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Methylation of Softwood Kraft Lignin with Dimethyl Carbonate

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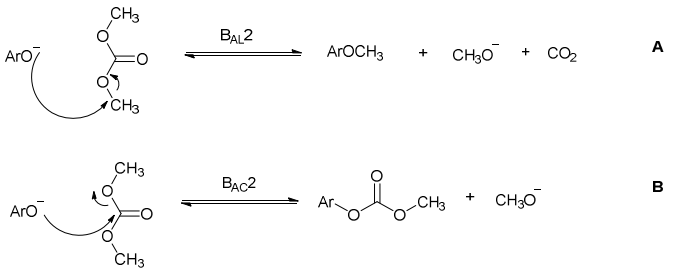
The reactivity and functionality of technical lignin requires reliable modulation in order to be used as precursors for a variety of applications. A green alternative for lignin derivatization via methylation reaction using dimethyl carbonate (DMC) is reported and this paper discusses our efforts toward optimization and structural elucidation for such methylation reactions. It is demonstrated that softwood kraft lignin can be progressively and reproducibly methylated to different extents using DMC in the presence of sodium hydroxide or cesium carbonate as bases with the latter requiring milder reaction conditions. ^{13}C NMR, FT-IR, and quantitative ^{31}P NMR spectroscopic analyses were used to document and understand the structural changes occurring within the methylated lignin derivatives. While the phenolic hydroxyl groups of lignin are methylated, the reduction in aliphatic –OHs is also observed in control and methylation reactions, most likely via a solvent mediated intramolecular rearrangement reaction. As anticipated, the methylation induced thermal stability, elimination of thermally induced crosslinking, and lowering in the glass transition temperature of the lignin is observed. Overall, the developed chemistry offers a green alternative to a much sought derivatization reaction that adds value to an otherwise intractable and underutilized biopolymer.

1. Introduction

Lignin is the most abundant aromatic biopolymer and second most abundant natural polymer after cellulose on the planet.[1] This three dimensional amorphous polymer is primarily found in the vascular plant cell walls cemented between the cellulose and hemicellulose. The structural component of lignin is mainly composed of phenyl propane units (C_6-C_3) of variable phenolic and aliphatic hydroxyl substitution levels in amounts that vary by the botanical origin and the method of isolation of the material.[2] Other functional groups present in lignin are methoxy, carbonyls, and carboxylic acids, again present in varying amounts depending on its origin. A complex structural pattern of connectivity amongst the various phenyl propane (C_6-C_3) units of lignin is also present as described by the following bonds; β-O-4, 5-5, β-5, 4-O-5, β-1, dibenzodioxocin, and β-β linkages.[2-4]

Every year a large amount of lignin is generated as a byproduct of the pulp and paper industry known as technical or kraft lignin[5] and as such it is mainly used as a source of energy. However, due to its highly aromatic and polymeric structure, enormous abundance, and highly functional character lignin can be considered as a serious candidate for replacing petro chemically based polymers and monomers with significant financial ramifications.[6-8] The main constraints on lignin's commercial usage are its random structure and instability at higher temperatures.[9] Previously, our group reported that at elevated temperatures (130 ^{o}C and above) lignin undergoes radically initiated self-polymerization leading to dramatic increase in its molecular weight.[10] This thermal instability restricts the processing of lignin at elevated temperatures. We also reported that this radically initiated self-polymerization can be completely prevented by the selective methylation of phenolic hydroxyl groups in lignin.



Scheme 1. Representing DMC as A) a methylating reagent via $B_{AL}2$ mechanism and as B) a carboxymethylating reagent via $B_{AC}2$ mechanism.

A completely methylated softwood kraft lignin sample does not show any increase in its molecular weight even when heated at 150 °C (20 °C above its Tg) for 3 hours.[10] These studies confirmed that the selective methylation of the phenolic hydroxyl groups of lignin is an appropriate method to control and modulate its reactivity and thermal stability. Consequently, the methylation reaction of lignin is becoming an extremely significant operation for the purposes in commercialization of this highly abundant natural polymer.[10] At present the available methods for lignin methylation are based on nucleophilic aromatic substitution reaction (S_NAr) with dimethyl sulfate (DMS) or methyl iodide[11] however, both of these reagents are highly toxic and hazardous.[12-14]

Literature precedence reports that dimethyl carbonate (DMC) can be used as a potential methylating agent for

phenolic hydroxyl groups either in a continuous or batch processes.[14-17] DMC is a non-toxic reagent and widely used as a green solvent in organic synthesis.[18-21] Unlike DMS and methyl iodide, DMC is not hazardous or mutagen, making its handling safe and facile. Moreover, carbon dioxide and methanol are the byproducts of this reaction with the potential of methanol being recycled and reused for the synthesis of DMC.[22, 23] The main drawback of using DMC as a methylating reagent is its variable chemical reactivity which depends on the reaction temperature. More specifically, DMC can either act as a methylating agent through a base mediated bimolecular alkyl cleavage nucleophilic substitution mechanism ($B_{AL}2$) at elevated temperatures (above 120 °C) or as a carboxymethylating agent through a base mediated bimolecular acyl cleavage nucleophilic substitution mechanism ($B_{AC}2$) at comparatively lower temperatures (ca. 90 °C); (Scheme 1).[17] Since the use of DMC as a methylating agent requires heating above 120 °C (which is above the boiling point of DMC (90 °C)), such reactions needs to be conducted in a sealed high-pressure reactor.

The development of a simple and safe method to methylate and produce a less reactive, chemically modulated, thermally stable technical lignin, using DMC, offers distinct environmental and safety considerations. Also, the utilization of technical lignins for other than incineration purposes offers additional advantages by avoiding carbon dioxide emissions. A literature account that examined the methylation reactions on lignin using DMC only in passing left many significant mechanistic, operational, and other details unanswered,[24] whereas a recent article on reactions of lignin model compounds with DMC has provided valuable foundations for this work.[25]

Consequently, in this effort, we have examined in detail the effect of DMC on softwood kraft lignin. To achieve this, we initially focused toward creating an understanding the effect of temperature and base on the reaction and its mechanism followed by detailed structural investigations of the methylated lignins. Finally, the methylated lignin derivatives were examined with respect to their polymer characteristics and thermal stability.

2. Experimental

2.1 Fractionation of kraft lignin: A prewashed and dry sample of softwood kraft lignin (supplied by Domtar Corporation) was suspended in acetone (1g/10 mL) and extracted for 10 h at room temperature. The solid residue was then removed by filtration. The acetone soluble fraction of the kraft lignin (ASKL) was recovered by evaporating the solvent on a rotary evaporator followed by drying in a vacuum oven at room temperature for 12 h. The functional group content and molecular weight of ASKL were determined using quantitative ^{31}P NMR and gel permeation chromatography (GPC) respectively.[26-29]

2.2 Methylation of lignin: 800 mg of ASKL (containing 4.66 mmol of phenolic, 1.54 mmol of aliphatic and 0.50 mmol of carboxylic hydroxyl groups respectively) were dissolved in 15 mL of dimethyl sulfoxide (DMSO). Sodium hydroxide (373 mg, 9.32 mmol; corresponding to 2 eq. to the phenolic hydroxyl group present in the ASKL sample) or cesium carbonate (3.031 g, 9.32 mmol; corresponding to 2 eq. to the phenolic hydroxyl group present in the ASKL sample) and DMC (varying from 1 to 10 eq. to the phenolic hydroxyl group present in the ASKL sample depending on the extent of methylation) were added to the above mixture. The reaction mixture was then transferred to a glass lined Parr reactor. The reactor was tightly sealed during the span of the reaction. The reaction mixture was heated at the specified temperatures and times (see results and discussion, Tables 1 and 2). After the completion of the reaction, the mixture was allowed to cool to room temperature and was then acidified with 2N hydrochloric acid to precipitate the lignin. The precipitated lignin was washed with water (50 mL X 4) and then freeze dried overnight. The details of the methylation reaction are shown in Tables 2 and 3. The progress of the methylation reaction was monitored by quantitative ^{31}P NMR spectroscopy.[26-28]

2.3 Control reactions: To examine and understand the effect of solvent, base, and temperature on the methylation reaction, control reactions were conducted in the absence of DMC. For all control reactions, 800 mg of ASKL were heated at 150 °C with the base (330 mg of sodium hydroxide or 3.031 g Cs_2CO_3) dissolved in 15 mL DMSO. The reaction time was extended to 24 h to examine for side reactions at elevated temperatures and extended times. The product was recovered by acidification by 2N HCl and was characterized by ^{31}P NMR. The data showed a negligible reduction in the amount of phenolic hydroxyl group (about 6%), confirming that any variations in the amount of phenolic hydroxyl groups of lignin were due to methylation by DMC.

2.4 ^{31}P NMR spectroscopy: The methylation of the kraft lignin was monitored and analyzed by quantitative ^{31}P NMR using a Bruker 300 MHz spectrometer as discussed in the earlier literatures.[26-28] An accurately weighed amount (40 mg) of a dried lignin sample was dissolved in 600 µL of anhydrous pyridine/$CDCl_3$ mixture (1.6:1, v/v). A total of 200 µL of an endo-N-hydroxy-5-norbornene-2,3-dicarboximide solution (9.23 mg/mL) as the internal standard and 50 µL of a chromium(III) acetylacetonate solution (5.6 mg/mL) as the relaxation reagent were added in the above pyridine/$CDCl_3$ solution . Finally, 100 µL of phosphitylating reagent II (2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane) was added and transferred into a 5-mm NMR tube for subsequent NMR acquisition using 256 scans, 12,000 Hz sweep width and 5 sec delay time.

2.5 Quantitative ^{13}C NMR analysis: An accurately known amount of 100 mg of a dried lignin sample was dissolved in 400 µL of anhydrous DMSO-d^6. A total of 100 µL of 1,3,5-trioxane solution (45.8 mg/mL in DMSO) was added serving as an internal standard and 100 µL of a chromium (III)

acetylacetonate solution (20 mg/mL in DMSO) serving as a relaxation reagent. The solutions were then transferred into a 5-mm NMR tube for subsequent NMR acquisition. Quantitative ^{13}C NMR spectra were collected using a 700 MHz NMR spectrometer equipped with a cryoprobe. Acquisition conditions were: 40,800 Hz sweep width, 1.7 s delay time and 34,000 scans.

2.6 FT-IR: FT-IT spectra were measured on a Frontier 94253 spectrometer. Spectra in the range of 4000-800 cm^{-1} were obtained with a resolution of 4 cm^{-1} by accumulating 16 scans using a Universal ATR and MIR TGS detector.

2.7 Acetobromination: Approximately 5 mg of a dried lignin sample were mixed in 2mL of glacial acetic acid/acetyl bromide mixture (92:8, v/v). The mixture was stirred at room temperature for ca. 2 h or until complete dissolution. Finally, the solvents were completely removed under reduced pressure at room temperature using a rotary evaporator connected to a cold-trap-protected vacuum pump.[29]

2.8 Gel permeation chromatography (GPC): All GPC measurements were carried out using a Waters GPC instrument equipped with UV (254 nm) detectors using tetrahydrofuran (THF) as an eluent at a flow rate of 0.7 mL/min at 35 °C. An injection volume of 100 µL and a sample concentration of 0.3 mg/mL were used. Two ultra styragel linear columns (Styragel HR 1 and Styragel HR 5E) were linked in series. A series of polystyrene narrow standards were used for calibration (the molecular weights of the polystyrenes used for the calibration were: 820 g/mol, 2,330 g/mol, 3,680 g/mol, 18,700 g/mol, 31,600 g/mol, 44,000 g/mol, 212,400 g/mol, 382,100 g/mol, 570,000 g/mol, 994,000 g/mol, and 1,860,000 g/mol).

2.9 Differential scanning calorimetry (DSC): All glass transition temperature measurements were performed on a TA-Instrument model TA-Q100 using a temperature range of 30-250 ºC. All samples were dried at 40 ºC for 12 h in a vacuum oven prior to the DSC analyses. Approximately 5 mg of a sample was weighed directly into a DSC hermetic aluminum sample pan, which was then covered by its lid and sealed by cold pressing; a small hole was pierced on the lid. After being loaded into the TA-Q100 all samples were heated up to 105 ºC at the rate of 5 ºC/min, isothermally conditioned for 40 min prior to being quenched to 30 ºC and isothermally kept for 5 minutes. Finally, the DSC thermograms were recorded by increasing the temperature to 250 ºC at a rate of 10°C/min.

2.10 Thermal gravimetric analysis (TGA): All thermal gravimetric analyses were carried out on a TA-Instrument model TGA-Q500 using a temperature range of 40-600 ºC and a nitrogen flow rate of 60 mL/min. The sample size for each analysis was approximately 15 mg. The samples were initially heated to 105 ºC with a heating rate of 10 ºC /min and maintained at this temperature for 20 min before being heated to 600 ºC with a heating rate of 10 ºC /min.

2.11 Thermal stability analysis: To simulate real processing conditions, about 60 mg of the unmethylated and nearly fully methylated kraft lignin samples were placed within the furnace of the TGA-Q500 instrument. The samples were subjected to three consecutive cycles of thermal treatment by heating (under a nitrogen atmosphere; flow rate of 60 mL/min) at 20 ºC above their respective glass transition temperatures (145 ºC for the unmethylated ASKL and 130 ºC for the methylated ASKL) for a total of 180 min. After every 60 min the heating was stopped and a portion was withdrawn for derivatization (acetobromination) followed by molecular weight distribution measurements.

3. Results and Discussion

The commercial utilization of kraft lignin is limited due to its heterogeneous structure and unpredictable reactivity. Earlier, literature accounts have reported that the lignin fractionation via organic solvent extraction protocols offer lignins of lower molecular weight and of lower polydispersity indices [30, 31] Recently, our group developed a systematic lignin fractionation method that offered homogeneous monodispersed lignins which after chemical modification allows the synthesis of higher molecular weight polymers[32, 33] Accordingly in this work, we used the acetone soluble kraft lignin (ASKL) fraction which was about 70% of the whole kraft lignin. The weight average molecular weight (Mw) and polydispersity index (Mw/Mn) of the starting kraft lignin was about 6300 g/mol and 6.6 respectively. However, the ASKL was of a considerably lower molecular weight (Mw=3800 g/mol) and of lower polydispersity (Mw/Mn=4.3) (all the molecular weights of the starting kraft lignin and ASKL were measured after acetobromination (see experimental section)). Quantitative ^{31}P NMR data for the fractionated sample also showed that the ASKL contains 5.83 mmol/g of phenolic-OH and 1.93 mmol/g of aliphatic-OH while the unfractionated starting lignin contains 4.6 mmol/g and 2.2 mmol/g of phenolic and aliphatic –OHs respectively. In this respect, the material used in the study was much better defined in terms of functional group distribution and consequent chemical reactivity.

3.1 Methylation of lignin using DMC- Optimization studies and selection of solvent and base: The objective of this paper is to examine and discuss efforts towards the systematic methylation reaction of acetone soluble kraft lignin (ASKL) using DMC as a methylating reagent. This is aimed at creating the foundations for the larger scale utilization of this reaction. Early methylation reactions were carried out in neat DMC as a solvent at 80 °C for 3h using Cs_2CO_3 as a base. However, these conditions only showed a 5% reduction in phenolic hydroxyl groups pointing out to the need to alter the solvent and the temperature of the reaction so as to promote complete methylation. Consequently, it became essential to use a higher boiling solvent such as DMSO allowing for better solubility of ASKL in it and the ability to increase the reaction temperature.

Table 1. Initial DMC methylation of lignin and comparative studies of bases used for the reaction.

Sample	Temp. (°C)	Time (h)	DMC (equivalent to phenolic –OH)	% Reduction in Aliphatic –OH (g/mol)	% Reduction in Phenolic –OH (g/mol)
Control reaction ASKL/ 2 eq. NaOH	120	5	-----	28	0
Methylation ASKL/2 eq. NaOH	120	5	6	66	85
Control reaction ASKL/ 2 eq. Cs_2CO_3	120	5	-----	53	26
Methylation ASKL/2 eq. Cs_2CO_3	120	5	6	77	82
Control reaction ASKL/2 eq. K_2CO_3	120	5	-----	56	0
Methylation ASKL/2 eq. K_2CO_3	120	5	6	81	89

Furthermore, it was observed that not only elevated temperature (120 °C - 150 °C) is crucial for this reaction but the polar aprotic nature of DMSO also possibly promotes this substitution reaction by solvating the nucleophile. This was confirmed by reaction performed with catalytic amounts of DMSO in DMC at low temperature (80 °C), which showed increased reduction in hydroxyl groups indicating the important role of solvent (DMSO).

Literature precedence reports that either a strong (NaOH) or a weak (K_2CO_3/Cs_2CO_3) base can be used in DMC methylation reactions of small phenolic molecules.[34, 35] Accordingly, our efforts focused at a comparative study of base selection for the DMC methylation reaction of lignin. Early optimization studies were conducted using three different bases (NaOH, K_2CO_3, and Cs_2CO_3) at 120 ºC for 5h in the presence of six eq. of DMC. The reaction temperature was selected to be 120 ºC in order to minimize documented carboxymethylation side reactions, which predominantly takes place at temperatures lower than 120 ºC.[17] Moreover, DMC has been documented to be stable at this temperature, decomposing by about 2% at ca. 300 °C.[36] The gauge pressure (95 PSI) also ensures the stability of DMC in the reaction mixture. The functional group analysis of the various methylated derivatives, when carried out using quantitative ^{31}P NMR spectroscopy, showed that the phenolic hydroxyl groups were significantly reduced (Table 1). Control reactions (in the absence of DMC) carried out under the same conditions, showed minor changes in the amounts of phenolic hydroxyl groups, pointing out the methylation occurring only in the presence of DMC. Overall, the quantitative ^{31}P NMR data showed that the reductions of phenolic –OHs were almost the same (within experimental error) for all examined bases (Table 1) indicating that any of the three bases examined could be used for the sought substitution reaction. Surprisingly, however, both control and the DMC methylation reactions showed a very significant reduction in the amounts of aliphatic -OH groups especially when K_2CO_3 was used. A postulated mechanism, offered for the rationalization of this effect will be discussed in detail in latter parts of this paper. Additional optimization efforts were thus focused on in using either a strong (NaOH) or a weaker (Cs_2CO_3) base. Cesium carbonate became especially attractive since it displays higher solubility in polar solvents, like DMSO and a stronger basicity compared to other alkali metal carbonates (Na_2CO_3 and K_2CO_3).[37]

3.2 Methylation of lignin using DMC, and NaOH as a base:

Initial methylation reactions were carried out using 3 equivalents of sodium hydroxide and 6 equivalents of DMC at 120 °C for 5h (Table 1). To further comprehend the progress and the chemistry of the reaction, quantitative ^{13}C NMR spectra of the starting material, control reaction products, and methylated products were examined in detail. The presence of a broad peak between 150 and 155 ppm in the methylated sample (which was absent in the starting material and the control reaction) signified the presence of carbonate carbonyl carbons arising from carboxymethylation reactions in lignin.[38] As discussed earlier, DMC can act both as a methylating and a carboxymethylating agent (Scheme 1) but preferring methylation over carboxymethylation at elevated temperatures.

Table 2. Optimization of the DMC methylation reaction of softwood kraft lignin using NaOH as the base.

Sample	Temp. (°C)	Time (h)	Reduction in Aliphatic –OH (%)	Reduction in Phenolic –OH (%)	Reduction in Carboxylic –OH (%)
Control reaction	150	24	48	6	10
Methylation 1	150	2	60	3	3
Methylation 2	150	5	61	39	-
Methylation 3	150	15	67	93	-

Previous studies have shown that simple phenols when heated between 180 ºC to 200 ºC were selectively methylated.[17, 25, 39] However, the thermal lability of lignin at higher temperatures[10] precluded the use of such high temperatures. Therefore, an optimum lower temperature was required to be selected so as to minimize the carboxymethylation reaction and maximize the methylation pathway. Therefore our work was carried out at 150 ºC by keeping all other reaction parameters same. By using quantitative ^{31}P NMR spectroscopy the profiling of all labile hydroxyls in lignin was monitored in detail (Table 2) as a function of time. Reaction periods ranging

from 2 to 5 h were seen to be inadequate in promoting phenolic methylation but after 15 h the levels of phenolic methylation were observed to be elevated (93%, see Table 2). Consequently, heating the reaction mixture in DMSO at 150 ºC for 15 h was selected as being the optimum time for the DMC lignin methylation reaction when NaOH is to be used as the base.

3.3 Methylation of lignin using DMC, and Cs_2CO_3 as a base: As stated earlier the initial reactions were conducted at 120 ºC for 5h in presence of six eq. of DMC using Cs_2CO_3 base (Table 1). Quantitative ^{31}P NMR data suggested that ca. 88% of the phenolic hydroxyl groups could be methylated under these conditions (Table 1). A series of additional methylation reactions were conducted with variable amounts of DMC ($N_{DMC/PhOH}$ = the ratio of equivalents of DMC used per total moles of phenolic OH present in lignin) (Table 3) to obtain a gradual increase in the degree of methylation. It was thus concluded that with increasing amounts of DMC, the degree of methylation progressively increases and a maximum of about 90% methylation could be obtained using 10 eq. of DMC (Figure 1A) with no further reduction beyond this level (Table 3).

3.4 Comparison of methylation reactions conducted with NaOH and Cs_2CO_3:
In experimental studies we have reported that both NaOH and Cs_2CO_3 can be used as a base for the quantitative methylation of ASKL using DMC as the methylating reagent. Figure 1 attempt to compare the efficiency of the two bases examined towards inducing methylation on the phenolic and the aliphatic –OH groups of lignin as a function of DMC concentration used. The data in Figure 1A shows that the reduction in the amount of phenolic –OHs is somewhat higher when NaOH is used as a base compared to Cs_2CO_3. The difference may be due to the different temperatures used for the two bases (150 ^oC for NaOH and 120 ^oC for Cs_2CO_3). It is likely that the increase in the reaction temperature may improve the efficiency of the Cs_2CO_3 base in promoting methylation levels above 90%. However, since the objective was to develop a mild and green reaction protocol, we examined lower temperatures for Cs_2CO_3 as optimal. The latter parts of this study will reveal that the minor differences in the degrees of methylation attained between NaOH and Cs_2CO_3 bases and no significant alterations in the properties of the end products were observed. Another reason for the observed differences in the degrees of methylation between the phenolic and the aliphatic –OHs using NaOH and Cs_2CO_3, (while identical batches of ASKL were used) could be the presence of a chemical variety of phenolic and aliphatic –OHs present in lignin.[40] A stronger base and a smaller anion may be advantageous toward promoting phenoxide nucleophile formation and this could be reflected in the higher efficiency of NaOH towards the methylation of the phenolic –OHs.

Since softwood kraft lignin most likely contains phenolic OH's of variable structure and consequently Pka values,[40] it is not surprising that the methylation profiles of the groups is variable for the two bases used. The differences however, in the reduction efficiency of the aliphatic OHs are somewhat more consistent between the two bases (Figure 1B). This could be due a slight lower chemical variability in the structure of aliphatic OHs present in softwood kraft lignin. Additional experiments to support the discussion on these differences is reported in the following sections.

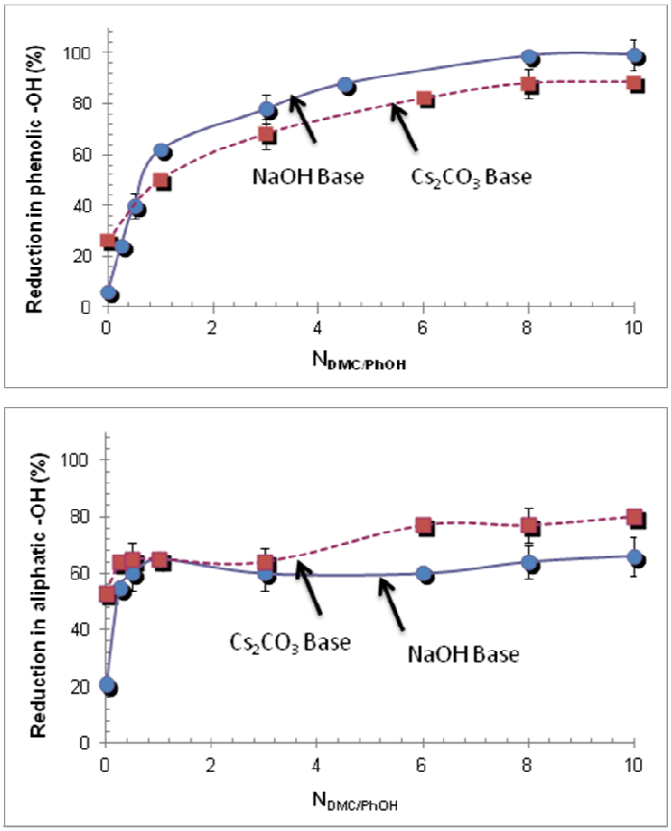


Figure 1. (A) Percent reduction of phenolic –OH groups as a function of DMC concentration (eq.) Results show that the reduction is slightly more using NaOH as a base. **(B)** Percent reduction of aliphatic –OH groups as a function of DMC concentration (eq.). Results show that the reduction is more using Cs_2CO_3 as a base.

It is important to note that since a detailed structure for softwood kraft lignin does not exist, the above hypotheses are proposed on the basis of known chemistry occurring during the kraft delignification process. It is to be noted here that the efficiency of Cs_2CO_3, in methylating phenolic OHs under the considerably milder conditions (to those of NaOH) is about 90% (within experimental error). This level of methylation is adequate in imparting the sought thermal and chemical stability characteristics in softwood kraft lignin.

3.5 Detailed hydroxyl group profiling via quantitative ^{31}P NMR spectroscopy: Detailed studies aimed at lignin utilization in copolymer and other systems, conducted by our group have shown that the phenolic hydroxyls groups in it need to be selectively methylated and their frequency be reliably modulated by partial methylation.[11,32,33] As such it was imperative that this effort arrives at a detailed reactivity map of all labile hydroxyl groups in lignin with emphasis on its various

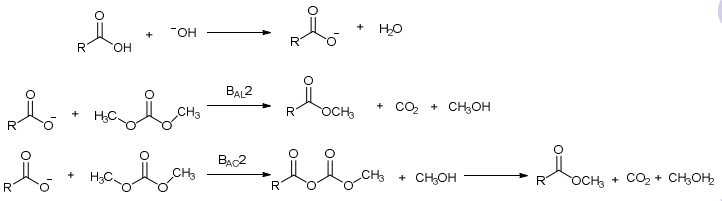
phenolic moieties. For both bases a series of methylation reactions were conducted with varying molar equivalents of DMC to the total moles of phenolic –OHs present in lignin ($N_{DMC/Ph-OH}$) as shown in Table 3 and Figure 1.

Table 3. Reduction (%) of the different hydroxyl groups in lignin as a function of DMC equivalents used, using NaOH and Cs_2CO_3 as bases.

Base	$N_{DMC/Ph-OH}$ *	Time/ Temperature (h/°C)	Reduction in phenolic –OH (%)			Reduction in aliphatic –OH %	Reduction in carboxylic –OH %
			Non-condensed	Condensed	Total		
NaOH	0.25	15/150	26	2	24	55	19
	0.50	15/150	56	24	40	60	23
	1	15/150	74	50	62	65	82
	3	15/150	86	70	78	60	87
	4.5	15/150	96	80	88	56	90
	6	15/150	97	86	92	60	91
	8	15/150	99	99	99	64	99
	10	15/150	100	99	100	75	99
Cs_2CO_3	0.25	5/120	22	20	21	64	15
	0.50	5/120	38	22	30	65	18
	1	5/120	62	38	50	65	77
	3	5/120	74	62	68	64	80
	4.5	5/120	75	65	70	65	95
	6	5/120	88	76	82	77	90
	8	5/120	96	80	88	77	90
	10	5/120	97	80	88.5	82	91

*NDMC/PhOH denoted the ratio of equivalence of DMC used with respect to the total phenolic OH present in lignin.

Product analyses were carried out using quantitative ^{31}P NMR spectroscopy (supporting data S1) in the presence of an internal standard.[26-28] Consequently, we used these methods to profile the reactivity of the different types of –OH groups present in lignin towards the methylation reaction (Table 3). This study suggests that the amount of phenolic –OHs reduces rapidly when the reaction is conducted in the presence of DMC. However, in case of the control reaction, only a negligible reduction in the amount (about 6%) of phenolic –OHs was observed. As such the data indicates that the reduction in the amount of phenolic –OHs (in presence of DMC) is strictly due to the methylation of the lignin. The quantitative ^{31}P NMR study further shows that lower equivalents of DMC only partially methylate the phenolic –OHs. For example when NaOH was used as the base and for a ratio of DMC equivalents to total phenolic –OH of 1, about 62% of the phenolic hydroxyl groups were methylated, while when cesium carbonate was used and for same DMC/PhOH ratio only about 50% of the phenolic OH were methylated (Table 3, Figure 1). Increasing amount of DMC ($N_{DMC/Ph-OH}$ = 8) leads to almost 100% reduction of the phenolic –OH groups (for NaOH as the base) can be seen (Figure 1A) indicating complete methylation of the phenolic hydroxyl groups.



Scheme 2. Carboxyl hydroxyl group methylation using DMC via $B_{AL}2$ and $B_{AC}2$ mechanisms

As such it can be concluded that the degrees of methylation of the phenolic hydroxyl groups can be adequately controlled

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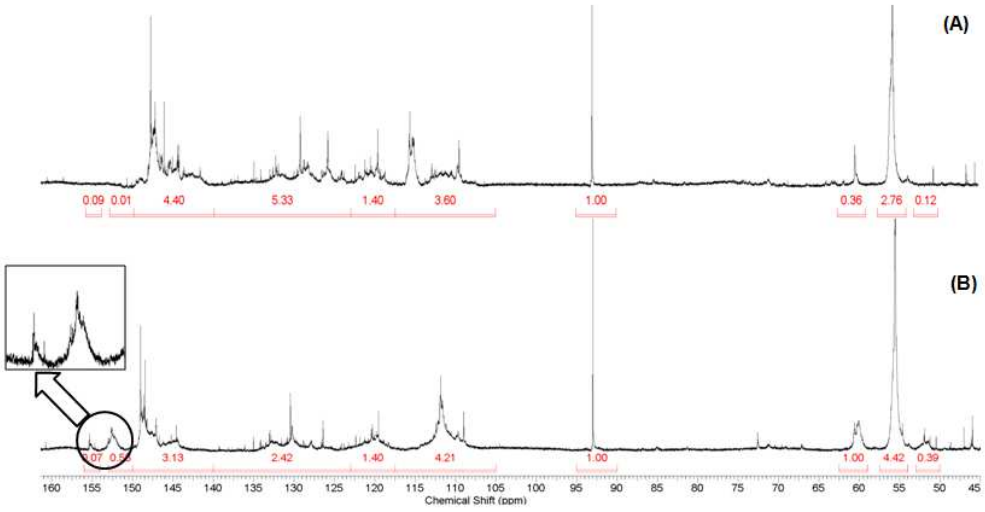


Figure 2. Quantitative ^{13}C NMR analysis of ASKL (A) before and (B) after DMC methylation. The chemical shifts at 55 ppm and 153 ppm show increase in the amounts of methoxy groups (from methylation) and the appearance of new carbonate carbonyls (from carboxymethylation) respectively.

based on equivalent amounts of DMC used. The data displayed in Figure 1 may thus serve as a guide in selecting the desired degree of methylation required and then using the appropriate amount of DMC equivalents.

Condensed phenolic –OH in softwood lignin are defined as those that belong to aromatic groups that have a substituent in the 5 position of the aromatic ring, while non-condensed phenolic –OH have no such substituents. Quantitative ^{31}P NMR studies indicate that the reaction rate of the condensed phenolic —OHs is slower than that of the non-condensed phenolic –OHs (Table 3). However, upon increasing the amount of DMC and using NaOH as the base, almost 100% of the condensed phenolic –OHs can be substituted (Table 3). The differences in reactivity of the condensed and non-condensed phenolic –OHs are due to the sterically-hindered environment of the condensed phenolic –OHs and the electronic effect of the functional groups as discussed in our previous work.[33]

Earlier efforts have shown that carboxylic acids undergo methylation when treated with DMC. As anticipated, the data in Table 3 shows that the lignin carboxylic acids are also methylated and the corresponding ester derivatives can be synthesized. The postulated reaction mechanism for this transformation is shown in Scheme 2.[41-43]

Furthermore, and almost invariably and irrespective of the base used, significant reductions in the amounts of aliphatic –OH groups (Figure 1B) were also observed for all reactions of lignin with DMC, including the control reactions. This is likely the result of certain simultaneous side reactions which will be discussed in the latter part of this paper.

3.6 Quantitative ^{13}C NMR analysis: In an effort to elucidate side-reactions and to confirm that the reduction of the phenolic -OH groups observed is the result of DMC induced methylation, quantitative ^{13}C NMR studies were carried out on the starting material and the corresponding methylated samples. Lignin itself contains a large amount of aromatic methoxy (-OCH_3) substituents, which can easily be identified in the region of 55 – 60 ppm in such NMR spectra (Fig. 2).[38] These signals were quantified in the starting material and the product with the aid of the internal standard 1,3,5-trioxane (92.5 ppm) as reported in our earlier effort.[44] The quantitative ^{13}C NMR studies indicate that the amount of methoxy groups present in the initial ASKL material (1.64 mmol/g) increases substantially after reacting with DMC in the final product (3.01 mmol/g). The increase in the amount of methoxy group confirms the methylation of ASKL.

^{13}C NMR analyses also indicate the generation of a new signals between 150 -156 ppm (Figure 2) due to carbonate carbonyl carbons. This observation suggests that a small portion of the lignin is also carboxymethylated by DMC most likely via the $B_{AC}2$ mechanism depicted in Scheme 1. Our work showed that approximately 5% of carboxymethyl groups are introduced in the lignin when the methylation is conducted using NaOH as the base at 6 eq. DMC to phenolic –OHs.

3.7 FT-IR analysis: The FT-IR spectra of the starting material and various methylated samples (using NaOH base) using variable concentrations of DMC are depicted in Fig. 3. A broad peak can be seen between 3200-3700 cm^{-1} for the starting material, which is assigned as the O-H stretching peak of the hydroxyl group present in lignin. However, upon methylation this peak reduces dramatically. Simultaneously, the peak between 2800- 3200 cm^{-1} (corresponding to C-H stretching frequencies) increases substantially upon methylation. Both O-H stretching peak between 3200-3700 cm^{-1} and the C-H

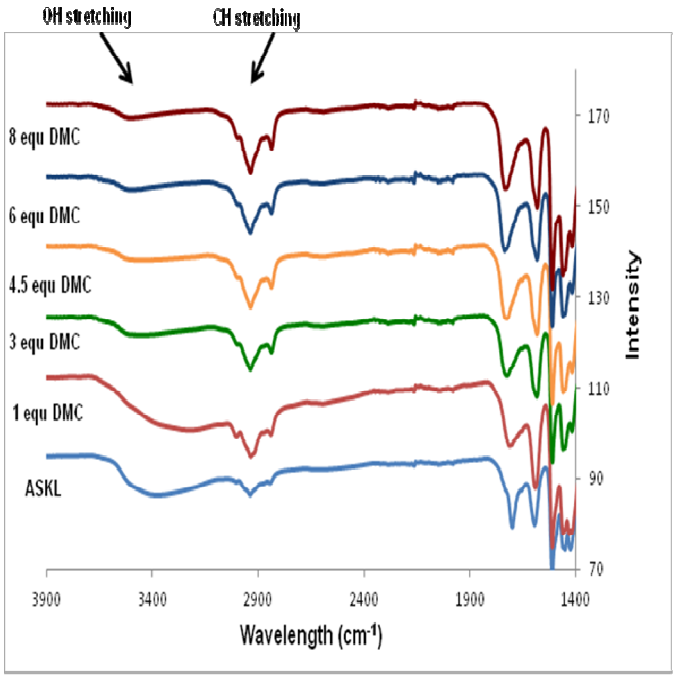
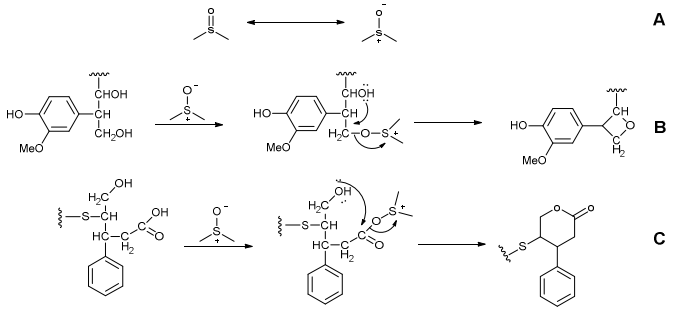


Figure 3. Overlay of FT-IR spectra of ASKL and methylated samples using NaOH as a base.

stretching peak between 2800 – 3200 cm^{-1} remain unaltered after the control reaction (supporting data Figure S2). Therefore, it is evident that during the reaction of lignin with DMC, its hydroxyl groups are converted to the corresponding methoxy groups. FT-IR studies of the methylated samples using Cs_2CO_3 as the base similarly showed that with increasing amounts of DMC the broad peak due to the O-H (between 3200 – 3700 cm^{-1}) stretching reduces gradually while the peak for C-H (between 2800 – 3200 cm^{-1}) stretching increases (supporting data shown in Figure S3). This also supports that in the presence of Cs_2CO_3 the hydroxyl groups of lignin are substituted by methoxy groups.

3.8 The fate of aliphatic –OH groups during DMC methylation of lignin: Quantitative ^{31}P NMR studies show that the aliphatic –OHs are dramatically reduced during the control reactions when carried out in the presence of either NaOH or Cs_2CO_3 bases (48% and 53% for NaOH and Cs_2CO_3 respectively). Additional reduction in aliphatic –OHs were also observed during the methylation reactions in the presence of DMC (Table 3 & Figure 1B). However, the quantitative ^{13}C NMR study (supporting data shown in Figure S4) of the control reaction shows no increase in the amount of methoxy groups. This likely rules out the possibility of methylating the aliphatic –OHs via DMSO (the reaction solvent) as the methylating agent. As such it is likely that another parallel side reaction could also be proceeding. In previous efforts regarding the reaction of lignin model compounds with DMC in basic media, Stanley et al. has shown that the aliphatic hydroxyl groups present in lignin model compounds are highly reactive.[25]

Moreover, these functional groups are more reactive in DMSO than in water under highly basic conditions.[45] At higher temperatures and under basic conditions DMSO is known to generate an active DMSO anion (Scheme 3A).[45] According to our hypothesis these DMSO anions react with the aliphatic –OHs present in kraft lignin followed by an intra-molecular rearrangement (Scheme 3C) resulting in the depicted cyclic products. Consequently, this could lead to the reduction in the aliphatic hydroxyl groups of the softwood kraft lignin. Despite the complexity of ^{13}C NMR spectra of lignin the new signals generated in the region (50 – 55 ppm) (Figure 2) after methylation may represent the ring methylene carbons formed during the intra-molecular rearrangement discussed above (Scheme 3). An additional reduction in the amount of aliphatic –OHs (Table 2) was observed during the reaction of lignin with DMC. This can be attributed to the transesterification reaction of the aliphatic –OHs conducted via $aB_{AC}2$ mechanism as reported earlier.[25, 42, 46, 47] Corresponding carbonate carbonyl peaks can be seen between 150 -156 ppm of the ^{13}C NMR spectra.



Scheme 3. (A) Activation of DMSO **(B)** Nucleophilic attack of –OH from lignin on to electrophilic DMSO followed by intramolecular cyclization leading to a four membered ring **(C)** Nucleophilic attack of –OH from lignin on to electrophilic DMSO followed by intramolecular cyclization leading to a six membered ring

3.9 Molecular weight distributions studies: The molecular weights of the ASKL, the control reaction, and the methylated lignin samples (using both NaOH and Cs_2CO_3 as bases) were examined after acetobromination to facilitate sample solubility in the THF mobile phase[30] (Figure 4). The Mn, Mw and PDI values are available in supporting data S5. Despite some negligible changes in the modality of the chromatograms after methylation, the molecular weight distributions of the initial and the methylated ASKL were nearly identical. These data are in excellent agreement with earlier reports by Sadeghifar et al. where the methylation of softwood kraft lignin was carried out using dimethyl sulphate as the methylating reagent.[11] Furthermore this data confirms the absence of any degradation or radically initiated polymerization reactions occurring during the heating of the reaction mixtures at the elevated temperatures and for the prolonged times used for the methylations (especially acute in the case of NaOH base).

3.10 Thermal Stability and Glass Transition Measurements: The thermal stability of the starting ASKL and the methylated samples (using both NaOH and Cs_2CO_3) were examined using

thermogravimetric analyses (TGA). The accumulated data shows a marginal improvement in the thermal stability of the methylated samples (shown in supporting data Figure S6). Most significantly this study suggests that the small amount of carboxymethylation observed to occur during the DMC methylation of the lignin does not actually affect the thermal stability of the substituted lignin.

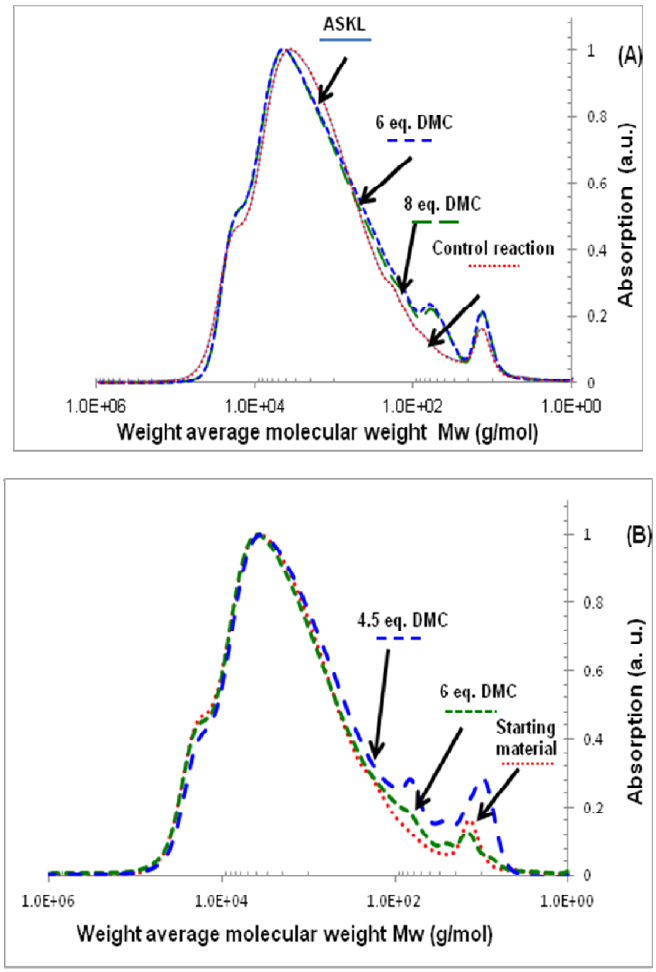


Figure 4. Normalized size exclusion chromatograms of ASKL and methylated samples using **(A)** NaOH as a base **(B)** Cs_2CO_3 as a base. chromatograms indicate that there are no significant changes in the molecular weight distributions after DMC methylation.

A comparative study of the DSC traces of the ASKL starting material and methylated samples shows that the glass transition temperature decreases slightly upon methylation (Fig. 5A) in accordance with previous studies.[10,11] The decrease in the glass transition temperatures with increasing reduction of free phenolic hydroxyl group (increase in the degree of methylation) (Figure 5B) is anticipated since methylation would restrict the intermolecular hydrogen bonding of the phenolic –OH groups. A higher degree of methylation when NaOH is used as the base lead to a slightly higher reduction in Tg compared to Cs_2CO_3 based methylation.

3.11 High Temperature Stability Studies. Since thermoplastic polymers are always processed above their glass transition temperatures, it is crucial for these materials to be stable at elevated temperatures.

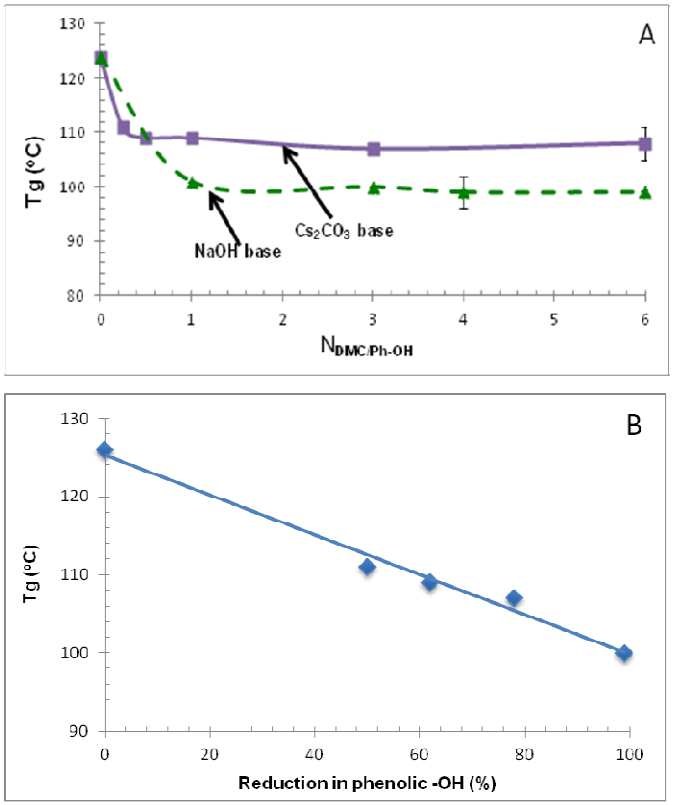


Figure 5. **(A)** Glass transition temperatures (Tg) of ASKL and methylated samples, against DMC concentration. **(B)** Decrease in Tg with the reduction in free phenolic -OHs

As such in an effort to document the anticipated thermal stability of the methylated ASKL both unmethylated and methylated samples were subjected to three consecutive cycles of a thermal treatment. Initially unmethylated ASKL was heated at 145 ºC (20 ºC above its glass transition temperature) for three consecutive cycles of 60 min (see experimental). The molecular weight distributions of the treated samples (after each cycle) were then determined by GPC following acetobromination. The GPC traces indicate that the molecular weight distributions of the ASKL sample shift towards the higher molecular weight side after each heating cycle (Fig. 6A). The broadening of the molecular weight distribution of the underivatized ASKL further supports our earlier work[11] that showed that during heating, phenoxyl radical induced self-polymerization of lignin is proceeding and the shapes of the chromatograms are becoming increasingly broader as anticipated when gelation statistics operate.[48-50,10] The methylated ASKL sample was also subjected to three consecutive cycles of thermal treatment by heating it at 130 ºC (20 ºC above its glass transition temperatures) for 60 min (see experimental). The molecular weight distributions of the treated

samples were then determined by GPC following acetobromination. Other than some minor differences in the modality (most likely caused by the thermally induced variations in the lignin's physical association),[51, 52] GPC traces show no significant increase in the molecular weights (Figure 6B).

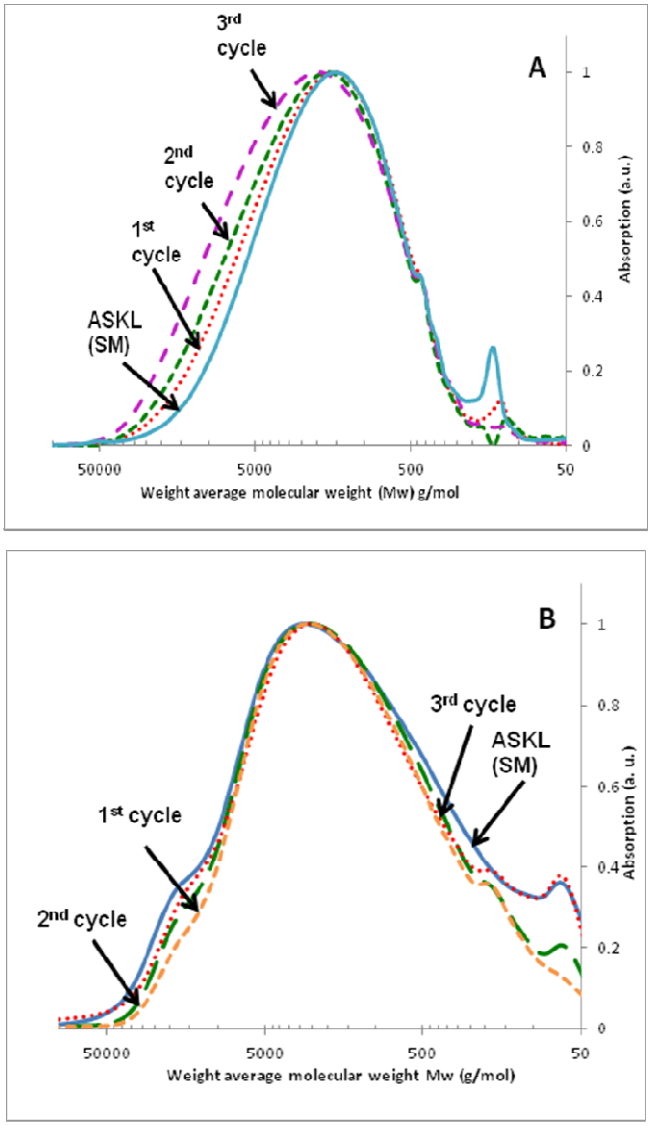


Figure 6. Molecular weight distributions of **(A)** Unmethylated lignin (ASKL) shows progressively wider molecular weight distributions as a result of heating. **(B)** Methylated lignin shows minor changes in the modality of the chromatograms with no increase in the breadth of the molecular weight distributions.

Corresponding molecular weights and PDIs are reported in the supporting data S7. As such it can be concluded that the methylation of lignin prevents the thermal polymerization events that most likely proceed via the generation of phenoxy radicals. Methylation of the phenols prevents phenoxyl radicals formation and thus the elimination of the thermally induced polymerization of lignin.

4. Conclusions

The progressive methylation of acetone soluble softwood kraft lignin has been demonstrated using DMC as the methylating agent. The reactivity of the different types of hydroxyl groups present in softwood kraft lignin has been elucidated. In this effort, it has been shown that the degree of methylation can be controlled based on the amount of DMC used. The products were characterized by ^{13}C NMR and FT-IR spectroscopy, and the degree of methylation was quantified by ^{31}P NMR spectroscopy. The comparative studies of the GPC data for the starting materials and its methylated counterparts are identical indicating no crosslinking or degradation chemistry operating during the developed methylation protocol. The thermal stability of the methylated lignin also remains almost unchanged.

However, as anticipated, the glass transition temperature of the methylated sample was observed to reduce due to the elimination of the intermolecular hydrogen bonding as a result of methylation. The aliphatic –OHs were also documented to reduce during the control reaction and the methylation reaction most likely via a solvent (DMSO) mediated intramolecular rearrangement reaction at high temperature.

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6. Notes and references

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† Electronic Supplementary Information (ESI) available: [^{31}P NMR spectra, FT-IR spectra of starting ASKL and controlled reaction, FT-IR spectra of starting ASKL and methylated samples using Cs_2CO_3 base, quantitative ^{13}C NMR spectra of starting ASKL and control reaction, molecular weight distributions and PDI of the methylated lignin samples using NaOH and Cs_2CO_3, TGA traces of starting lignin and methylated samples, Molecular weight distributions and PDI of unmethylated and methylated lignin before and after heating 20 °C above respective glass transition temperatures]. See DOI: 10.1039/b000000x/

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Methylation of Softwood Kraft Lignin with Dimethyl Carbonate

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Methylation of lignin is essential for inducing thermal stability in lignin when a multitude of thermoplastic applications are envisaged.