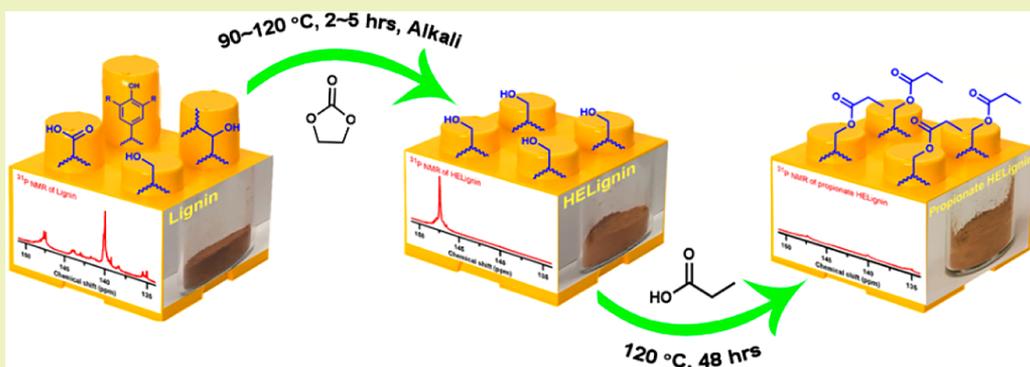


Uniform Chemical Functionality of Technical Lignin Using Ethylene Carbonate for Hydroxyethylation and Subsequent Greener Esterification

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Supporting Information



ABSTRACT: Full utilization of plant-based feedstocks for sustainable societies must include the valorization of lignin, an abundant aromatic component of the cell wall of plant stems, in processes that follow green chemistry principles. However, one of the major issues limiting lignin utilization is the chemical nonuniformity of the isolated polymer, along with the thermal sensitivity of the free phenolics which hinders processing at elevated temperatures. To address these issues, free phenolics and carboxylic acids of industrial lignins were hydroxyalkylated through the use of ethylene carbonate, which served as both the reagent and the solvent. This facile and safe reaction resulted in near complete conversion of phenolics and carboxylic acids into aliphatic hydroxyls resulting in uniform chemical functionality and enhanced thermal stability. However, the increased reaction temperature decreased the total hydroxyl content and increased the molecular weight of the lignin; the work identified a narrow processing window that achieved derivitization without extensive structural modification, which plagued earlier work with carbonate modification of lignin. ¹³C NMR spectroscopy of hydroxyalkylated lignin showed a low degree of condensation and limited to no copolymerization of the ethylene carbonate when reacted under modest conditions. The hydroxyethylated derivative had enhanced solubility in propionic acid, which was used as a solvent and reagent in order to directly esterify the lignin. The reaction achieved over 95% substitution of the lignin hydroxyls creating ethylpropionate derivatives where excess propionic acid could be recycled under vacuum. The hydroxyalkylation followed by direct esterification provided a route toward the development of greener lignin esters by avoiding added solvents, carcinogens such as ethylene oxide, and halogens like acid chlorides for lignin-based polymeric materials synthesized utilizing green chemistry principles.

KEYWORDS: Technical lignin, Hydroxyethylation, Ethylene carbonate, Molecular weight analysis, Fractionation

INTRODUCTION

Feedstocks derived from plant sources offer a potential alternative to petroleum feedstocks that fulfill one important tenant of green chemistry.¹ However, biobased polymers need significant chemical modification that limits the green nature of the feedstock in order to be processed using industrially relevant methods (i.e., extrusion).² One class of lignocellulosic-derived feedstock is technical lignin, an aromatic polymer that is isolated from the delignification process of woody biomass during pulp and paper production.³ The potential amount of

technical lignin from these methods, including biorefinery lignin, is 140 million tons per year, which equal 44% of plastic waste society produced annually.^{4–6} By utilizing this renewable resource as a building block in polymer applications, lignin has a great potential to reshape the materials consumed in our daily lives.^{7,8} Furthermore, new industrial recovery options for

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technical lignin during the paper making process, “Lignoboost” and “Lignoforce” have been implemented in order to reduce bottlenecks in the chemical recovery furnace at paper mills.^{9,10} These technologies offer a route to recover lignin in a powder form, potentially increasing the availability of technical lignin to the market for polymeric applications.

Lora and Glasser reviewed a diverse set of polymer applications for lignin that included epoxy-based circuit boards to polyurethane foams that provided proof-of-concept ideas relevant to help reshape the sources of different polymeric materials found within the built environment.¹¹ Further, Upton and Kasko provided an updated review for synthetic pathways toward lignin polymeric materials.⁸ The review highlighted a section on lignin esters, which included utilizing a variety of acid chlorides. Another approach reported the use of anhydrides for esterification and often included solvents like dioxane¹² or pyridine.¹³ These trailblazing studies were important to highlight the array of complex polymeric materials from lignin, but do not necessarily highlight how these materials can be synthesized utilizing green chemistry principles.

Unfortunately, unmodified lignin requires derivatization for widespread applications; lignin has poor solubility in typical organic solvents stemming from its heterogeneity, has a variety of reactivities based on its functional groups (include primary and secondary hydroxyls, phenolics, aldehydes, and carboxylic acids),^{14,15} and is sensitive to elevated temperatures where free radical reactions cause changes in molecular weight.¹⁶ Modification can be partially achieved with etherification of the aromatic hydroxyls, as well as methylation.¹⁷ While methylation leads to further stability, it does not provide a clear route for additional modification steps. Derivatization methods with alkyl oxides reported in the literature primarily use propylene oxide as the main derivatizing agent in alkaline mediums or in the melt.^{18,19} These alkyl oxide compounds have the advantage of no byproducts during etherification, providing good atom economy. The drawback is that both ethylene oxide and propylene oxide are reported to be possibly carcinogenic, and ethylene oxide is highly flammable and forms homopolymers during reactions. Still, there is a need for hydroxyalkyl lignin derivatives as they offer the opportunity to create reactive segments for step-growth polymers where the aliphatic hydroxyl groups serve as a handle for further modification.²⁰ The chemistry lends itself to produce polyesters, which as a polymer class offer a diverse array of properties based on the coreactants creating segments that can contain aliphatic or aromatic compounds allowing the polymers to be tuned. From this perspective, materials can be formed that are high modulus strong fibers to extremely flexible plastics and even coatings, based on the chosen chemical composition of the comonomers.^{21,22}

Because of the drawbacks, recent work has moved from hydroxyalkylation with alkyl oxides to carbonates such as ethylene carbonate (EC), glycerol carbonate, and propylene carbonate (PC) to reactants with unsaturated groups like diallyl carbonate, or methylation with dimethylcarbonate (DMC).^{17,23–25} Comparing with traditional oxide compounds, these carbonate compounds, including EC and PC, are attractive substitutes because they have low odor level, low evaporation rate, low toxicity, and high boiling/flashing point.^{26,27} However, caution is required when using such reagents with lignin, as these reactions are temperature dependent, which may also cause structural changes during

reactions at elevated temperatures with alkaline catalysts. For example, a recent study used different types of carbonate compounds with reactions conditions near 170 °C and 1,8-diazabicyclo-undec-7-ene (DBU) as a catalyst. At 170 °C, near pulping conditions, it opens the possibility of lignin modification and significant lignin structural changes at this temperature, which resulted in a significant increase in molecular weight and PDI.²⁵ These drawbacks would restrict their further application in copolymerization with other monomers.

In the current study, we investigated a range of reaction conditions (time, temperature, catalyst type, catalysts loading, solvent presence) to make lignin derivatives with more uniform chemical functionality and enhanced thermal stability. Moreover, we exploited the resulting uniform reactivity of the primary hydroxyls of the hydroxyethylated lignin derivative for direct esterification with an organic acid. As a result, the study provided insight into technical lignin derivatization methods that limit modification to lignin structures, such as cross-linking, and used greener reagents avoiding added solvents in the process. The novel methods resulted in an alkylether lignin ester that had nearly all available hydroxyls derivatized, which was in contrast to nonhydroxy alkylated lignin that had the majority of phenolics unmodified during direct esterification. Overall, the study lends itself to the scalable platform for lignin-based thermoplastics for lignin-based polyesters directly through condensation reactions utilizing safer reagents. This method is clearly safer for lab based lignin derivatives, and opens a path for scaled modification to create lignin with more uniform chemistry.

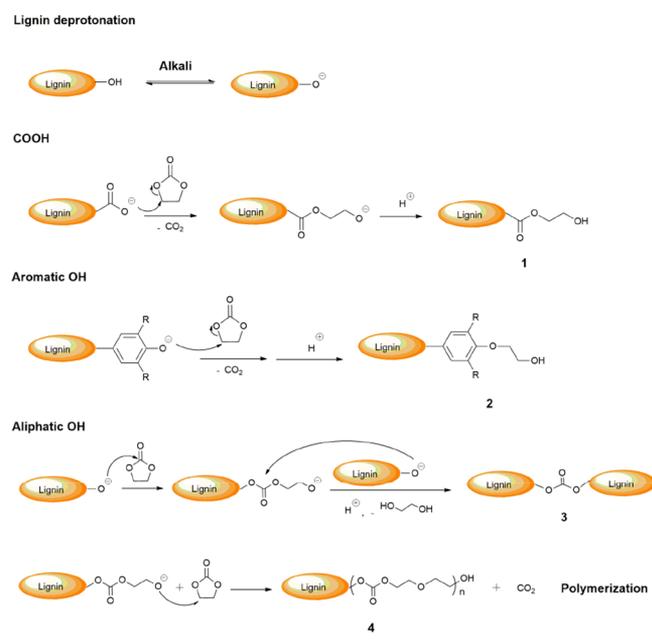
RESULTS AND DISCUSSION

Reaction Conditions for the Hydroxyethylation of Kraft Lignin. The hydroxyethyl derivatization of lignin using ethylene carbonate (EC) was systematically studied utilizing alkaline catalysts. Clements discussed the potential reaction conditions and mechanism using carbonate compounds in the reactions with phenolic hydroxyls, aliphatic hydroxyls, and carboxylic acids, which all can be found on technical lignin to various extents.²⁶ The possible reactions noted in [Scheme 1](#) accounted for (1) phenolate and carboxylate attack of the cyclic carbonate, with CO₂ off-gassing and (2) deprotonated aliphatic OH groups reacting with the carbonyl carbon in EC to possibly form polycarbonate linkages.

As noted in the polymer industry, EC has been widely used to modify carboxylic acid and phenol compounds with alkali catalysts under temperature ranges (100–150 °C).^{26,27} Therefore, hydroxyethylation reactions of the lignin were studied for the catalyst and reaction conditions (time, temperature, and solvent). In initial studies to enhance the uniformity of kraft lignin, we adopted a fractionation method to prepare acetone soluble softwood kraft lignin (ASKL) and acetone soluble hardwood kraft lignin (AHKL) with a greater amount of aromatic hydroxyl groups and lower polydispersity ([Table S1](#)). The catalysts had some differences in their basicity and were used for the deprotonation of the aromatic hydroxyl groups on lignin.²⁸ With these catalysts, initial reaction conditions were established at 120 °C for 20 h with excess EC relative to the aromatic content in DMF as a solvent used for comparison purposes ([Figure 1](#)).

Based on the quantitative ³¹P NMR analysis ([Figure S1](#)) results, [Figure 1](#) shows the amount of aliphatic hydroxyls (AlOH, 150–145 ppm), aromatic hydroxyls (ArOH, 144–136

Scheme 1. Possible Reactions between EC and Deprotonated Carboxylic Acid, Aromatic Hydroxyl, and Aliphatic Hydroxyl Groups in Lignin that Produces a Mixture of Hydroxyethyl Lignin Compounds 1 and 2, Carbonate Compounds 3, and Polyether Copolymers 4



ppm), and carboxylic acids (COOH, 136–133 ppm), which comprised the total hydroxyl content (150–133 ppm) for the softwood kraft lignin. As shown in Figure 1a, ArOH were readily converted into hydroxyethyl ethers using “control” conditions of 20 equiv of EC and 2 equiv alkali at 120 °C for 20 h in solvent. This reaction resulted in lignin containing over

95% of AlOH groups for all the catalysts utilized. In addition, deprotonated carboxylic acids on the lignin also reacted with ethylene carbonate (Scheme 1), achieving high substitution of this functional group as well. Negligible differences were detected in the derivatization of the lignin, as all catalysts were effective in hydroxyalkylating lignin at conditions of 120 °C and 20 h. This result was different from Over et al. and Kühnel et al., which required TBAB and DBU as alkaline catalysts for the reaction to proceed with carbonates used in their studies.^{23,25} The alkaline carbonate catalysts used in the current study have lower cost and toxicity than these compounds and satisfy requirements of green chemistry.

In a control reaction without ethylene carbonate, there was a slight change in aromatic content, with a reduction of free aromatic groups. The aromatic OH groups were reduced from 5.98 to 4.32 mmol/g, accompanied by the reduction of 5-substituted ArOH groups from 2.01 mmol/g (ASKL) to 1.41 mmol/g. These changes suggested that the alkaline catalysts at 120 °C may have led to potential repolymerization through the aromatic hydroxyls, indicating that lignin was very sensitive to structural modification when utilizing alkaline catalysts and heat for derivatization.²⁹

A series of additional hydroxyethyl lignin reactions were performed to optimize reaction conditions that included the quantities of DMF, alkali and ethylene carbonate content relative to the phenolic hydroxyl concentration in the lignin, and temperature/time. Complete substitution of the ArOH occurred with and without the presence of the additional solvent (Figure 1b). In so doing, excess solvent recovery was avoided during this reaction. Moreover, the yield increased for the DMF solvent-free conditions from 60% to 80%, which was attributed to the loss of hydroxyethyl lignin in the recovery and purification stages when using DMF. The comparison among these three catalysts without the addition of DMF showed that

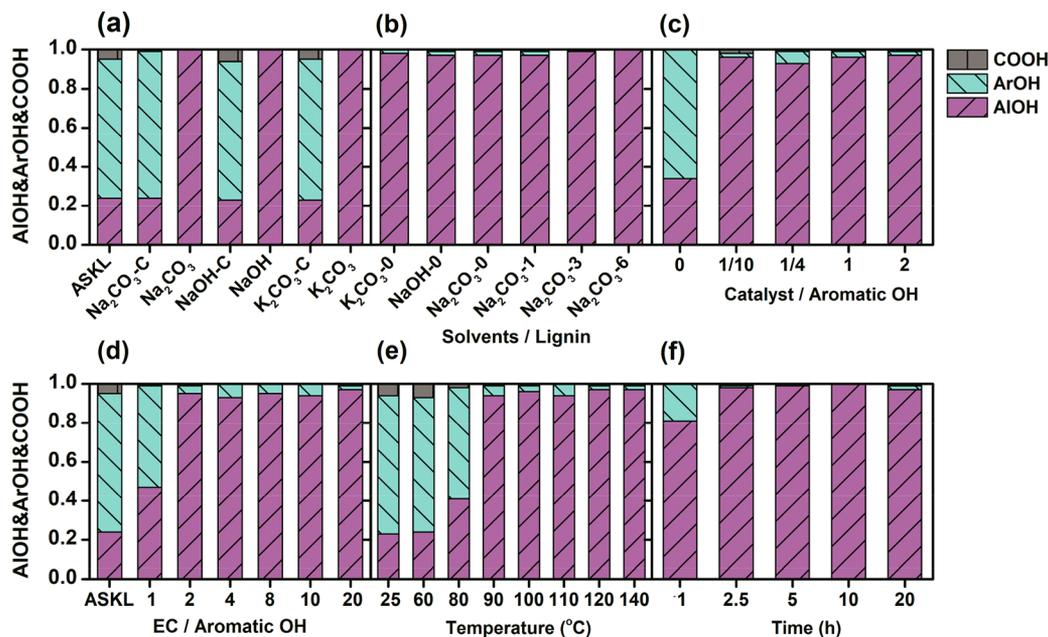


Figure 1. Functional groups of acetone soluble softwood kraft lignin considering six factors including: the different types of catalysts (a); the ratio of solvent (mL) to lignin (1 g) (6, 3, 1, and 0) (b); catalysts loading to phenolic OH (molar ratio) (c); ethylene carbonate (EC) to phenolic OH molar ratio (d); effects of temperature on the reaction at 20 h (e); and time on the reaction at 120 °C (f); initial conditions in panel (a): temperature = 120 °C, time = 20 h, EC/aromatic OH molar ratio = 20, alkali/aromatic OH = 2; -C, controlled reaction conditions without adding EC; (b) different amount of solvents (–6, 1 g mixing with 6 mL DMF); (c), (d), (e), and (f) use Na₂CO₃ as catalysis without the addition of DMF.

the total OH (4.85 mmol/g) and the percentage of AIOH group (97.3%) for Na_2CO_3 were similar to K_2CO_3 (4.60 mmol/g, 97.6%) and NaOH (4.81 mmol/g, 96.2%). Essentially, the catalyst type did not have a significant impact on this reaction and additional solvent was unnecessary for the hydroxyethyl reaction.

The catalyst loading had a minimum impact on the etherification of ArOH and COOH groups (Figure 1c). Complete substitution occurred for a range of conditions when the catalyst amount was twice the number of ArOH group content down to a level when the catalyst content was reduced to one tenth of the lignin ArOH group content. For the latter, the percentage of AIOH group content was nearly 97%. Overall, the smallest addition of the catalyst was enough to deprotonate the phenolic hydroxyl groups on lignin for the reaction. In the absence of catalyst, the control reaction revealed the aromatic hydroxyl content did not change, indicating the need for the catalyst for conversion of the phenolics into aliphatic hydroxyls.

Because ethylene carbonate can be the solvent and reagent at the same time during the reaction, we were able to remove DMF from the reaction scheme. By reducing the EC amount from 20 to 2 equiv, the percentage of AIOH group content remained over 90%. (Figure 1d); however, an obvious reduction of AIOH content occurred when the EC/ArOH was reduced to 1 equiv. Noteworthy, it was observed that a relatively low amount of ethylene carbonate led to high solvency of the lignin. Previous research indicated the complete liquification of biomass at relatively low temperatures demonstrating high solvency of biomass in alkyl carbonate compounds.³⁰

The reaction time was reduced to 2.5 h with the additional amount of EC at 120 °C (Figure 1f). However, it was dependent upon the temperature and the additional amount of EC. As shown in Table S2, the lower temperature (90 °C) required a higher amount of EC and longer reaction time to obtain over 90% AIOH content in the resulting lignin. These results were in agreement with previous results by Over et al., who studied the allylation of organosolv lignin.²³ In addition, the ASKL data (Table S2) was used to analyze the interactive impacts of temperature, time and EC loading. Results of standardized effects (Table S3) showed that temperature and interactive impacts of temperature and EC loading had the most significant impacts on AIOH, ArOH, and COOH group modification. To realize the complete modification of ArOH and COOH, temperature and EC loading must be well controlled.

Temperature of the reaction had a significant impact on the lignin structure as the total hydroxyl content decreased as a function of temperature (Figure 2). Further, Figure 1e shows that the significant changes in the hydroxyalkylation reaction occurred when the temperature increased from 80 to 90 °C. The percentage of AIOH group content increased from 41.0% to 93.8% with the reduction of total hydroxyl group from 5.82 mmol/g to 4.74 mmol/g. Above 90 °C, there was nearly complete substitution of ArOH groups with only minor modification of total hydroxyl groups for samples reacted in a range from 90 to 120 °C (5.02 mmol/g, Figure 2). Reactions that occurred above 120 °C, showed significantly lower AIOH groups content; from this observation higher temperature also caused side reactions, that would lead to condensed structures. This cross-linking reaction had been further revealed in the following results on gel permission chromatography analysis.

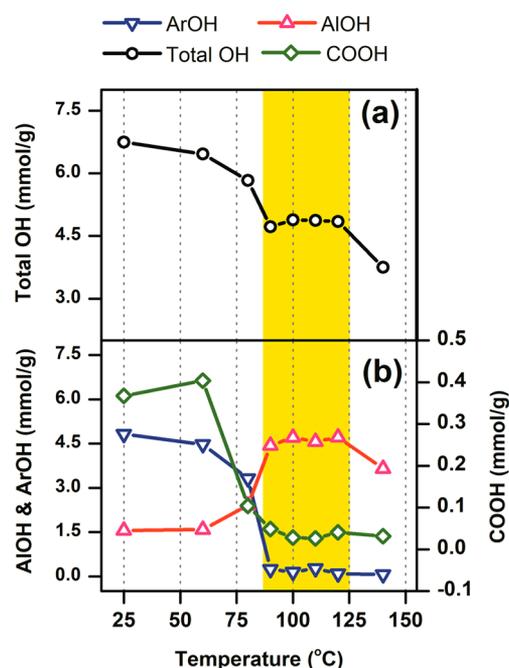


Figure 2. Impact of temperature on total OH, AIOH, ArOH, and COOH for the hydroxyethyl ASKL. Reaction conditions: time = 20 h, EC/aromatic OH = 20, Na_2CO_3 /aromatic OH = 2.

Further, these reaction conditions were investigated for a hardwood lignin substrate (acetone soluble hardwood kraft lignin, AHKL). The AHKL had a lower substitution of the phenolics compared with ASKL when using the same conditions of the softwood lignin (No. 4 and No. 9 in Table S2). Therefore, complete substitution required longer reaction time or higher reaction temperature to complete the reaction. This result may be explained based on the structure of hardwood lignin that contained syringyl units (Table S1), and thus had additional steric hindrance arising from the additional methoxy group near the phenolic during the reaction with ethylene carbonate. As a result, the reaction conditions were modified for the lignin type or source. Additional lignin types and reaction conditions (comparison to reference conditions at 170 °C) are listed in Table S2.

Gel Permeation Chromatography Analysis. Acetylated lignins (ASKL and AHKL) and hydroxyethyl lignin (Table S4) with different reaction conditions were dissolved in THF and analyzed for molar mass. Hydroxyethyl lignin for both hardwood and softwood lignin showed a shift to higher molecular weight versus the lignin precursor (Figure 3). Lignin molecular weight values, M_n , M_w , and polydispersity (PDI), were calibrated based on a series of polystyrene standards (Table S4). After modification, lignin had higher PDI and this value increased with the temperature and reaction time indicating the sensitivity of kraft lignin to this reaction. The outcome suggested that a narrower distribution of molecular weight required lower reaction temperatures for lignin modification.

As indicated earlier, the increased temperature led to structural changes of the modified lignin with a reduction in the overall hydroxyl content. A loss in total hydroxyl content would be an indication that the AIOH content will react with the EC by transesterification or polymerization reactions (Scheme 1). Further, with lignin in alkali, free radical reactions may have also occurred through phenoxy radicals reacting with

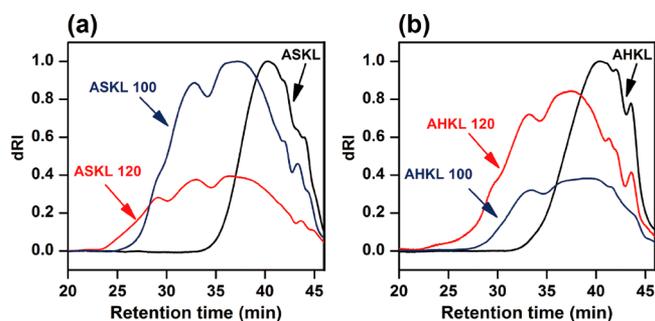


Figure 3. GPC traces of softwood (a) and hardwood (b) lignin before and after hydroxyethylation with different temperatures (100 or 120 °C).

other lignin segments at open ortho positions on adjoining aromatic rings. Hence, the temperature was a highly important factor to control lignin derivatization without significant lignin copolymerization with polycarbonate segments and lignin cross-linking.³¹

Impact of Modification on Structure (Quantitative ¹³C NMR Analysis). From the ¹³C NMR spectrum of acetylated lignin samples (Figure 4), we distinguished the different hydroxyl groups in the resulting lignin. Similar to ³¹P NMR analysis, the AIOH group (Peak 1 and 2) increased with the corresponding reduction of ArOH (Peak 3 and 4) for the samples after hydroxyethylation (Table 1 and Figure 4). Also, the total hydroxyl group content reduced for both modified ASKL and AHKL as previously noted above with ³¹P NMR analysis (Figure 2). Additionally, an unexplained phenomenon was observed, the secondary AIOH groups (Peak 2) were reduced, which also was correlated with an emergence of a new peak 5 (77–72 ppm).

Noteworthy, the increased amount of primary AIOH groups, 48 per 100 C₆ units (Peak 1, Figure 4), was lower than the reduction of ArOH groups, 60 per 100 C₆ units (peak 2, Figure

4), after the hydroxyethyl reaction for both hardwood and softwood kraft lignins (Table 1). This difference in AIOH group content when accounting for the substitution of the ArOH groups was suggested to arise from the reaction of lignin into compounds like 3 or 4 in Scheme 1 during the modification and/or lignin condensation reactions. The substitution of AIOHs can create carbonate linkages (Scheme 1), which would lead a reduced total hydroxyl group content (Figure 2) and an increased molecular weight (Figure 3). Peak 7 was related to the formation of carbonate bonds between AIOH groups and ethylene carbonate during the hydroxyethylation process (compound 3 and 4 in Scheme 1). Further, the peak clusters in a range from 155 to 154.4 ppm (Figure S3) revealed carbonyl signal from compounds 3 and 4 in Scheme 1. The existence of these carbonate groups had also been shown by the FT-IR spectrum, because a distinctive increase in absorbance for the carbonyl peak $\nu = 1748 \text{ cm}^{-1}$ after hydroxyethyl reaction was observed (Figure S4).

Further evaluation of the degree of carbonate linkage formation was found as follows: a range of 72–58.0 ppm showed new peak clusters (peak 6 and 8) appearing after the modification for both hardwood and softwood lignin. These two peaks corresponded to the hydroxyethyl carbons in the resulting lignin. The peak clusters labeled as peak 6 appeared with greater intensity (68–65 ppm) in the modified softwood lignin than clusters in the modified hardwood lignin. This difference may partly arise because of the structural differences between hardwood lignin and softwood lignin. The peak clusters 8 (65–58 ppm) represents the C_γ of the side chain in unmodified lignin, which directly relates with the native primary AIOH groups. The peak of C_γ will change depending on the chemical structure of original compounds. By comparing peak 7 and peak 8, the carbonate carbon was identified and related to the amount of primary AIOH groups to determine the degree of copolymerization. Because the ratio was 0.18 (HE_ASKL) and 0.11 (HE_AHKL) (Table 1), there

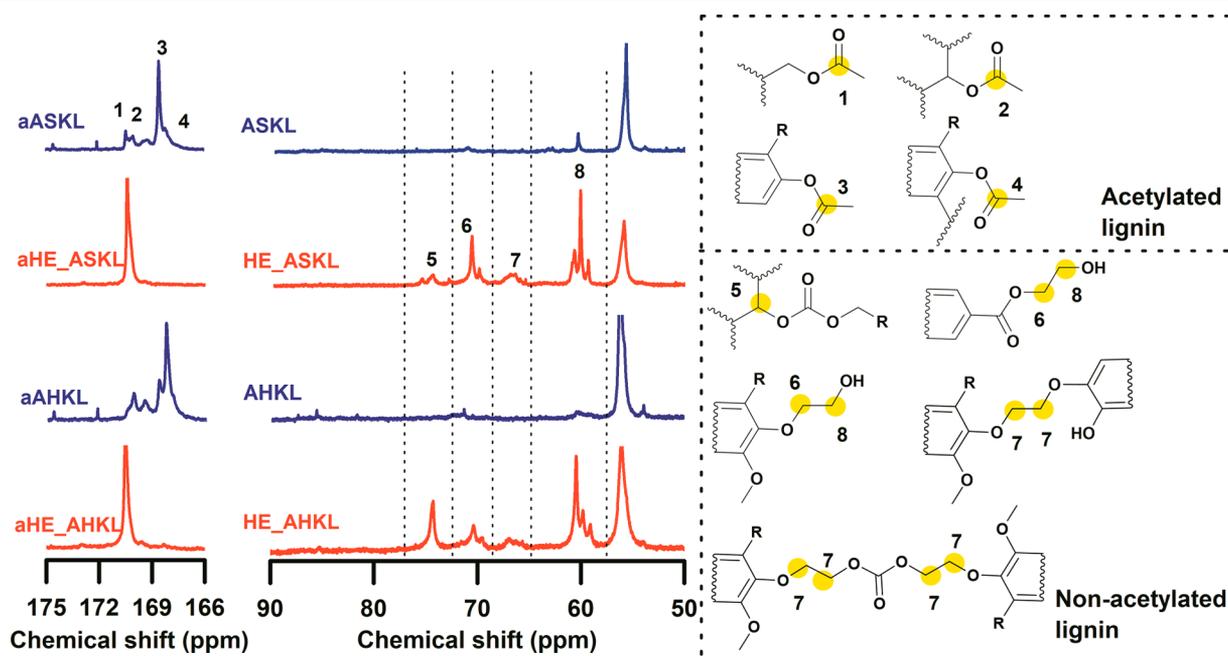


Figure 4. ¹³C NMR spectra of lignins before and after hydroxyethyl reactions; in DMSO-*d*₆ ($\delta = 39.5 \text{ ppm}$) for both nonacetylated (ASKL, HE_ASKL, AHKL, and HE_AHKL) and acetylated lignin (aASKL, aHE_ASKL, aASKL, aHE_AHKL).

Table 1. Quantitative ^{13}C NMR Analysis of Major Functional Groups in Softwood and Hardwood Lignin before and after Hydroxyethyl Reaction Including Acetylated and Non-Acetylated Lignin (per 100 Ar)

peak no.	assignment	peak range [ppm]	ASKL	HE_ASKL	AHKL	HE_AHKL
acetylated lignin ^a						
1	AlOH primary	172–169.8	20	68	18	66
2	AlOH secondary	169.8–168.9	15	4	15	5
3	ArOH 5-free	168.9–168.3	42	1	22	2
4	ArOH 5-substituted	168.3–166	19	0	42	1
	total AlOH	172–168.9	35	72	32	71
	total ArOH	168.9–166	61	1	64	3
	total OH	172–166	96	73	96	75
nonacetylated lignin						
5	$-\text{C}(\text{H})(-\text{R})-\text{O}-\text{C}=\text{O}-$	77–72 ^b	10	31	19	42
6	$-\text{O}-\text{C}(\text{H})_2-\text{CH}_2-\text{OH}$	72–68	9	55	17	33
7	$-\text{O}-\text{C}(\text{H})_2-\text{C}(\text{H})_2-\text{O}-\text{C}=\text{O}$, $\text{Ar}-\text{O}-\text{C}(\text{H})_2-\text{C}(\text{H})_2-\text{O}-\text{Ar}$	68–65	4	31	8	19
8	$-\text{O}-\text{C}(\text{H})_2-\text{C}(\text{H})_2-\text{OH}$	65–58	21	88	32	85
	copolymerization ^c			0.18		0.11
	degree of condensation		57	76	38	56

^aThe acetylated lignin samples were used to analyze the hydroxyl group content of lignin. ^bUnknown compounds may contribute this peak area.

^cCopolymerization = $1/2 \times \text{peak 7}/\text{peak 8}$.

had been limited copolymerization between modified lignin and ethylene carbonate (compound 4 in Scheme 1) with our optimized conditions. This result was quite different from the traditional ethylene oxide modification of lignin in which ethylene oxide reacts with itself to form poly(ethylene oxide) chains.¹¹

The degree of condensation of lignin after the modification was one of the primary reasons for the reduction of a total hydroxyl group and increased molecular weight. The degree of condensation was calculated based on the formulation by Balakshin et al.³² After the modification, the degree of condensation increased, and the hydroxyethylated softwood lignin had a higher degree of condensation than that of modified hardwood lignin (Table 1). Most likely syringyl units found in hardwood lignin prevented the condensation of lignin at the open C₅-position. This data agreed with the changes in the molecular weight (Figure 3).

Moreover, quantitative ^{13}C NMR analysis was performed by using trioxane as internal standard (Table S5). Noticeably, softwood samples contained 94% primary AlOH group (4.91 mmol/g), accompanied by the reduction of secondary AlOH from 1.20 to 0.28 mmol/g. For the other changes of OH group, it was in line with ^{31}P NMR results described above. Overall, ethylene carbonate was used to create hydroxyethylated derivatives that contain nearly only primary hydroxyl groups: this result contrasted with the starting material that also had carboxylic acids, secondary hydroxyls, and phenolics. Hence, ethylene carbonate is a unique reagent to create lignin with uniform chemical functionality and limited copolymerization.

Thermal Properties of Lignins. The thermal stabilities of unmodified and hydroxyethylated lignin were analyzed by TGA under a nitrogen atmosphere. The $T_{D5\%}$ (the temperature with 5% degradation) of softwood and hardwood kraft lignin occurred at 213 and 218 °C, (Table 2). After hydroxyethylation the $T_{D5\%}$ of ASKL and AHKL shifted to 251 and 273 °C, respectively. As shown in Figure S5, ASKL and AHKL had higher weight loss rate at a range from 200 to 450 °C compared to the modified samples. Below 300 °C, about 15% weight of original lignin was lost due to the degradation of thermally sensitive groups with the increased temperature.

Table 2. Thermal Properties of Lignin before and after Hydroxyethyl Reaction

	ASKL	HE_ASKL	AHKL	HE_AHKL
$T_{D5\%}$, °C ^a	213 ± 2	251 ± 1	218 ± 2	273 ± 2
$T_{g,DSC}$, °C ^b	86 ± 2	73 ± 4	122 ± 9	108 ± 5
$T_{g,G'}$, °C ^c	99	81	129	112

^aThe temperature with 5% degradation. ^bThe glass transition temperature from the differential scanning calorimetry (DSC) analysis. ^cThe glass transition temperature by the storage modulus (G') data from the dynamic rheological analysis.

From this result, it is clear that after the hydroxyethyl reaction, lignin became more thermally stable as less than 10% weight lost occurred below 300 °C, which stability is critical when processing thermoplastic materials at elevated temperature.

Lignin can be potentially used as thermoplastic materials, dependent upon its glass transition temperature (T_g). In this study, DSC and thermo-rheological analysis were used to obtain the T_g of lignin before and after hydroxyethylation. Based on the thermal scans (Figure S6), there were clear endothermic changes in the baseline for all lignin samples, allowing the determination of the T_g by DSC. Comparing the parent materials after annealing treatment, hardwood lignin had a T_g of 128 °C which was greater than softwood lignin (T_g of 88 °C). While methoxy groups usually decreased the T_g , the hardwood had higher molecular weight than ASKL, which can impact the chain mobility. After the hydroxyethyl reactions, both types of lignin had a slightly lower T_g , which may have arisen from the additional bulking from the ethylene groups. This result was supported by the fact that higher temperature reactions increased the amount of alkyl content of the lignin as illustrated by the FT-IR (Figure S4).³³

Parallel plate dynamic rheological analysis was used to investigate the change of mechanical properties, including storage modulus (G'), loss modulus (G''), and $\tan \delta$, as a function of temperature (Figure 5). With a normal force applied to the sample during the temperature ramp, there was densification of the material seen with an increase in G' . When the samples reached their T_g there were nearly 2 orders of magnitude decrease in storage modulus with continued

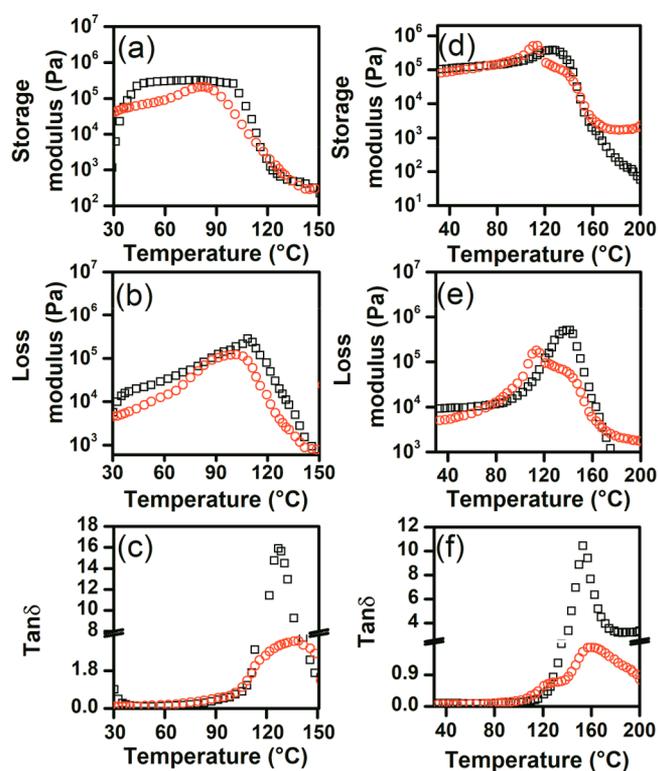


Figure 5. Storage modulus (G' , a ASKL, d AHKL), loss modulus (G'' , b ASKL, e AHKL), and $\tan \delta$ (degrees, c ASKL f AHKL) of lignin before (black squares) and after hydroxyethyl reaction (red circles).

heating. The unmodified lignin had higher T_g than the hydroxyethylated lignin (Table 2). The onset of G' decrease was similar in value to the DSC data for these lignin samples. The peak of $\tan \delta$ values for both hydroxyethyl lignin derivatives was lower than the parent lignin. The temperature range width of the transition for the softwood was slightly wider than the unmodified lignin, indicating a broad relaxation profile. Total $\tan \delta$ profiles for both samples of the hardwood kraft lignin were above the testing conditions of the experiment; however, the hydroxyethyl derivatives had a significant shoulder on the peak. This shoulder or wider

peak temperature ranges may belong to the wider distribution of polymer's molecular weight, in agreement with GPC results (Figure 3).

Esterification of Hydroxyethyl Lignin. The above study showed that the hydroxyethylation reaction provided an efficient route to obtain lignin with uniform functionality, which contained over 90% primary AOH groups. This hydroxyethyl lignin, as a building block, has the possibility to be used as a precursor in preparation of biopolymers for polyesters.

Figure 6a shows a direct esterification of lignin using propionic acid without any catalysts. As shown in Figure 6b, the propionic acid reacted with the hydroxyethyl groups on the modified lignin giving nearly complete substitution. The ^{13}C spectrum of the propionate ester, revealed the methylene and methyl carbons of the ester, along with the new carbonyl groups from the reaction of the free hydroxyls (Figure 6c). It was interesting to compare the esterification of hydroxyethyl lignin to the unmodified lignin; the propionate softwood lignin showed a lower AOH (0.35 mmol/g) group conversion, and only a slight change of the ArOH (3.89 mmol/g) and COOH groups (0.60 mmol/g). The direct esterification of the hydroxyethyl lignin allowed for a fully substituted lignin ester, as the free phenolics in the technical lignin did not get converted leaving a lignin with a mixed functionality.

Of course, anhydride modification can esterify both types of hydroxyls readily. Thielemans and Wool studied the solubility of these esterified kraft lignins, which showed a higher solubility in nonpolar solvents and could be used in unsaturated thermosets.¹² Luo et al. mixed the propionate softwood kraft lignin with thermoplastics to be biodegradable materials as green fillers, which showed higher compatibility than unmodified lignin.³⁴ However, when compared with esterification methods using anhydride compounds or halogenate compounds, direct condensation is industrially used for polyesters and avoids further use of solvents and catalysts. With water as a byproduct during condensation and the propionic acid serving as the solvent and reactant, the E-factor is lower than those other methods to make a fully substituted lignin ester.

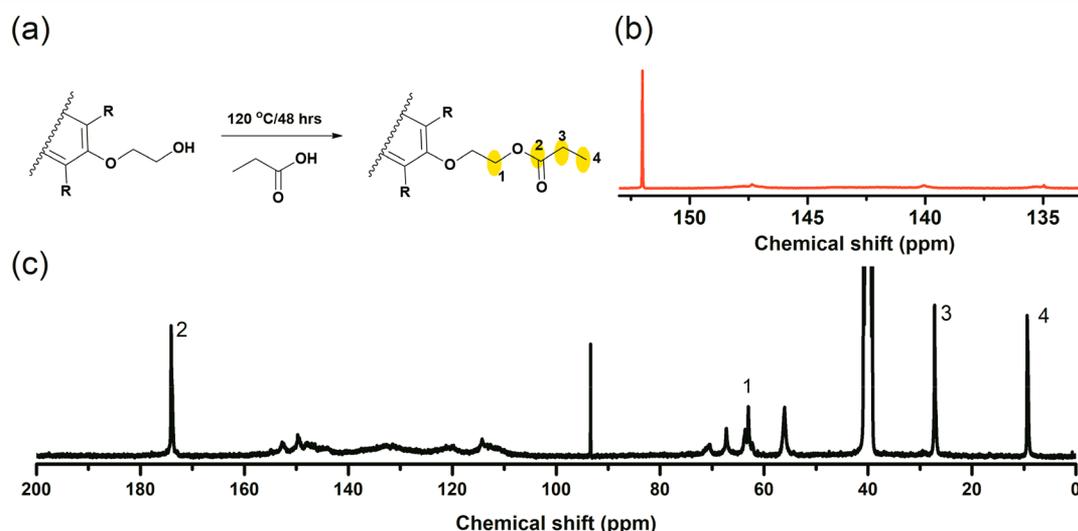


Figure 6. Direct esterification of HESKL (a), ^{31}P NMR spectrum of propionate HESKL (b), ^{13}C NMR spectrum of propionate HESKL (c).

CONCLUSIONS

Ethylene carbonate, as a greener reagent with lower toxicity and higher stability (boiling point = 243 °C), was reacted with lignin aromatic hydroxyl groups and carboxylic acids to form hydroxyethyl ethers for subsequent greener esterification reactions. Optimized reaction conditions for softwood kraft lignin led to 95% conversion of phenolics into primary hydroxyalkyl ethers (90% for hardwood kraft lignin) with a total hydroxyl content of 5.02 mmol/g (4.56 mmol/g hardwood kraft lignin).

Further, ^{13}C NMR analysis was utilized to reveal that the alkyl carbons of the derivatives corresponded with the phenolic ethers, indicating there was mainly derivatization and not polymerization of the ethylene carbonate at the optimized conditions. Further, the lignin derivatives were more thermally stable compared to the unmodified analog, while hydroxyalkylation at optimized conditions caused a slight decrease in T_g relative to the unmodified sample. Hydroxyethyl lignin samples were readily modified with high conversion into lignin esters, by direct condensation reactions. Hydroxyethylation using ethylene carbonate with common catalysts may serve as a robust route to create lignin with more uniformity, avoiding carcinogenic reagents typically used in these reactions; however, reactions conditions should be carefully selected with technical lignin in order to minimize further structural changes to the lignin. Overall, during these reactions of hydroxyalkylation and subsequent esterification, the main byproducts were water, CO_2 , and ethylene glycol, which are valuable precursors for preparing ethylene carbonate.³⁵ Moreover, propionic acid and ethylene carbonate can be obtained from renewable resources by fermentation or efficient processes with catalytic chemistries.^{27,30,36} These characters make the reactions possibly more sustainable to create biobased precursors for plastics from lignin feedstocks based on green chemistry principles.

EXPERIMENTAL SECTION

Materials and Instrumentation. Industrial softwood kraft lignin (SKL) including Indulin-AT (WestRock Company) and BioChoice (Domtar Corporation), hardwood kraft lignin (HKL), (FPInnovations) and organosolv hardwood lignin (OSHL), (Fibria Innovations) were used in this work. Prior to use, lignin was dried at 50 °C in a vacuum oven until no weight change was recorded. All reagents were obtained from Sigma-Aldrich, Fisher Scientific, and VWR Corporation and used as received. Deuterated chloroform (CDCl_3) was obtained from Cambridge Isotope Laboratories.

Nuclear magnetic resonance (NMR) was performed with a Bruker Avance 300 MHz spectrometer (USA) at 25 °C.

Synthesis of Hydroxyethyl Lignin. The amount of hydroxyl groups was calculated based on ^{31}P NMR for molar ratios. Dried lignin powders were mixed with ethylene carbonate (EC) in a molar ratio: EC/aromatic OH equaled 1 to 20 in a 100 mL round-bottomed flask. Three types of alkaline catalysts including Na_2CO_3 , NaOH, and K_2CO_3 , were added to the flask in a molar ratio of alkali/aromatic OH equaled 0 to 2, respectively. The flask was then closed with a rubber septum bound with steel wire. For the system with solvent, dimethylformamide (DMF) was added via syringe (0–6 mL/g, v/v). The flask was then purged with nitrogen for 5 min, placed in an oil bath (preheated to 60–170 °C), and stirred for 1 to 20 h. At completion, the hot solution was added dropwise into 400 mL of 0.01 mol/L hydrochloric acid (HCl) to precipitate the modified lignin. The supernatants were filtrated by vacuum filtration with 0.45 μm nylon membrane, and the residue was thoroughly washed by another 400 mL 0.1 mol/L HCl. Solid lignin powders were dried via lyophilization for 24 h and then vacuum-dried in the 50 °C oven for

another 48 h. Reaction yield was calculated based on the original lignin content of 1500 mg.^{37,38}

Quantitative ^{31}P NMR Analysis. A solution mixture was prepared by mixing pyridine and CDCl_3 in a ratio of 1.6/1 v/v. The pyridine was protected from the moisture with molecular sieves. The relaxation reagent and internal standard were prepared by dissolving the chromium(III) acetylacetonate and *N*-hydroxy-5-norbornene-2,3-dicarboximide into the solution with a concentration of 5.6 and 9.0 mg/mL, respectively. An exact amount of 20 mg of dried lignin powders was then dissolved in 400 μL of the above solution, followed with the addition of 100 μL of internal standard solution, 40 μL of relaxation reagent solution, and 50 μL of 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane (TMDP). This lignin solution was thoroughly mixed until no solid was left in the solution and transferred into a 5 mm NMR tube for immediate analysis. An inverse gated decoupling pulse was employed to obtain quantitative ^{31}P NMR with parameters: number of scans 800, relaxation delay 5 s, acquisition time 1.4 s, pulse length 6 μs , and 90° pulse width. The chemical shift of each phosphorylation product was calibrated with a product of TMDP with residual moisture at 132.2 ppm. Different functional groups were assigned (Figure S1).^{14,39}

Acetylation of Lignin for NMR and Molecular Weight (MW) Analysis. 300 mg of dried lignin powders was dissolved in a solvent, composed of 9 mL of anhydrous pyridine followed by the addition of an equal volume of anhydrous acetic anhydride. Mixtures were reacted at room temperature for 48 h in a nitrogen atmosphere with continuous stirring. To recover the product, the solution was added dropwise into 600 mL of 0.01 mol/L hydrochloric acid. Precipitated acetylated lignin was collected by filtration using 0.45 μm nylon membrane and washed by another 200 mL of 0.01 N hydrochloric acid three times and 200 mL of distilled water three times. Acetylated lignins were dried in a vacuum oven at 50 °C.⁴⁰

Quantitative ^{13}C NMR Analysis. Approximately 150 mg of acetylated lignin and nonacetylated lignin samples were dissolved into 450 μL of $\text{DMSO-}d_6$, followed by the addition of 60 μL of a solution of the relaxation agent chromium(III) acetylacetonate (50 mg/mL) in $\text{DMSO-}d_6$ and 15 mg of trioxane as an internal standard. The mixture was fully dissolved using a vortex mixer and transferred into a 5 mm NMR tube. The inverse-gated decoupling sequence was applied using the parameters: number of scans 20 000, relaxation delay 2 s, acquisition time 1.4 s, pulse length 8.15 μs , and 90° pulse. Signals were calibrated using DMSO as a reference (39.5 ppm). The relative concentration of functional groups is presented per 100 aromatic units. This was achieved by integrating the aromatic regions (100–160 ppm) and setting this to a value 60, then all chemical groups would be expressed based on this value.^{32,41}

Gel Permeation Chromatography (GPC). 5 mg of acetylated lignin samples was dissolved in 1 mL of anhydrous THF and stored at room temperature for 48 h. Lignin samples were then filtrated via 0.45 μm PTFE syringe filters. GPC measurements were carried out using Agilent 1100 GPC equipment (USA) consisting of a pump, an autosampler, and a column oven set at 35 °C. 100 μL of lignin solution was injected into the system and separated by three columns including Styragel HR4 (5–600 kDa), HR3 (0.5–30 kDa) and HR1 (0.1–5 kDa) with eluting solvent THF (degassed with helium) at a flow rate of 0.7 mL/min. Fractionated lignins were analyzed by the Wyatt Optilab T-Rex refractive index detector (dRI, USA) with 785 nm at 35 °C. All data were collected and analyzed by Wyatt ASTRA 6.0 (USA) installed with standard calibration with six different polystyrene which had standard molecular weight 1.3, 2.5, 5.8, 9, 17.5, and 30 kDa.^{40,42}

Thermal Gravimetric Analysis (TGA). TGA experiments were performed in triplicate using the TA 500 TGA (USA). 15 mg of dried lignin powders was loaded onto a platinum pan and heated to 105 °C with holding for 10 min to remove residual moisture, then further heated to 650 °C at a rate of 10 °C/min. All of samples were analyzed under a nitrogen atmosphere.

Differential Scanning Calorimetry (DSC). The glass transition temperature (T_g) measurements were measured in triplicate using a TA Q1000 DSC (USA). Approximately 7 mg of dried lignin powders

was sealed into 40 μL aluminum aluminum pans and lids. An annealing procedure was adopted by heating the sample up to 100 $^{\circ}\text{C}$ at the rate of 10 $^{\circ}\text{C}/\text{min}$, before cooling down to 0 $^{\circ}\text{C}$. Finally, the DSC thermograms were recorded by increasing the temperature from 15 to 125 $^{\circ}\text{C}$ (softwood kraft lignin) or 165 $^{\circ}\text{C}$ (hardwood kraft lignin) at a rate of 10 $^{\circ}\text{C}/\text{min}$.³¹

Thermorheological Analysis. Thermorheological analysis was conducted with in a TA Instruments AR 2000 rheometer (USA). Dried and finely ground lignin powders (mortar/pestle) were loaded between two 25 mm diameter stainless steel parallel plates. Samples were heated from room temperature to 150 $^{\circ}\text{C}$ at a rate 3 $^{\circ}\text{C}/\text{min}$. The normal force was held at 3 N below 100 $^{\circ}\text{C}$ and was reduced to 2 N above 100 $^{\circ}\text{C}$ to help prevent significant densification.⁴³

Direct Esterification of Hydroxyethyl Lignin. Around 1 g of softwood kraft lignin (SKL, Lignoboost) and hydroxyethyl SKL (HESKL) was obtained by the reaction conditions in Table S7. SKL-Lignoboost was mixed with 10 mL of propionic acid in a 25 mL round-bottomed flask. The solution was then reacted in the oil bath at 120 $^{\circ}\text{C}$ for 48 h. At the end of reaction, the solution was poured into 20 mL of THF, and the mixture was centrifuged at 5000 rpm for 10 min. The supernatants were kept, following the removal of THF and propionic acid by rotary evaporator. The resulting lignin was thoroughly washed by distilled water and dried by lyophilization. The yield of esterified lignin was about 70% (propionate SKL) and about 90% (propionate HESKL).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b02649.

Tabulated data for the NMR analysis, ³¹P, ¹H, and ¹³C NMR spectra of lignin samples, photographs of modified lignin, solubility test results, the hydroxyethylation of a variety of technical lignins, TGA, and DSC thermograms (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

SKL, softwood kraft lignin; HKL, hardwood kraft lignin; ASKL, acetone dissolve softwood kraft lignin; AHKL, acetone dissolve hardwood kraft lignin; HELignin, hydroxyethyl lignin; ALOH, aliphatic hydroxyl group; ArOH, aromatic hydroxyl group; COOH, carboxylic acid; EC, ethylene carbonate; SC, sodium carbonate; SH, sodium hydroxide; PC, potassium carbonate; -C, controlled reaction running without EC; OMe, me-

thoxy; T_g , glass transition temperature; T_{max} , maximum mass loss rate

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