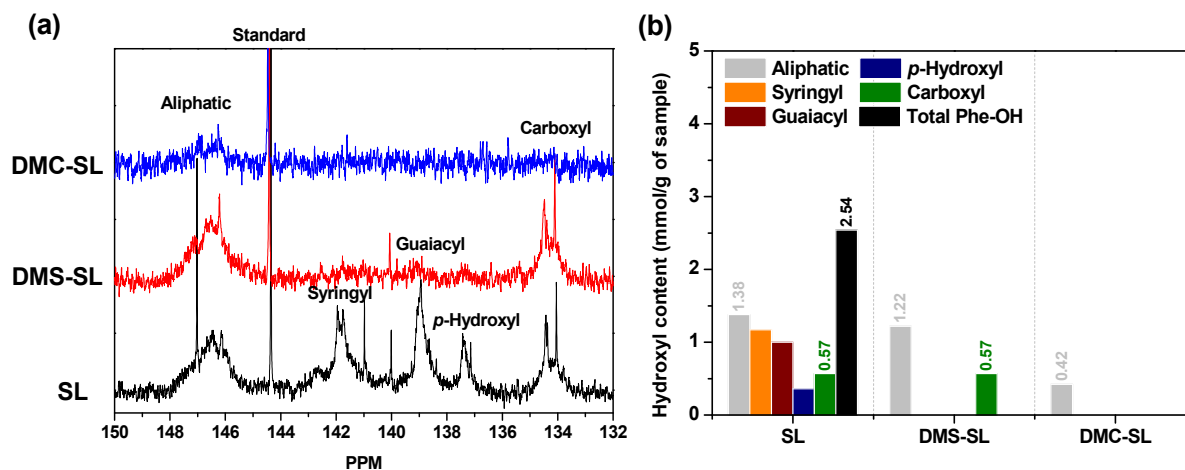


Figure 1. (a)  $^{31}\text{P}$ -NMR spectra and (b) quantification of functional groups of lignins

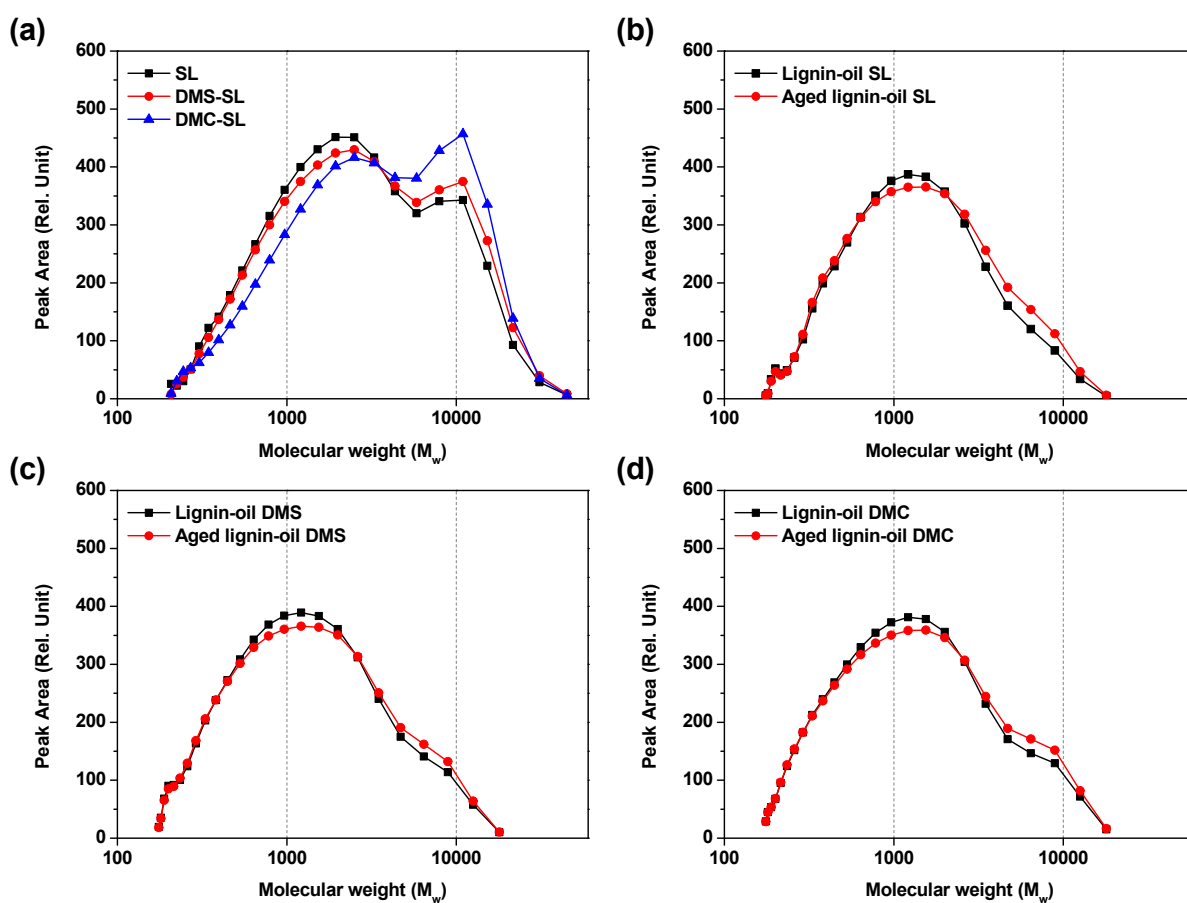
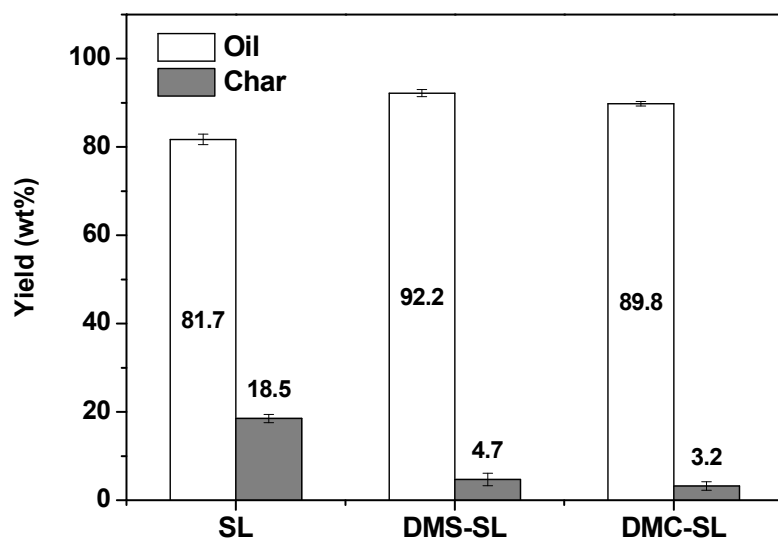
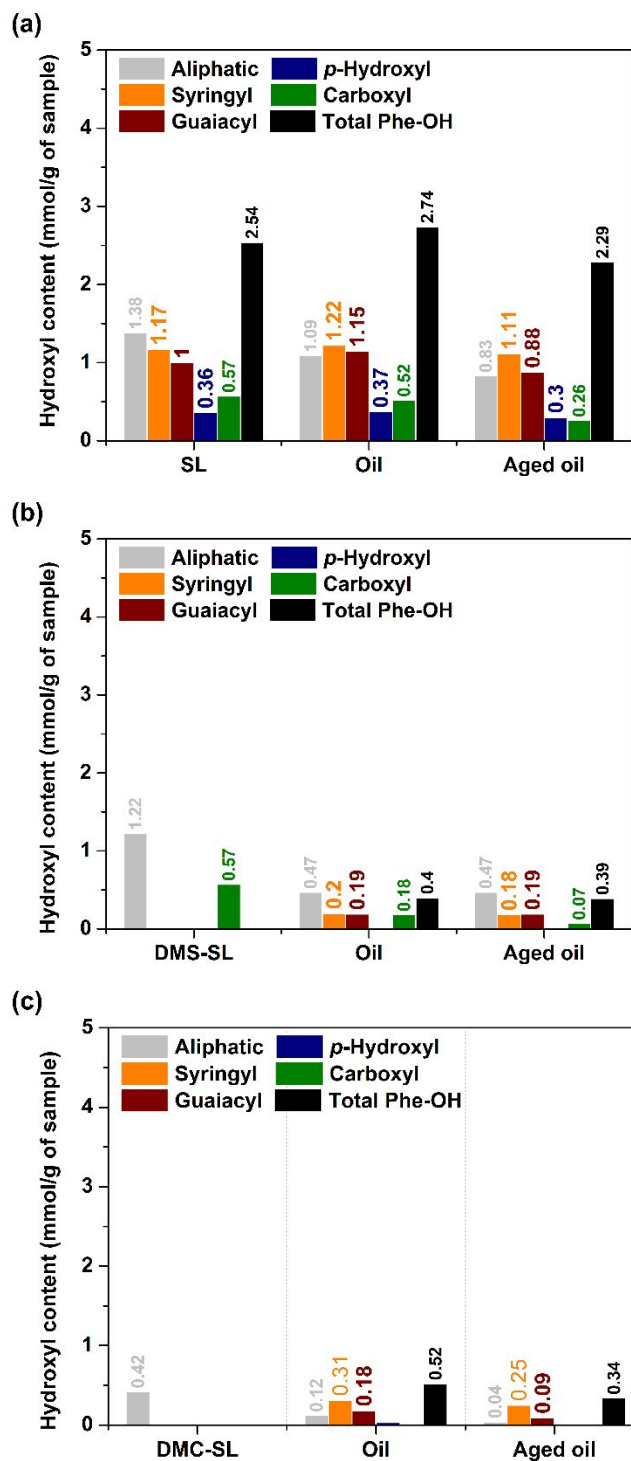


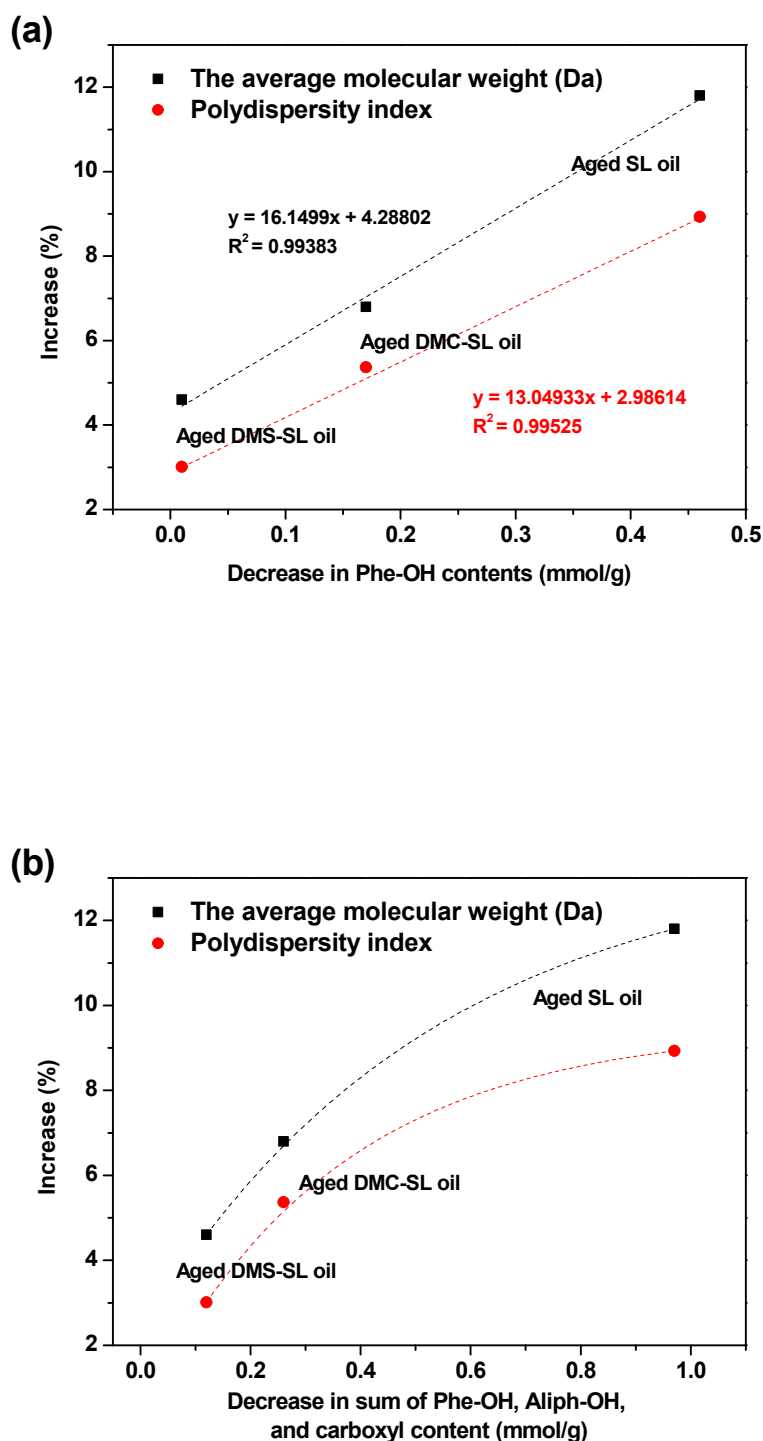
Figure 2. The GPC curves of (a) lignins, (b) oil and aged oil from SL, (c) oil and aged oil from DMS-SL, and (d) (b) oil and aged oil from DMC-SL



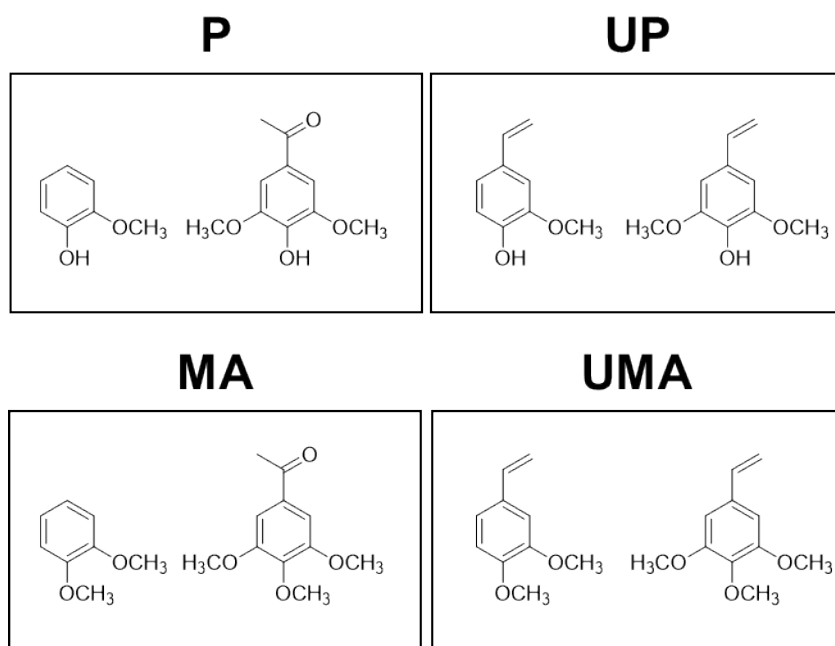
**Figure 3. The yield of oil and char from lignins**



**Figure 4. Quantification of functional groups of (a) oil and aged oil from SL, (b) oil and aged oil from DMS-SL, and (c) oil and aged oil from DMC-SL)**



**Figure 5. Correlation between (a) decrease in Phe-OH content and the  $M_w$ /PDI and (b) decrease in all functional groups contents and the  $M_w$ /PDI (y-axis indicates increase percentage (%) in the  $M_w$  and PDI of oils after aging)**



**Figure 6. Classification of monomeric compounds detected by GC/MS**

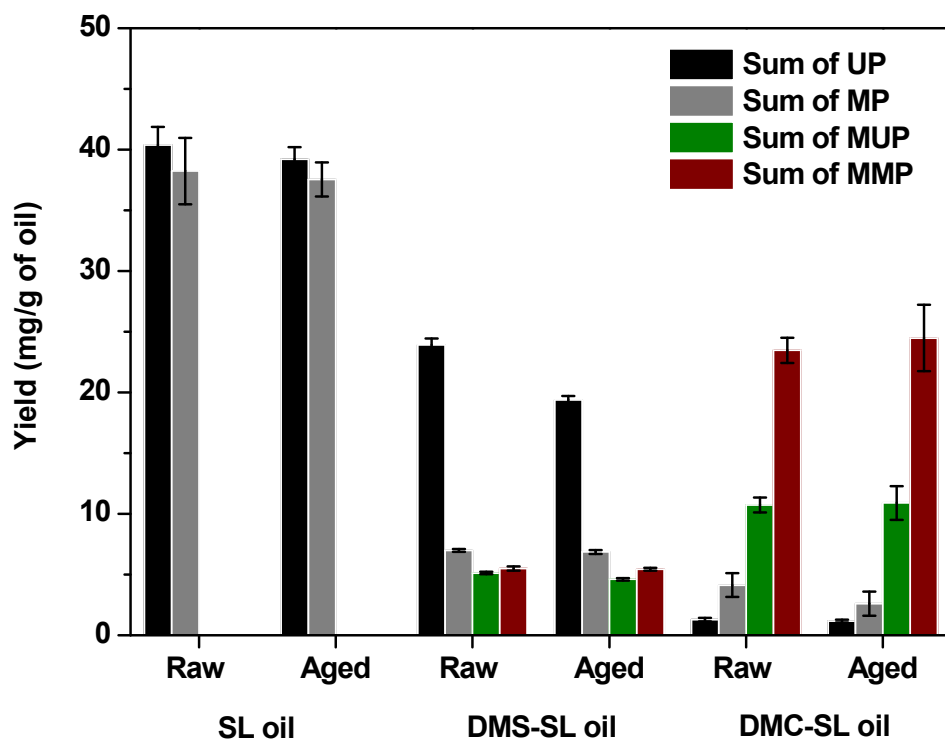
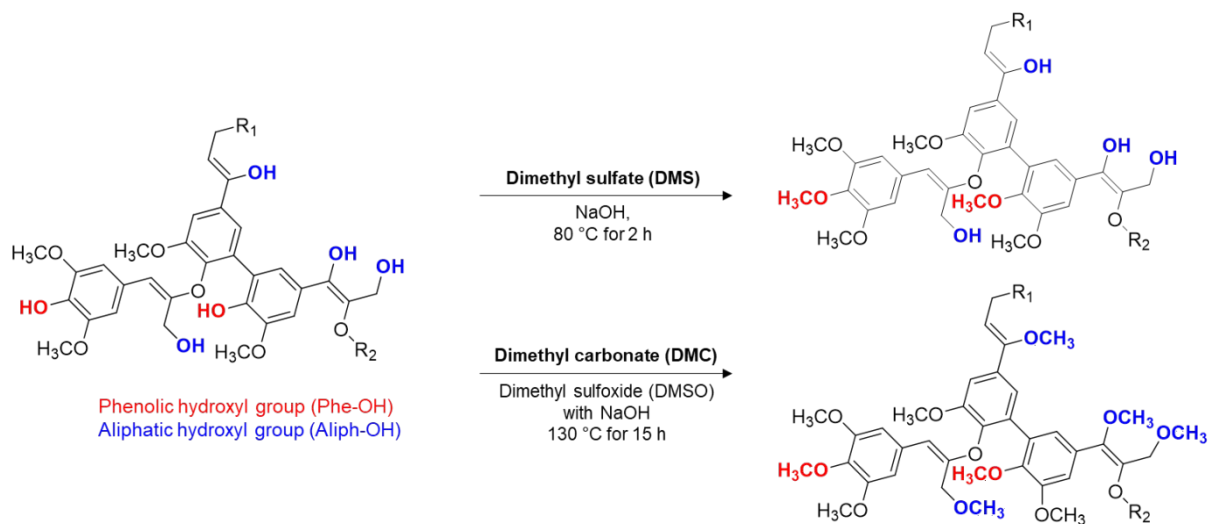


Figure 7. Comparison of monomeric compounds yields of oils before and after accelerated aging



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**Scheme 1. Preparation of methylated lignins**