

Fractionation of wood polymers by carboxymethylation: Exploring the strategy

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ABSTRACT: We explored the feasibility of fractionating wood polymers in situ by carboxymethylation to yield the carboxymethyl derivatives of cellulose (CMC), hemicelluloses, and lignin for potential industrial applications. The initial water-soluble materials formed were a mixture of hemicelluloses and cellulose derivatives, and also contained some lignin (3%–5%). Interestingly, the water-insoluble residue after another carboxymethylation treatment gave essentially a CMC product containing less than 1% of residual lignin. Thus, the bulk of wood lignin is less reactive than the polysaccharide components under typical carboxymethylation conditions. Also, a hot water pre-extraction or dilute acid pre-treatment of wood samples was found to significantly enhance the reactivity of the cellulose component. A preextraction approach would facilitate CMC preparation and also provide the flexibility to convert the extracted hemicelluloses to other bio-based fuels or materials.

Application: Direct preparation of cellulose from wood substrates, if successful, would greatly simplify the overall process for CMC synthesis compared with preparation from dissolving pulps.

The current interest in biorefinery and developments for improved use of lignocellulosic materials may provide a means to cope with continuously soaring fossil fuel prices and the increasing global demand for energy. Current uses of woody polymers [1–6] are centered largely on the polysaccharide components (hemicelluloses and cellulose) for making fiber-based paper products or for converting into biofuels. For all those applications, the lignin component generally plays a negative role and has to be modified, partially degraded, or removed, depending on the nature of the end products. A modification of lignin in wood by thermal and/or chemical pretreatments is often necessary to produce chemimechanical pulps [1] or to facilitate the enzymatic hydrolysis of the cellulose component for the biofuel conversion [5,6].

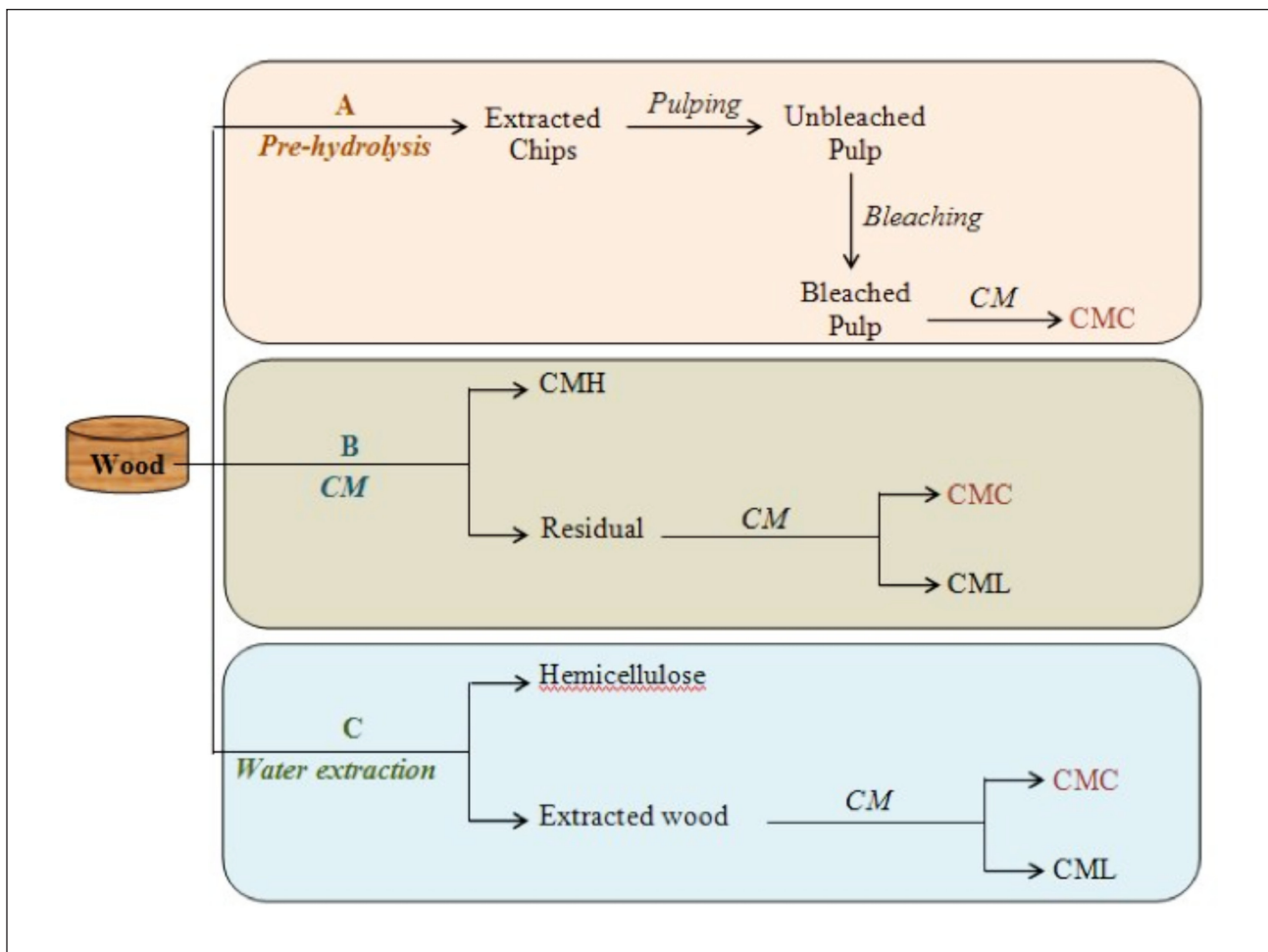
The paper industry represents the largest-scale industrial process for isolation of wood polysaccharides that are predominantly used as papermaking fibers [1]. In the production of pulp fibers for making stable white papers, the lignin component has to be removed by a series of pulping and bleaching operations [1,2]. Although kraft pulping is the dominant process and is effective for pulping all different kinds of plant materials, it is not an efficient operation; approximately one-third of the polysaccharides are degraded and lost as a consequence of alkaline degradation reactions [7–9] in the process.

Naturally, many current wood-based biorefinery projects emphasize extraction and isolation of hemicelluloses [3,4,10–14], which otherwise would be degraded in a typical kraft cooking process. The extraction methods examined ranged from a hot-water (auto-hydrolysis) extraction (HWE) to a mild

alkali treatment. The extent of the hemicellulose extraction would vary, depending on the intent to use those extracted chips for the production of papermaking fibers or solid-wood products such as wood pellets.

At our institute (SUNY-ESF), a technology based on the HWE of sugar maple in the 160°C–170°C range has been extensively studied with respect to the characteristics and potential applications of the water extracts and the extracted chips [3,4,10,11]. For example, the sugar components of water extracts after hydrolysis and component separation were shown to be very responsive to fermentation for the production of biofuels (ethanol and butanol) or biopolymers such as polyhydroxy-alkanoates (PHA). The extracted chips could then be used for the production of papermaking fibers or reconstituted wood products with improved properties. Interestingly, the water-extraction step significantly enhanced the subsequent alkaline (kraft) delignification process [15].

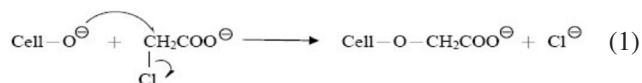
In addition to the papermaking fibers, the paper industry also produces a pulp product called dissolving pulp (a very pure cellulose) [1] for making cellulose products such as rayon, cellophane, and cellulose derivatives. To prepare that cellulose pulp, extra operations are needed for complete removal of the hemicellulose components. For example, a prehydrolysis stage prior to kraft pulping is often used in the current production of dissolving pulps. Also quite often, an extraction stage may be necessary to remove the residual hemicelluloses remaining in the pulp. Considerable efforts [16,17] have been made to recover those partially degraded hemicelluloses from the prehydrolysis stage for biofuel or polymer applications.



1. Different approaches for the synthesis of carboxymethylcellulose (CMC) from wood.

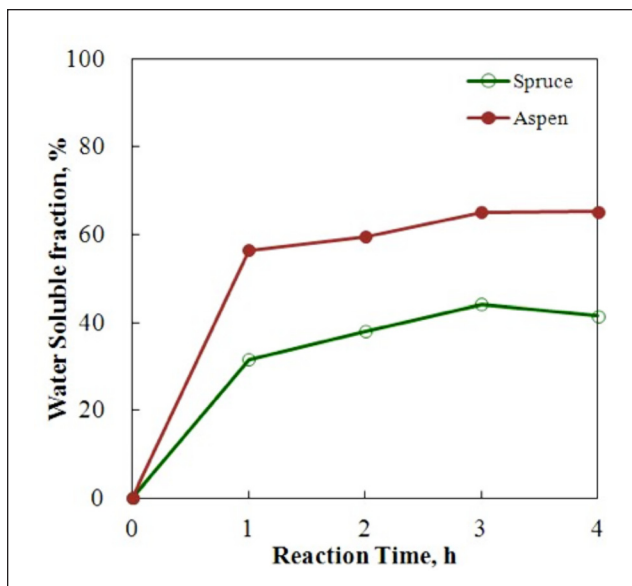
Thus, the current production of cellulose derivatives such as carboxymethyl cellulose (CMC) from a woody substrate is a very tedious process, as it includes a prehydrolysis stage to remove hemicelluloses and a series of pulping and bleaching operations to remove the lignin component followed by a carboxymethylation (CM) process, as illustrated in Process A (Fig. 1). CMC is a widely used industrial polymer with applications ranging from the food industry, to pharmaceuticals, paper coatings, and oil drilling fluids [2,18].

The CM process is an important etherification reaction for the modification of polysaccharides [2,18–20] and has also been investigated for improving solid wood use [21,22] or for the separation of wood components [23–29]. The CM process is generally conducted in alkalis in the presence of an organic solvent such as 2-propanol, which traditionally has been the solvent used in CMC synthesis [30]. The process involves the reactions of hydroxyl groups with monochloroacetic acid (MCA), as illustrated in Eq. (1) for cellulose. The underlying hypothesis is that the general reaction in Eq. (1) is expected to be applicable to both major polysaccharide components of woods and the lignin components, and that the reaction kinetics might enable separation of the components.



Lam et al. [24–28] and Jin et al. [29] had reported on the CM process of wood meal samples conducted in a 2-propanol system [30]. The resulting CM mixture was then separated into water-soluble and water-insoluble fractions. The soluble materials were derived mainly from the polysaccharide components and contained some residual lignin (3%–7%), while the water-insoluble materials were mainly a mixture of the lignin and cellulose. Surprisingly, the water-insoluble materials, similar to the water-soluble fraction, were reported as having a high degree of substitution (1.5–1.6) based on the ¹H-NMR technique [28, 31]. This interesting phenomenon [29] was attributed to the presence of lignin-carbohydrate complexes (LCC) inhibiting the solubility of some derivatized materials.

This work was aimed at understanding the extent to which the separation of wood polymers could be improved by modifying the CM process conditions. Initial results [32] indicated that the nature of organic solvents used and the chemical charges (alkalis and MCA) have considerable influence on the



2. The rate on the formation of water-soluble fraction and its lignin content from the carboxymethylation of the acid-treated spruce wood. (Conditions: wood [600 mg] in 2-propanol [33 mL], MCA [450 mg], and 30% NaOH [2 mL] at 50°C).

CM of wood polymers in terms of the formation of water-soluble materials and its residual lignin content. However, a clean separation of wood polymers could not be achieved by a single CM of wood substrates.

Figure 2 illustrates the rate on the formation of water-soluble materials from the CM of wood samples conducted in a 2-propanol system. A similar two-phase pattern was observed for both spruce and aspen wood. The initial rapid phase was essentially completed within 1 h. On the basis of the sugar analysis by the $^1\text{H-NMR}$ technique [28,31], the initial rapid phase was attributed to the CM of the hemicelluloses plus a cellulose component, while the subsequent slow phase was attributed mainly to the CM of cellulose.

We observed that the degree of substitution (DS) was significantly higher for the water-soluble materials obtained after 1 h reaction – 1.4 (spruce) and 0.9 (aspen) – as compared with that of the water-insoluble fraction – 0.5 (spruce) and 0.4 (aspen). Those results differed significantly from those reported by Jin et al., as noted earlier [29]. Our results suggested that the cellulose component remaining in the water-insoluble fraction was attributable mainly to an insufficient CM reaction. This contention will be examined further.

In connection with our biorefinery program [3,4,10,11], the influence of the hot-water preextraction on the subsequent CM of wood is of special interest, as it might be expected to enhance the accessibility of wood cellulose toward the CM reaction and thus facilitate the CMC preparation. Also, this preextraction process would provide the flexibility for converting the extracted hemicelluloses to biobased fuels and other products.

Our paper represents an update of our attempts to develop a simpler process than the current synthesis of CMC from dis-

solving pulps (Path A) by a direct CM process of woody substrates (Path B) or by a combined prehydrolysis and CM process (Path C), as shown in Fig. 1. The proposed approaches B and C would represent concepts for maximizing the amounts of products recovered from use of lignocellulosic material as biomaterials or biofuels.

EXPERIMENTAL

Wood samples

Extractives-free wood meal samples (40–60 mesh) from Norway spruce and aspen were prepared by extraction with acetone overnight and then air-dried. The hot water-extracted wood was prepared by heating extractive-free wood (5 g) with distilled water (50 mL) in small autoclaves at 160°C for 1.5, 2, and 3 h. After filtration and thorough washing with distilled water, the extracted wood was air-dried, and the yield and lignin content were determined.

The acid-treated wood was prepared by heating the extractive-free wood (4 g) with 0.05M sulfuric acid (40 mL) at 160°C for 1 and 2 h. After being washed thoroughly with distilled water and air-dried, the yield and lignin content of the treated samples were determined.

Carboxymethylation of wood

The CM of wood was conducted as described earlier [32]. In general, wood samples (600 mg) were mixed with a solvent (33 mL) in a flask (125 mL) followed by the addition of 30% (NaOH) (1 mL) and MCA (450 mg) and then heated in an oil bath at 50°C for 4 h. The cooled mixture, after centrifugation to remove the solvent, was washed several times with a water/methanol (1:9 by volume) solution and then with methanol. The resulting CM-wood yield and lignin content were measured after drying over phosphorus pentoxide (P_2O_5) in a desiccator.

A sample of carboxymethylated wood (200 mg) was stirred with distilled water (10 mL) for 2 h and then kept overnight at ambient temperature. After centrifugation, the lignin content of the water-soluble material was estimated based on the ultraviolet (UV) absorption at 280 nm, whereas yield was measured for the insoluble material after drying.

Analytical methods

The lignin content of carboxymethylated wood samples was measured by a modified TAPPI standard method as described earlier [32]. The modified procedure used a smaller sample (100 mg), and the results were very comparable to that of the TAPPI standard method. The lignin content of the Norway spruce and aspen wood samples was established to be 30.7 and 22.0, respectively (**Table I**). The sugar analysis of the carboxymethylated products followed the reported procedures [28,31].

RESULTS AND DISCUSSION

Figure 2 illustrates the overall CM process of wood in terms of the formation of water-soluble materials and could serve, if

Wood	Lignin Content (%)			PhOH* No./100 C ₉
	Klason	Acid-Soluble (%)	Total (%)	
Spruce	28.3	2.4	30.7	12.6
Aspen	18.9	3.3	22.2	10.8

*Determined by periodate oxidation method.

I. Content of lignin and phenolic hydroxyl groups (PhOH) of spruce and aspen wood.*

the reaction kinetics supported it, as a basis for approach B to fractionate wood polymers (Fig. 1). As discussed earlier, the initial formation of water-soluble materials from the CM of wood was largely derived from the CM of hemicelluloses and cellulose components plus some lignin. Thus, it is essential to identify optimal conditions for selective CM of the hemicellulose components and also to evaluate the extent that the water-insoluble residue can be further separated into the CMC and CML products. The latter cellulose-lignin separation task, along with the influence of preextraction of hemicelluloses on the subsequent CMC formation (approach C), is also discussed in the following section.

Characteristics of carboxymethylated wood

To understand the nature of the slow-phase reaction, we conducted another CM of wood with a larger sample size (15 g) to prepare enough water-insoluble materials to examine their reactivity. **Table II** summarizes the characteristics of the carboxymethylated wood.

As indicated, the apparent weight gain was slightly higher for spruce (44%) than aspen wood (37%). Weight gain is the percent weight increase for the carboxymethylated wood (Eq. [2]) and is closely related to the extent of the CM of wood polymers. Also, the apparent lignin content of carboxymethylated spruce (20.4%) was significantly lower than that of the original wood (30.7%) (Table I). However, by taking into account the weight gain from the CMC process, it was found by calculation that the total amount of lignin present in the whole carboxymethylated spruce was 29.3%, which was very close to that of the original value of wood

(30.7%). Thus, the bulk of spruce wood lignin (95%) was retained in the carboxymethylated wood. A similar calculation was made for the aspen wood.

$$\text{Weight gain (\%)} = \left(\frac{\text{weight of product} - \text{weight of sample}}{\text{weight of sample}} \right) \times 100 \quad (2)$$

The lignin content of the water-soluble fraction was lower for spruce (3%) as compared to aspen (5%). Those values indicated that the proportion of lignin in the carboxymethylated wood that was made soluble in water was low for spruce (4% of the original lignin content) as compared to aspen (21% of the original lignin content). Thus, the aspen wood lignin was found to be more responsive to the CM reaction than the spruce wood lignin.

Table III shows the extent of CM based on the formation of carboxylic groups for both the water-soluble and water-insoluble fractions. The carboxylic groups were determined by a conductometric titration as described by Beatson [33]. The water-soluble material had a higher content of carboxylic groups than the water-insoluble material by a factor of 1.6 for spruce and 1.5 for aspen wood. Because the exact composition of those materials remains to be determined, the DS was estimated from Eq. (2) based on the assumption of the products being 100% of xylan (DS₁), cellulose (DS₂), or lignin (DS₃).

Equation (3) is often used in the DS calculation for CMC samples (with M = 0.162 [34]) or for CMH (for xylan hemicellulose using a different M of 0.132 [20]. Lignin has a value for M of 0.180,

$$DS = \frac{M \times A}{1 - 0.08 \times A} \quad (3)$$

where A is the total carboxyl group content (g.mmol gram of material; M is the mass (g.mmol⁻¹) of the basic unit of a polymer, i.e., 0.132 for a xylose, 0.162 for a glucose, and 0.180 for a C₉ unit of lignin); and 0.08 (g.mmol⁻¹) is the net increase in mass for each carboxymethyl group introduced.

As shown in Table III, the water-soluble fraction has a noticeably higher DS than the water-insoluble material for both spruce and aspen wood. For example, for spruce wood, the DS₂ of water-soluble materials was 1.05 compared to 0.56 for the insoluble material. Thus, the solubility of wood

Sample	Carboxymethylated Wood					
	Weight Gain (%)	Lignin (%)	Water-Insoluble Fraction		Water-Soluble Fraction	
			Prop.(%)	Lignin(%)	Prop.(%)	Lignin(%)
Spruce	43.8	20.4	36.3	2.5	63.7	27.9
Aspen	37.4	15.2	59.1	5.3	40.9	26.1

*Conducted with 15 g of wood sample in 2-propanol (400 mL), 18.7 g of MCA, 7.5M of NaOH (40 mL) at 55°C for 3 h.

II. Characteristics of the carboxymethylated spruce and aspen wood.*

Sample	CO ₂ H mmol/g	Degree of Substitution**		
		DS ₁	DS ₂	DS ₃
Spruce				
Water-soluble	4.27	0.86	1.05	1.17
Water insoluble	2.69	0.45	0.56	0.62
Aspen				
Water-soluble	3.65	0.68	0.84	0.93
Water-insoluble	2.40	0.39	0.48	0.54
CMC***	3.32	-	-	0.73
*From Table II. ** DS was estimated based on products assumed being 100% xylan (DS ₁), 100% cellulose (DS ₂) or lignin (DS ₃). ***A commercial sample from Aldrich having a DS of 0.7.				

III. Contents of carboxylic groups and estimated degree of substitution for the water-soluble and water-insoluble materials.*

polymers appears from this data to depend on the extent of CM reaction.

Carboxymethylation of water-insoluble materials.

The water-insoluble residues derived from the carboxymethylated wood shown in Table II were then subjected to another CM treatment. As shown in **Table IV**, the CM of the water-insoluble materials resulted in a relatively high yield of the water-soluble fraction for both the spruce (46%) and aspen (61%) wood. This phenomenon further supported our earlier contention that the water-insoluble material was attributed largely to insufficient CM reactions, as an alternative explanation to the presence of LCC as claimed by Jin et al. [29].

Interestingly, the new water-soluble materials formed contained less than 1% of the residual lignin and appeared to be a rather pure CMC product. Those observations supported our hypothesis that the reaction kinetics of the CM reaction might be used to progressively fractionate the wood polymers.

Sample	Carboxymethylated Water-Insoluble Materials**			
	Weight Gain (%)	Lignin (%)	Water-Soluble Fraction	
			Prop. (%)	Lignin (%)
Spruce	41.2	21.9	45.5	0.9
Aspen	29.3	17.3	60.7	1.0
*Conducted with 300 mg of the water-insoluble residue in 2-propanol (33 mL), 900 mg of MCA (sodium salt), and 2M NaOH (4mL) at 50°C for 4h. **Obtained from the CM of wood (Table II).				

IV. The carboxymethylation* of the water-insoluble materials.**

Wood Sample	Time (h)	Yield (%)	Lignin Content (%)		
			Klason (%)	Acid-Soluble (%)	Total (%)
Spruce	0	100	28.3	2.4	30.7
	1.5	83.7	31.5	1.8	33.3
	2	80.2	32.4	1.9	34.3
	3	81.5	32.7	1.8	34.5
Aspen	0	100	18.9	3.3	22.2
	1.5	73.7	21.3	4.6	25.9
	2	72.5	21.1	3.8	24.9
	3	74.2	23.2	3.9	27.1

V. The hot-water extraction of spruce and aspen wood conducted at 160°C.

On the basis of the lignin content data in Table IV, the proportion of the water-soluble material formed was about 46% for spruce, which would account for only 60% of the total polysaccharides present. Similarly for aspen, the water-soluble materials (61%) would account for about 70% of the polysaccharide components. Those findings imply that significant amounts of the cellulose components (30%–40%) are still resistant to the second stage of CM reaction.

Hot-water preextraction

Table V illustrates that the hot-water preextraction of wood at 160°C resulted in a significant extraction of material, especially for the aspen wood. That extracted material was expected to be predominately from the removal of the hemicellulose components.

The responses of the water-extracted wood samples to the CM reactions were evaluated in two systems. The CM of the 1.5 h-treated wood was conducted in a solvent mixture of acetone and ethanol (7:3), and **Table VI** summarizes the results. For longer-treated samples (2 and 3 h) (Table V), the CM reaction was conducted in 2-propanol with a slightly higher alkali (**Table VII**).

Sample	Water-Hydrolysis (h)	Yield (%)	Carboxymethylated Wood		
			Weight Gain (%)	Water-Soluble Fraction	
				Prop. (%)	Lignin (%)
Spruce	0	54.6	20.0	26.9	3.7
	1.5	52.7	22.1	40.8	3.6
Aspen	0	50.3	12.9	42.9	7.8
	1.5	41.7	15.8	66.2	6.6
*Conducted with 600 mg of wood in a 7:3 mixture of acetone/ethanol with a charge of MCA (450 mg) and 1 mL of 30% NaOH at 50°C for 4 h.					

VI. The carboxymethylation* of hot-water extracted wood (at 160°C for 1.5 h).

Sample	Water-Hydrolysis (h)	Carboxymethylated Wood			
		Weight Gain (%)	Lignin (%)	Water-Soluble Fraction	
				Prop. (%)	Lignin (%)
Spruce	0	41.4	20.1	41.5	1.6
	2	51.9	25.5	54.7	2.1
	3	49.4	24.8	58.5	2.4
Aspen	0	50.0	14.1	65.6	4.5
	2	45.7	15.3	77.3	4.4
	3	38.2	15.6	78.1	5.0

*Conducted with 600 mg of wood in 2-propanol with a charge of MCA (450 mg) and 2 mL of 30% NaOH at 50°C for 4 h.

VII. The carboxymethylation* of hot-water extracted wood (at 160°C for 2 and 3 h).

As indicated, the preextraction enhanced the subsequent CM reactions, resulting in a higher formation of the water-soluble materials, especially for the aspen wood. Also, the HWE slightly increased the residual lignin content of water-soluble materials (Table VII). The hot-water pretreatments slightly enhanced the CM of lignin, especially for the aspen wood. A higher lignin reactivity in the preextracted wood can be related to the hydrolysis of labile aryl ether structures [35], leading to formation of phenolic hydroxyl (PhOH) units. This was consistent with our earlier observation that a mild acid treatment of wood enhanced the subsequent sulfonation conducted at pH 7.5 [36]. The preextraction conditions need to be further optimized to minimize the lignin reaction to develop a selective CMC production process.

Because those preextracted samples contained smaller amounts of residual hemicelluloses, the water-soluble material should contain mainly the CMC polymer. For the 2 h-treated samples (Table VII), the high proportion of soluble materials for aspen (77%) would account for about 90% of the polysaccharide components. That would imply that 10% of the cellulose was resistant to the CM reaction. For spruce wood, a lower proportion of water-soluble materials (55%) would represent 73% of total carbohydrates in the carboxymethylated wood and imply 37% of the cellulose being resistant to the CM process. Thus, the hot-water treatment significantly enhanced the CM of cellulose and, to a lesser extent, that of the lignin component.

The data in Table VI also indicated that the water preextraction had slightly enhanced the CM of lignin especially for the aspen wood. That contention was based on the observations that the preextraction process considerably enhanced the formation of water-soluble materials and their lignin contents were also increased by the pretreatments.

Dilute-acid pretreatment

The dilute-acid treatments (conducted in 0.05M H₂SO₄ [sulfuric acid] at 160°C for 1 h) of wood (Table VIII) resulted in more extensive removal of the hemicelluloses as compared to

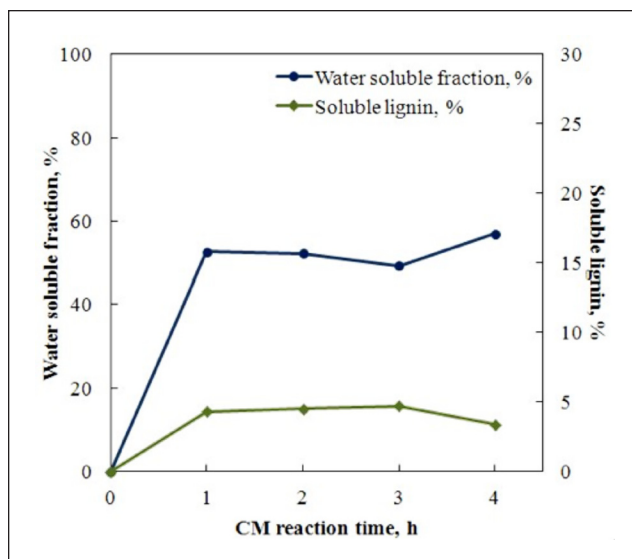
Species	Acid Treatment (h)	Yield (%)	Lignin Content (%)		
			Klason (%)	Acid-Soluble (%)	Total (%)
Spruce	0	100	28.3	2.4	30.7
	1	73.8	40.0	1.9	41.9
Aspen	0	100	18.9	3.3	22.2
	1	74.4	26.2	4.8	31.0

VIII. The dilute-acid treatment of spruce and aspen wood with 0.05M H₂SO₄ at 160°C for 1 h.

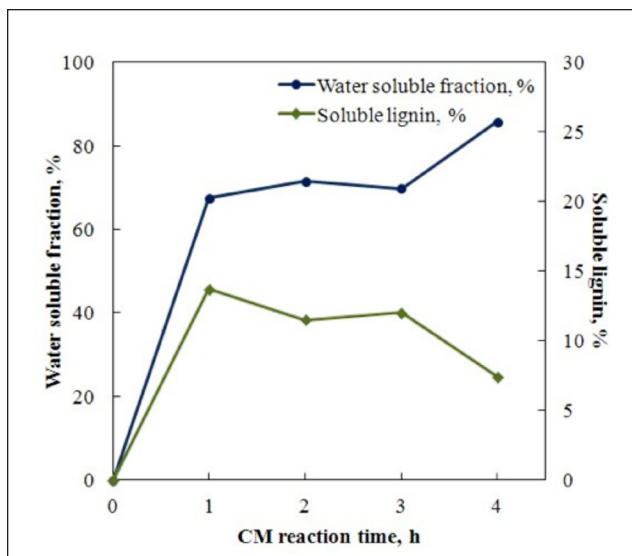
the HWE (Tables VI and VII). Also, those acid-treated samples retained practically all the wood lignin.

The response for acid-treated samples to the CM reaction was conducted in a 2-propanol system. Figure 3 illustrates the rate on the formation of water-soluble materials for the acid-treated spruce wood, and the initial reaction (mainly the CMC formation) is essentially completed within 1 h. The water-soluble fraction contained about 4% of residual lignin, which was slightly higher than that from the untreated or hot-water preextracted wood samples. On the basis of the lignin content data, approximately 70% of cellulose component in the acid-treated spruce wood was accessible to the CM reaction.

The 1-h acid-treated aspen wood (Fig. 4) was more reactive toward CM than that of the acid-treated spruce wood, resulting in a higher formation of the water-soluble materials of over 80%. That soluble fraction also contained a relatively higher content of the residual lignin (7%–14%) as compared to that of spruce wood (~4%). Thus, the reactivity of both cellulose and lignin components in aspen wood was considerably enhanced by the dilute-acid pretreatment.



3. The rate on the formation of water-soluble fraction and its lignin content from the carboxymethylation of the acid-treated spruce wood. (Conditions: wood [600 mg] in 2-propanol [33 mL], MCA [450 mg], and 30% NaOH [2 mL] at 50°C).



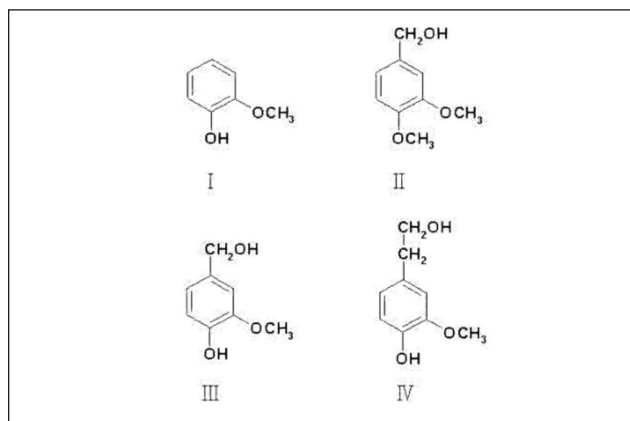
4. The rate on the formation of water-soluble fraction and its lignin content from the carboxymethylation of the 1h acid-treated aspen wood. (Conditions: wood [600 mg] in 2-propanol [33 mL], MCA [450 mg], and 30% NaOH [2 mL] at 50°C).

Reactivity of lignin

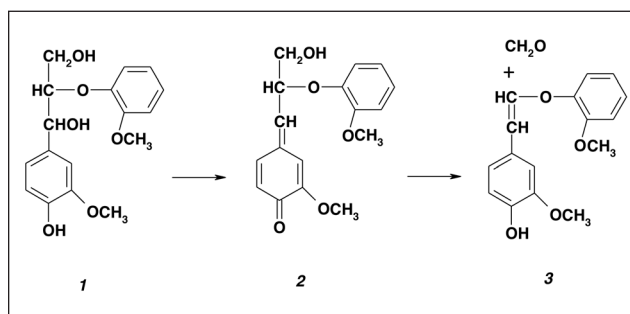
The chemistry involved in the CM of wood lignin is still not well understood. We have examined the relative reactivity of simple lignin model compounds toward the CM reaction [37]. These included the PhOH unit of guaiacol (I), benzyl hydroxyl group of veratryl alcohol (II), combined phenolic and benzyl hydroxyl groups of vanillyl alcohol (III), and combined phenolic and primary hydroxyl groups of homo-vanillyl alcohol (IV) (**Fig. 5**).

We have observed [37] some interesting phenomena related to the reactivity of key functional units of lignin. For the guaiacol (I), the CM of the PhOH unit as expected was a very reactive one. However, for the vanillyl alcohol (III), no direct CM products were obtained from the phenolic unit and the bulk of product mixtures were derived from the well-known alkali-catalyzed condensation reactions [38]. Also unexpectedly, the CM of the benzyl hydroxyl group in veratryl alcohol (II) appeared to be a very slow process under the CM conditions used. In addition, the CM of homo-vanillyl alcohol (IV) occurred mainly at the β -hydroxyl group and not at the PhOH unit. Those observations suggested that the CM of the phenolic unit would vary significantly with the nature of the side-chain unit.

Regarding the reactivity of lignin in the CM of wood, we observed that the carboxymethylated wood still contained significant amounts of PhOH units. That was consistent with the lignin model compound reaction; that is, the reactivity of PhOH varied with the nature of the side-chain units. Also, the phenolic units present in the carboxymethylated wood were shown to contain noticeable amounts of the conjugated types as revealed by the UV difference spectra analysis [39]. Because wood lignin in situ is expected to have very few PhOH units



5. Simple lignin model compounds [37].



6. Alkaline degradation of phenolic β -aryl ether unit [9].

of the conjugated type, the presence of those structures has to be generated during the CM process. A major reaction is likely to involve the alkali-catalyzed degradation of the phenolic β -aryl ether unit leading to the generation of the C_6C_2 -enol ether-type structures (**Fig. 6**). The relative reactivity of these different phenolic structures in CM reactions will be discussed further in a separate paper.

CONCLUSIONS

Current results supported the concept that the fractionation of wood polymers could be achieved by in situ CM based on their relative reactivity. Although the initial soluble products formed from a direct CM of wood were mainly a mixture of CMH and CMC containing some CML (3%–5%), the water-insoluble residue after another CM treatment provided a CMC product containing only 1% of residual lignin. Thus, the bulk of wood lignin was less reactive than the cellulose component toward the CM reaction. With those encouraging results, further refinements of the process conditions may lead to a novel process for a direct synthesis of CMC from wood without the involvement of pulping and bleaching operations.

The hemicellulose extraction of wood by the hot-water or dilute-acid treatments had a significant impact on the subsequent CM process. The treated wood containing mainly cellulose and lignin were shown to be more reactive toward the CM reactions, providing a high yield of the water-soluble materials. The content of soluble CML depended considerably on

the extent of the pretreatments and was generally higher for the aspen wood. Although the pretreatment approach has the flexibility to use the extracted hemicelluloses for other applications such as biofuels, both the pretreatment and CM conditions have to be optimized further to improve the quality of the CMC product if a viable process is to be developed. **TJ**

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ABOUT THE AUTHORS

The concept of biorefinery has stimulated much interest in improved use of wood polymers. In researching a subject of fundamental interest with industrial applications, we sought new products or improved processes for making existing products more efficiently. The proposed fractionation process, if successful, would represent a new concept for nearly total utilization of all wood polymers. Our work confirmed the concept that wood can be fractionated in situ by carboxymethylation to yield individual polymers for industrial applications.

Removing small amounts of residual lignin from the cellulose component was challenging, and we are investigating that task further. Interestingly, the bulk of wood lignin was less reactive than the cellulose under the carboxymethylation conditions. The results were very encouraging, and improved fractionation of wood polymers as chemical derivatives can be envisioned in the future. Mills that aim to prepare cellulose derivatives will benefit from a fundamental understanding of the relative reactivity of



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polysaccharides and lignin toward the carboxymethylation reaction. Our next step is to prepare individual products and evaluate their properties and potential applications.

Chien is a doctoral candidate and Amidon and Lai are professors with the Department of Paper and Bioprocess Engineering, SUNY College of Environmental Science and Forestry, Syracuse, NY, USA. Email Lai at yzlai@syr.edu.

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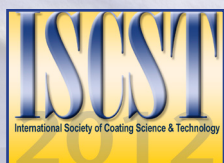
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