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The Effect of the Kraft Pulping Process, Wood Species, and pH on Lignin Recovery from Black Liquor

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Abstract: Lignin has shown a great potential to produce fuels, value-added chemicals, and functional materials due to its high-energy density and intrinsic aromatic-based structure. Yet, the lignin precipitation of different biomasses needs investigation because most of the work has been performed on softwood and much less is known about hardwoods. In fact, the lignin from these two wooden biomasses vary in composition and pulping performance, which can reflect on lignin precipitation. Therefore, the present study investigated the precipitation and composition of 40 distinct kraft lignins obtained from pine, acacia, sweetgum, and eucalyptus black liquors. Two lignin fractions were precipitated at different pHs, according to known industrial lignin separation practices (pH = 9.5 and 2.5) from black liquors taken at different levels of pulping. Overall, lignin recovery increased with increasing lignin concentration in the black liquor, i.e., higher amounts of lignin were obtained at higher levels of delignification. In addition, pine lignins showed superior yields than the hardwoods and were around five times purer. Among the hardwoods, lignin recovery increased with the S–G ratio of the native lignin, and eucalyptus showed the best performance by achieving the highest yields and purities. Finally, the present work compared the lignin recovery yield and the purity of softwood and different hardwood lignins in a systematic way, which will increase awareness of this underutilized green material and could potentially increase the interest in establishing new lignin plants across the globe.

Keywords: lignin precipitation; hardwood kraft lignin; material balance; purity

1. Introduction

Lignin precipitation from kraft black liquor (BL) has been discussed for almost a century; however, the complexity of this wood-based polymer and its variation among species, growth site, and modifications upon processing hinder its understanding and, hence, its utilization. Nevertheless, obtaining lignin from black liquor has been shown to be commercially viable; thus, it is reasonable to expect increasing amounts of kraft lignin to be available in future years at relatively low costs [1].

Softwood lignins have been well characterized and their precipitation behavior is relatively well understood. In addition, the precipitation and properties are not particularly species dependent. On the other hand, the behavior of hardwoods during lignin precipitation is not fully understood; thus, efforts to increase the fundamental knowledge of how pulping impacts hardwood lignin precipitation and its final properties are crucial.

Lignin extraction from BL is an attractive option for pulp mills as it allows for increased production capacity without increasing recovery boiler load [2]. It also enables the industry to become a biorefinery by allowing for the manufacture of multiple products from biomass.

In line with this concept, it has already been shown that 10–15% of the lignin dissolved in BL can be isolated without adversely affecting the chemical recovery [3].

In kraft pulping, sodium hydroxide (NaOH) and sodium sulfide (Na_2S) (white liquor) are applied to wood chips under pressure and high temperatures, targeting lignin hydrolysis/dissolution, and fibers are liberated from the wood via the dissolution of the lignin into the spent liquor. The most common technique for lignin recovery is LignoBoost™, which is based on the dissociation equilibria of the weak acid groups in lignin. Carbon dioxide (CO_2) is dissolved in BL to decrease the pH from ~13 to ~10. A key advantage of using CO_2 is that it does not disturb the balance between sodium (Na) and sulfur (S) in the recovery cycle [4]. The pKa value for the phenolic groups in lignin vary between 6.2 and 11.3, depending on the substitution pattern [5]. Thus, when the pH is reduced to ~10, these groups become protonated, which leads to lignin precipitation.

After precipitation, the solids are separated by filtration and then subsequently re-suspended in water and sulfuric acid (H_2SO_4) at pH ~2.5 to remove impurities [6]. An effective washing step is necessary because precipitated lignin contains high levels of Na^+, which must be washed out and returned to the mill to avoid disturbing the Na–S balance and, hence, requiring an excessive demand for make-up chemicals [4]. Moreover, several final uses for precipitated lignin require a high purity. When the filter cake is re-dispersed at pH and temperature values approximately equal to those of the final washing liquor, the concentration gradients are low. Thus, the change in the pH level and ionic strength, and any change in lignin solubility, take place in the slurry but not in the filter cake or in the filter medium during washing [7]. Another motivation for redispersion is lignin recovery because this step has been shown to improve lignin yield in the range of 6 to 7.5% [4]. The losses experienced in the system without this step are attributed to high pH and strong ionic strength gradients that lead to lignin re-dissolution. The final step in the precipitation process is an additional filtration to obtain solid lignin.

In general, lignin is a complex, racemic, cross-linked, and highly heterogeneous aromatic macromolecule, which is based on three major phenylpropanoids with various degrees of methoxylation (*p*-coumaryl, coniferyl, and sinapyl alcohol) [8]. By repetitive dehydrogenation and cross-coupling, the syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) units are formed in lignin. These structural building blocks are condensed by both ether and carbon–carbon linkages [9]. It is critical to highlight that every lignin is different, and neglecting such a fact leads to non-comparable results and irreproducible material portfolios, which substantially hinder progress toward a commercial lignin-based biorefinery [10].

Softwood native lignins have been reported to contain mostly G units and vary little between species [11,12]. Thus, softwood lignin is much better understood, whereas hardwood native lignins vary greatly between species and have a wide range of syringyl-to-guaiacyl ratios (S–G ratios) [13] within their structures. It has been conclusively shown that pine (softwood) and sweetgum (hardwood) behave very differently during lignin precipitation [14]. Thus, the present investigation aimed to establish a correlative relationship between wood species and subsequent lignin precipitation and lignin quality. Several kraft lignins obtained from four different important species that are used extensively in the global pulp and paper industry were evaluated. In addition, because most of lignin precipitation studies have been performed on pine black liquor samples, this species was treated as the control sample.

2. Experiment

2.1. Material

Pine (*Pinus taeda*), a softwood, and three hardwoods, acacia (*Acacia mangium*), sweetgum (*Liquidambar styraciflua*), and eucalyptus (*Eucalyptus globulus*), were investigated in the present study. The pine and sweetgum samples were obtained from the southern United States, whereas the acacia and eucalyptus were obtained from Taiwan and Chile, respectively. Wood logs were chipped in a lab chipper. The resulting chips were then screened according to the standard method "size distribution" (SCAN-CM 40:01, 2001).

2.2. Methods

2.2.1. Kraft Pulping

Batch cooks were carried out using 1000 g o.d. chips in a 10 L laboratory pulping digester (Greenwood Instruments, LLC; Andover, MA, USA). The digester was equipped with a temperature controller, liquor recirculation piping, and an indirect heating system. A liquor-to-wood ratio of 4:1 was applied for all cooks. The active alkali (AA) (such as Na_2O) for pine was 19% and 16% for hardwoods on oven dried (o.d.) wood. The sulfidity was 25% for all cooks, the temperature applied for the pine cooks was 170 °C and 160 °C for the hardwood cooks. Pulped chips were washed thoroughly with water, screened using a 150 mesh screen, and disintegrated. The pulp was subsenquetely centrifuged to ~30% consistency and stored in polyethylene bags for posterior characterization. The pulp yield was gravimetrically determined. The black liquor generated was characterized according to the protocols described by "solids content of black liquor" (TAPPI/ANSI T650 om-15) and "residual effective alkali" (REA) (SCAN-N 33:94). The black liquor samples were also stored in sealed Nalgene bottles for lignin precipitation.

Cooks were performed for 30, 60, 90, 120, and 150 min to obtain different levels of delignification. It is important to mention that the timing refers to the total cooking time and not the time at temperature. Overall, the target temperature was achieved ~30–40 min after the start of the cook. In total, five pulp samples and five black liquor samples were produced from each wood species.

2.2.2. Lignin Precipitation

Lignin precipitation was carried out at room temperature, atmospheric pressure, and constant slow stirring. A schematic representation of the precipitation and purification steps is shown in Figure 1.
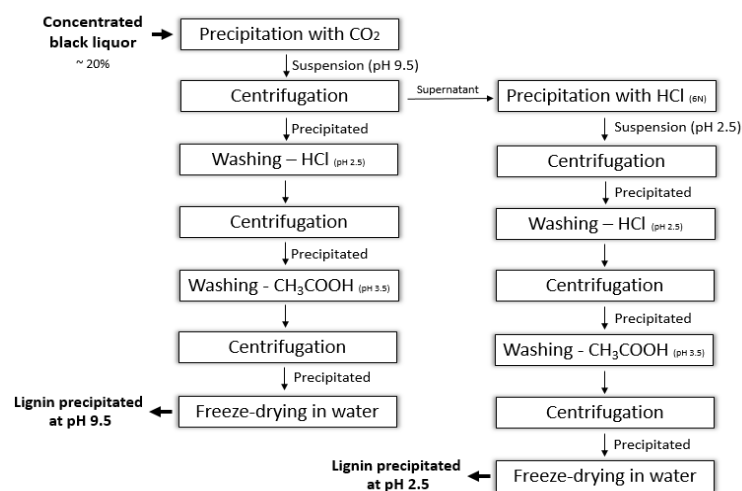
Figure 1. Protocol for lignin precipitation of two lignin fractions (at pH 9.5 and at pH 2.5) from kraft black liquor [14].

The generated black liquor samples were filtered through Whatman #3 filter paper to remove fines, then evaporated to a solids content of ~20% and subjected to precipitation experiments of two lignin fractions (pH 9.5 and 2.5). CO_2 was sparged into concentrated black liquors at a low flow rate to attain pH 9.5 and was then allowed to equilibrate for 30 min. The precipitated solids were obtained via centrifugation and the supernatants were stored for further precipitation. The solids were washed with hydrochloric acid (HCl) solution at pH 2.5 to remove ash and were subsequently washed with acetic acid at pH 3.5 to remove residual HCl. After the washing steps, the solids were obtained via centrifugation, suspended in deionized water, and freeze-dried. The freeze-dried solids,

called lignin fraction at pH 9.5, were obtained according to commercially known lignin isolation protocols (e.g., LignoBoost™).

The supernatants obtained after carbonation were further acidified with 6N HCl to pH 2.5 in order to precipitate a second lignin fraction, which was similarly washed with HCl and acetic acid and then freeze-dried. This second lignin fraction was obtained with the understanding that most of the theremaining lignin in the solution would be precipitated at pH 2.5.

The experimental conditions were kept constant for all precipitation experiments to establish a fair comparison between the behaviors of all lignin samples that were investigated.

2.2.3. Characterization of Wood, Pulp, and Precipitated Lignin

The wood samples were prepared by grinding them in a Wiley mill and then screening the resulting milled wood. The fraction passing through a 40-mesh screen and retained on a 60-mesh screen was collected for analyses. Subsequently, the milled wood was extracted in a Soxhlet apparatus for 6 h using a benzene–ethanol mixture (2:1 v/v ratio) (TAPPI standard test method T 264 cm-07 "preparation of wood for chemical analysis"). Carbohydrates and lignin contents were quantified according to the Technical Report NREL/TP-510-42618 Determination of structural carbohydrates and lignin in biomass. Ash content was measured according to "Ash in wood, pulp, paper and paperboard: combustion at 525 °C" (TAPPI standard test method T 211 om-16). The same procedures were applied to the characterization of the lignin samples precipitated from the black liquors.

The syringaldehyde–vanillin (Sr–V) ratio of the native lignins was determined according to the alkaline nitrobenzene oxidation (NBO) procedure reported in the literature [15,16]. As nitrobenzene oxidation accounts for only uncondensed structures, the equation below was used to obtain an accurate S–G ratio. This method was developed using a calibration line established by the S–V ratio that was obtained via nitrobenzene oxidation and the S–G ratio that was obtained via ^{13}C NMR of several milled wood lignins (MWLs) [13].

$$S/G = 0.806 \times Sr/V \tag{1}$$

2.2.4. Material Balance

The characterization of the wood, pulp, and lignin samples, as well as the determination of pulp yield and inorganics added into the process via the white liquor, allowed for a material balance. Solid and liquid mass flows were measured and used to determine the lignin yield for each of the precipitation experiments. The characterization of wood and pulps also allowed for an estimation of the composition of the black liquor used for the lignin precipitation experiments.

3. Results and Discussion

3.1. Kraft Pulping

Pine, acacia, sweetgum, and eucalyptus chips were subjected to standard batch kraft pulping conditions. This process generates pulp and a residual process stream (BL) that is rich in organic degradation products (lignin and carbohydrates) and spent inorganics. All four wood species were pulped at different levels of intensity (30, 60, 90, 120, and 150 min), the results for which are shown in Table 1.

Overall, longer cooks (higher H-factor) yielded less pulp and the black liquor samples showed lower REA levels and higher solid contents, which was expected. Throughout the pulping process, alkali was consumed in the reactions with lignin, in the dissolution of carbohydrates, in neutralizing various organic acids both present in the original wood and produced during pulping, by the wood extractives, and to some extent, by adsorption on the fibers [17], which decreased the REA. In commercial cooks, the REA is maintained at or above a certain threshold to ensure that the lignin is dissolved. Moreover, the dissolution of the degradation products is followed by an increase in the solids content of the BL. After 150 min of pulping, pine showed the lowest final pulp yield (43.5%), which is

reasonable because much harsher conditions were applied to this species. When considering only the hardwoods, acacia showed the highest pulp yield (56.4%), whereas sweetgum and eucalyptus showed similar values (~48%). Note that, at all levels of pulping, the REA for acacia was the highest among all four wood species, which could be attributed to its composition. Additionally, acacia has been shown to be harder to pulp in other investigations, mainly due to its high lignin content and lignin chemistry [18,19].

Table 1. The H-factor, pulp yield, residual effective alkali (REA), and solids content of black liquor for pine, acacia, sweetgum, and eucalyptus.

Species	Parameter	Cook Time (min)				
		30	60	90	120	150
Pine	H-factor	7	32	503	983	1400
	Pulp yield, %	93.2	69.1	51.4	47.4	43.5
	REA, g/L as Na_2O	19.2	17.0	11.5	10.0	5.9
	Solids in BL, %	11.1	13.8	16.6	17.3	16.6
Acacia	H-factor	0	19	227	469	688
	Pulp yield, %	91.3	74.9	66.1	62.5	56.4
	REA, g/L as Na_2O	26.4	17.3	11.8	8.9	7.3
	Solids in BL, %	9.0	11.1	12.8	13.6	13.8
Sweetgum	H-factor	0	51	273	487	650
	Pulp yield, %	85.5	62.6	50.7	48.7	47.6
	REA, g/L as Na_2O	20.5	12.5	9.0	4.7	3.5
	Solids in BL, %	8.9	12.1	14.1	14.4	14.4
Eucalyptus	H-factor	0	15	216	442	648
	Pulp yield, %	93.8	67.6	52.0	48.7	48.1
	REA, g/L as Na_2O	24.5	14.5	8.1	5.8	5.0
	Solids in BL, %	9.0	11.0	13.4	14.3	14.7

3.2. Composition of Wood and Pulps Produced

Extractive-free wood chips and pulps were characterized for lignin and carbohydrate contents, as shown in Table 2. The values for the pulps obtained after 30, 60, 90, 120, and 150 min depict the residual content after the pulping of 100 g (o.d.) of wood (wood basis).

Table 2. The composition analysis of pine, acacia, sweetgum, and eucalyptus wood chips and pulps.

Species	Compound	Sample/Cook Time (min)					
		Wood *	30	60	90	120	150
Pine	Glucan, g	40.0	38.7	36.1	35.1	35.4	32.8
	Total Lignin, g	31.7	28.7	19.2	6.7	3.9	3.3
	Xylan, g	6.1	5.8	4.9	3.6	3.5	3.4
	Galac + Man + Arab, g	19.7	16.9	7.8	7.3	5.9	5.3
Acacia	Glucan, g	42.7	41.7	40.5	40.4	40.3	39.5
	Total Lignin, g	27.9	25.1	20.1	8.1	6.1	4.1
	Xylan, g	10.0	8.6	8.1	7.2	7.3	6.7
	Galac + Man + Arab, g	1.3	1.0	0.6	0.5	0.0	0.0
Sweetgum	Glucan, g	45.2	39.6	36.4	33.8	33.8	33.5
	Total Lignin, g	25.9	21.6	10.8	2.9	1.4	1.2
	Xylan, g	14.8	12.3	9.9	8.7	8.5	8.6
	Galac + Man + Arab, g	6.3	5.2	3.0	2.4	2.6	3.0
Eucalyptus	Glucan, g	44.6	41.9	31.9	31.7	30.6	30.4
	Total Lignin, g	24.8	24.5	13.8	3.0	1.7	1.1
	Xylan, g	13.1	11.2	7.5	7.8	7.0	7.4
	Galac + Man + Arab, g	4.0	3.4	1.3	0.9	0.5	0.5

Where: galac is galactan; man is mannan; and arab is arabinan. * Content in 100 g (o.d.) (wood basis).

Pine and acacia wood chips displayed the lowest contents of carbohydrates and the highest contents of lignin. Thus, it can be speculated that these two wood species are good candidates for lignin precipitation because, throughout pulping, there is more lignin to be dissolved in the black liquor. Even though sweetgum and eucalyptus wood chips displayed lower lignin contents, they could also be considered suitable for lignin precipitation because most of the lignin was removed over the course of pulping. After 150 min, the residual lignin content was 1.1 g for eucalyptus and 1.2 g for sweetgum, whereas for pine and acacia, it was 3.3 g and 4.1 g, respectively.

Besides lignin content, the S–G ratio of the lignin was also determined, the results of which are shown in Table 3. Note that pine lignin is not listed because S is not one of the lignin building blocks in this species. This ratio was investigated because it is a key factor affecting the delignification rate of hardwoods during kraft pulping [18]. A lignin with high S content has a higher proportion of ether linkages because the C_5-position in this unit is blocked by a methoxyl group. Therefore, species with high S–G ratios are easier to pulp [20] because ether bonds are more easily ruptured than C–C bonds.

Table 3. The Sr–V and S–G ratios of acacia, sweetgum, and eucalyptus.

Species	Sr–V Ratio	S–G Ratio
Acacia	1.2	1.0
Sweetgum	2.8	2.3
Eucalyptus	4.5	3.6

In NBO, the moieties of the three lignin building units of *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) were degraded into *p*-hydroxybenzaldehyde (B), vanillin (V), and syringaldehyde (Sr) and then, in addition to a small amount of their corresponding acids, *p*-hydroxybenzoic acid (Ba), vanillic acid (Va), and syringic acid (Sa), respectively [17]. As NBO only quantifies uncondensed structures, an equation was used to obtain an accurate S–G ratio. Note that the highest S–G ratio was observed for eucalyptus, followed by sweetgum and acacia. This reinforces the effect of the S–G ratio on the kraft pulping process because acacia (S–G ratio = 1.0) was much more difficult to pulp than the other hardwoods. In addition, acacia showed similar behavior to pine throughout the pulping process, to which harsher pulping conditions were applied because of the higher lignin G unit content.

Figure 2 depicts the degradation curves for the wood compounds throughout pulping for all four wood species that were studied, including the delignification curves. Pulping undergoes three distinct phases as wood chips are cooked into pulp. The phases are classically referred to as initial, bulk, and residual [21]. Most of the lignin is removed over the initial and bulk phases whereas the residual phase is the much less selective part of pulping, in which very low levels of lignin are removed. This trend is observed independently of wood species, lignin content, and lignin type [22]. Note that most of the delignification for all four wood species took place up to 90–120 min.

The eucalyptus delignification took place at a faster rate than sweetgum, which was anticipated given its higher S–G ratio. However, we expected a more pronounced difference because of the significant S–G ratio difference. A possible explanation for this observation is wood chip porosity. It has been reported that *E. globulus* shows a vessel percentage of 8.5% and a vessel diameter average of 127.3 μm, whereas the vessel percentage and vessel diameter average for sweetgum are 35.9% and 54.6 μm, respectively [18]. It is likely that the higher porosity that is observed in sweetgum facilitated liquor impregnation and, consequently, enhanced pulpability. It is important to mention that alkaline pulping is complex and is affected by several factors, such as the morphological characteristics of the wood, location of lignin in the woody tissue, penetration pathway of the chemicals, swelling or thermal coalescence of the lignin-containing interface, cleavage of lignin–carbohydrate bonds, chemical degradation of the lignin macromolecule, condensation reactions, stabilization of the degradation products via solvation and by means of electrostatic forces, the

removal of degradation products from the reaction zone, and undesirable carbohydrates degradation reactions [17].
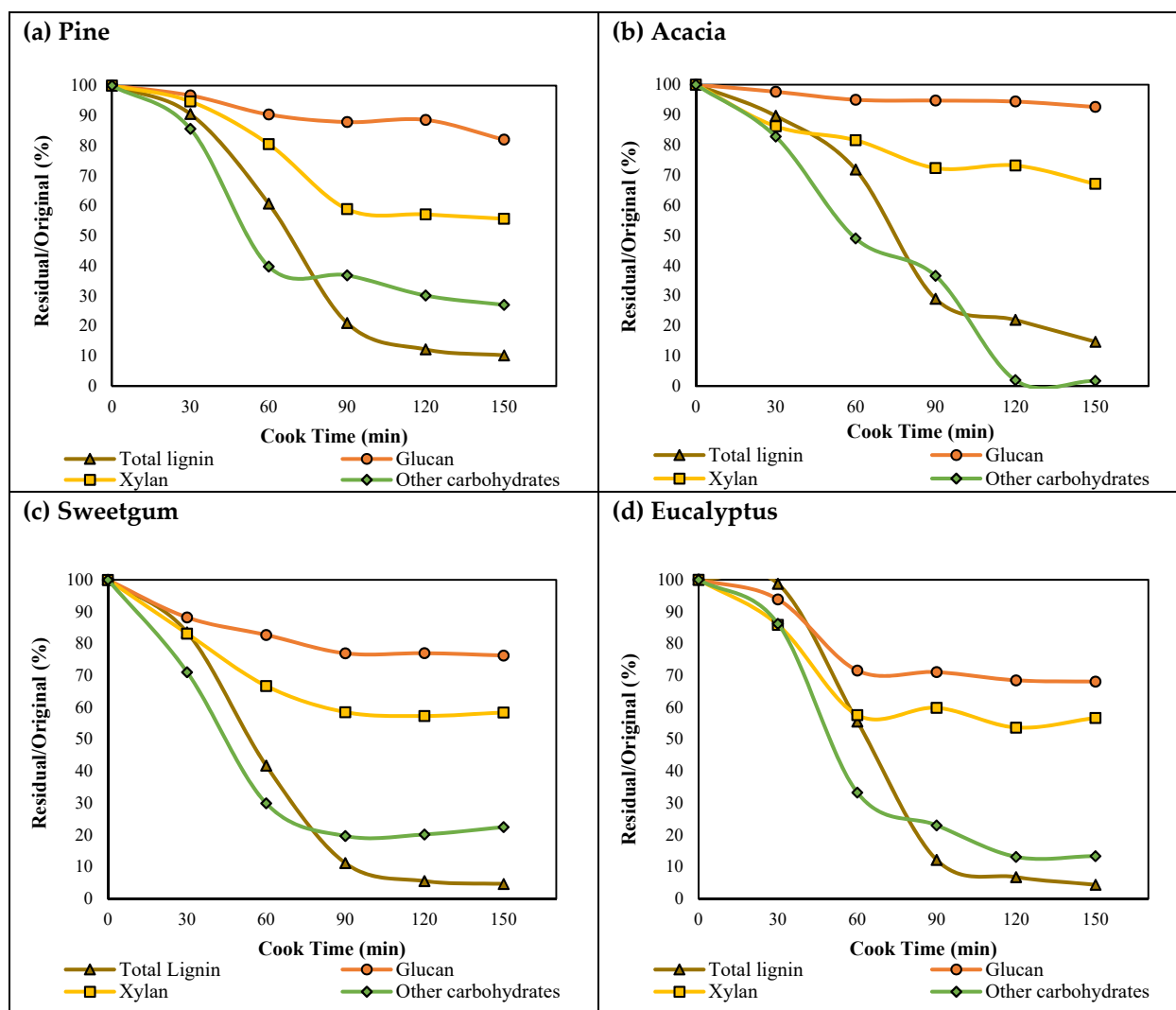

Figure 2. The lignin and carbohydrate degradation curves for (**a**) pine, (**b**) acacia, (**c**) sweetgum, and (**d**) eucalyptus.

As the kraft pulping process is designed to promote the removal of lignin and retain carbohydrates, the former are more degraded than the latter. The degradation profiles were explored in this study. Within the carbohydrates, glucan and xylan were more resistant to pulping, while galactan, mannan, and arabinan were more easily degraded. The great resistance of cellulose to degradation can be attributed to its crystallinity and high degree of polymerization. The resistance of xylans to pulping is due to the presence of the side group known as 4-*O*-methyl-α-D-glucuronic acid (MeGlcA), which protects the oligosaccharide structure against reducing endgroup hydrolyses reactions, referred to as peeling [23]. Additionally, the other hemicelluloses with lower molecular weights and more accessible chemical structures are more easily hydrolyzed and dissolved in the black liquor.

Moreover, xylan is the main hemicellulose in hardwoods, whereas glucomannan is the main hemicellulose in softwoods. Given the reduced resistance of glucomannan to pulping, a greater loss of this wood compound is observed for pine. For instance, after 90 min of pulping, 19.8 g of carbohydrates were lost for pine, in which 4.9 g were from cellulose and 14.9 g from hemicelluloses. Note that for eucalyptus, 23.6 g of carbohydrates

were lost at this level of pulping, where 14.0 g were from cellulose and only 9.6 g were from hemicelluloses.

After every cook, the BL was collected and filtered and the solids contents were adjusted to 20%. Subsequently, the BL samples were acidified to obtain two lignin fractions: one at pH 9.5, where the acidifying agent was CO_2, and another at pH 2.5, where the acidifying agent was HCl. Both fractions were precipitated from the same BL sample, which was performed with the objective of characterizing most of the dissolved lignin. The protonation of the phenolic groups during carbonation allowed for precipitation of the lignin fraction at pH 9.5. When the pH was further acidified to 2.5, the carboxylic groups in lignin were also protonated (pK_a 3 to 5), leading to the precipitation of a final lignin fraction. Thus, once the pH was lowered to 2.5, an increase in lignin recovery yield was observed.

The content of lignin dissolved at all levels of pulping, the total solids isolated in every precipitation experiment, and the characterization of the solids precipitated are shown in Table 4.

Note that the amount of lignin dissolved in the black liquor was calculated from the difference between the lignin content in the wood and the residual content of lignin in the pulp at a given pulping level. The lignin content in 100 o.d. grams of pine wood chips was 31.7 g and the residual content in the pulp was 3.3 g after 150 min of pulping; thus, the total amount of lignin dissolved in the black liquor was 28.4 g. Looking at the hardwoods, the total amount of lignin dissolved into the black liquor per 100 o.d. grams of chips, also after 150 min of pulping, was found to be 23.1 g for acacia, 24.7 g for sweetgum, and 23.7 g for eucalyptus. Considering only the lignin concentration in the BL, these results suggest that sweetgum would be the best candidate for lignin precipitation as it produces the highest concentration, followed by eucalyptus and acacia.

The total solids precipitated value, also shown in Table 4, represents the mass of material obtained after every precipitation experiment. For pine at 150 min, the total solids precipitated at pH 9.5 was 21.0 g, out of which 19.4 g was lignin, 0.4 g was carbohydrates, and 0.5 g was inorganics (ash). For the precipitation of the second lignin fraction (pH 2.5), the content of lignin in the black liquor was 9.0 g and the total solids precipitated was 7.1 g, out of which 6.4 g was lignin, 0.2 g was carbohydrates, and 0.1 g was ash. Note that the solids precipitated also contain other degradation products that were not determined, such as organic acids, extractives, and volatile compounds.

After 30 and 60 min of pulping, very little lignin was obtained for all four wood species, while the recovery significantly increased with the intensity of pulping, i.e., the lignin recovery increased with lignin concentration. In low lignin concentrations (at the onset of kraft pulping), the lignin macromolecules are surrounded by significantly more water molecules than in high lignin concentrations, which may influence lignin interactions/agglomerations [24] and, hence, precipitation.

Moreover, before the target pulping temperature at 30 min was reached, the amount of lignin recovered at pH 2.5 was higher than at pH 9.5 for all wood species that were studied. This can be attributed to the fact that mainly low molecular weight lignin is removed during the initial phase of delignification and that the lower molecular weight lignins are precipitated at lower pHs [14,25]. Overall, as pulping proceeds, larger lignin fractions are removed and condensation reactions take place, leading to an increase in the molecular weight. Thus, more lignin is recovered at pH 9.5 than at pH 2.5.

Figure 3 depicts the lignin precipitation yields at the two different pHs and the lignin-to-carbohydrate ratio (L–C ratio) of the solids precipitated, also at both pHs, as a function of the pulping level for all four wood species.

Hardwood lignins showed much lower L–C ratios than pine, regardless of the pH and pulping level. It is reasonable to assume that the presence of lignin–carbohydrate complexes (LCCs) and/or lignin association in hardwoods led to the co-precipitation of carbohydrates with lignin. In addition, the structure of lignin that is linked to xylan is different than lignin that is linked to glucomannan [26], because the glucomannan–lignin

seems to contain more condensed bonds and lower contents of β-O-4 bonds than the xylan–lignin [27]. Thus, it has been suggested that the higher content of xylan and β-O-4 bonds in hardwoods may lead to a higher content of LCCs [26].

The physical interactions between lignin and carbohydrates in the cell walls have not been fully understood. However, it has been shown that the number of physical contacts with carbohydrates correlates with the number of methoxyl groups in lignin and decreases in the order: S > G > H [28]. Thus, this physical contact is more significant in hardwoods than softwoods, which are primarily composed of G units.

Table 4. The material balance of lignin precipitation from pine, acacia, sweetgum, and eucalyptus black liquors (BL) [a].

Species	pH	Parameter	Sample / Cook Time (min)				
			30	60	90	120	150
Pine	9.5	Lignin in the BL	3.0	12.4	25.0	27.8	28.4
		TS [b] precipitated	0.4	4.6	6.9	19.4	21.0
		Total lignin	0.3	4.3	6.4	16.4	19.4
		Carbohydrates	0.0	0.0	0.2	0.5	0.4
		Ash	0.0	0.1	0.1	0.4	0.5
Pine	2.5	Lignin in the BL	2.7	8.1	18.6	11.4	9.0
		TS [b] precipitated	1.2	3.0	16.9	9.0	7.1
		Total lignin	1.0	2.6	13.9	7.6	6.4
		Carbohydrates	0.0	0.1	0.6	0.3	0.2
		Ash	0.0	0.0	0.2	0.1	0.1
Acacia	9.5	Lignin in the BL	2.8	8.4	19.3	21.1	23.1
		TS [b] precipitated	0.2	2.3	5.2	0.9	0.8
		Total lignin	0.1	1.8	4.3	0.4	0.3
		Carbohydrates	0.1	0.3	0.4	0.4	0.3
		Ash	0.0	0.0	0.0	0.0	0.0
Acacia	2.5	Lignin in the BL	2.8	6.6	14.9	20.8	22.7
		TS [b] precipitated	0.5	2.0	8.3	17.7	20.5
		Total lignin	0.4	1.8	7.2	15.8	18.7
		Carbohydrates	0.0	0.1	0.6	0.8	0.8
		Ash	0.0	0.1	0.1	0.4	0.2
Sweetgum	9.5	Lignin in the BL	4.3	15.1	23.0	24.5	24.7
		TS [b] precipitated	0.6	5.5	12.4	14.7	12.3
		Total lignin	0.1	3.1	9.0	10.9	9.4
		Carbohydrates	0.4	1.7	2.0	2.1	1.6
		Ash	0.0	0.1	0.3	0.3	0.3
Sweetgum	2.5	Lignin in the BL	4.2	12.0	14.0	13.5	15.3
		TS [b] precipitated	0.8	4.2	3.6	4.4	8.4
		Total lignin	0.3	3.2	3.2	4.0	7.8
		Carbohydrates	0.3	0.4	0.2	0.2	0.4
		Ash	0.0	0.0	0.0	0.0	0.1
Eucalyptus	9.5	Lignin in the BL	0.2	9.8	19.1	20.0	20.6
		TS [b] precipitated	0.0	2.5	9.8	13.5	13.6
		Total lignin	0.0	1.7	7.9	11.3	11.6
		Carbohydrates	0.0	0.5	1.1	1.4	1.3
		Ash	0.0	0.0	0.2	0.2	0.2
Eucalyptus	2.5	Lignin in the BL	0.1	8.1	11.2	8.7	9.0
		TS [b] precipitated	0.0	1.2	4.2	5.2	5.9
		Total lignin	0.0	1.0	3.5	4.7	5.4
		Carbohydrates	0.1	0.1	0.3	0.3	0.3
		Ash	0.0	0.0	0.0	0.0	0.0

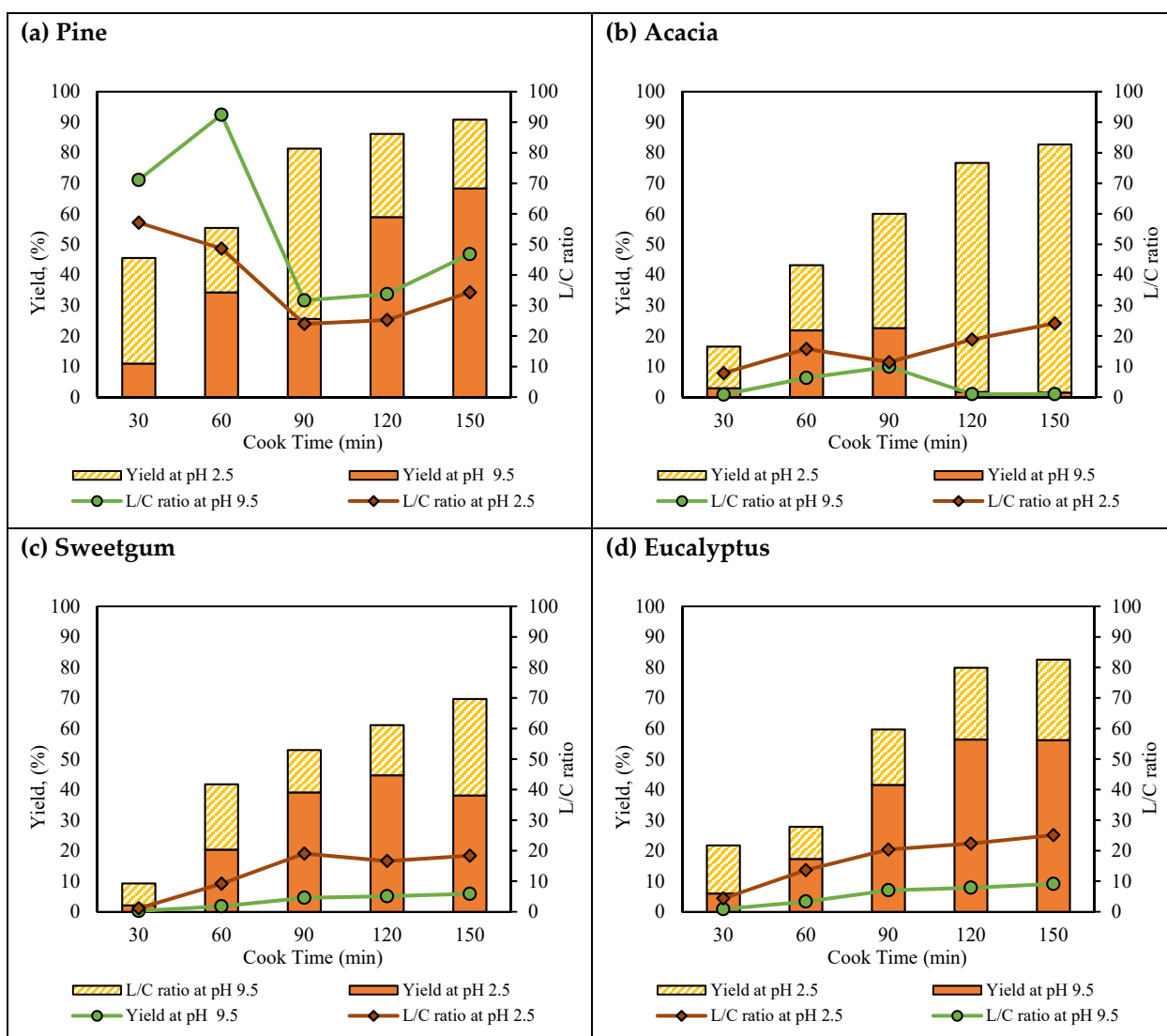[a] Values in g (wood basis). [b] Total solids.

Figure 3. The lignin precipitations yield and L–C ratios as a function of the pulping level for (**a**) pine, (**b**) acacia, (**c**) sweetgum, and (**d**) eucalyptus. Where L–C is the lignin-to-carbohydrate ratio in the solids precipitated.

Another study has shown that the S–G ratio and lignin content influence LCC content [29]. The research revealed that, for samples with similar S–G ratios, the level of LCCs increased with increasing lignin content, and for samples with similar lignin contents, the level of LCCs increased with increasing S–G ratios. In the present investigation, a clear relationship was not observed between the L–C ratio and lignin content nor between the S–G ratio and lignin.

Finally, acacia lignins showed a unique behavior in the precipitation experiments relative to the other three species. Very little amounts of lignin were precipitated at pH 9.5 at high pulping levels (120 and 150 min), whereas for the other species, most of the lignin was obtained at this pH. The explanation for such a discrepancy cannot yet be determined. Thus, a more rigorous characterization of the chemical structure of these lignins is recommended.

Additionally, improved elucidation via the determination of molecular weight, functional groups, and other chemicals structures would greatly contribute to the understanding of this biomaterial and, hence, amplify the utilization of lignin as a green material. For instance, the linkage or association between lignin and carbohydrates should be further investigated. Even though LCCs are suggested to display recalcitrance during biomass

processing and fractionation [30], LCCs have been associated with important properties relating to antiviral, antioxidant, and antitumoral activities [31,32]. Such functionalities, however, are more likely due to the co-preservation of moieties, such as lignin and carbohydrates, rather than the LCCs themselves [33].

4. Conclusions

- Lignin precipitation from pine, acacia, sweetgum, and eucalyptus black liquor samples were investigated, and it was shown that the lignin content in the black liquor and the subsequent recovery increased with pulping level. In the initial phase, the total lignin recovery ranged from ~9 to 55%, while in the later phase, the total lignin recovery varied from ~61 to 91%, depending on the species and pH. The increased lignin recovery was due to the increasing lignin concentration toward the end of pulping.
- Softwood showed higher lignin recovery and lower contamination with carbohydrates than the hardwoods, regardless of pH and pulping intensity.
- Hardwood lignin recovery was affected bythe S–G ratio, which resulted in higher yields at pH 9.5 with the increasing S–G ratio.
- Overall, more lignin was precipitated at pH 9.5 than at pH 2.5. However, lignin precipitation at pHs lower than 9.5 should be taken into consideration for samples that achieve low recovery yields. The precipitation of the lignin fraction at pH 2.5 contributed a ~7 to 81% recovery increase, depending on the pulping level, S–G ratio, and species.
- Acacia lignins, which have the lowest S–G ratio amongst the hardwoods, behaved very differently from the other species that were investigated, and the reasons for this are not yet fully understood. The further characterization of all lignins obtained herein will be performed using different spectroscopy and chromatography techniques, which will likely further amplify the lignin characteristics that account for such discrepancies.

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References

1. Hubbe, M.; Alén, R.; Paleologou, M.; Kannangara, M.; Kihlman, J. Lignin recovery from spent alkaline pulping liquors using acidification, membrane separation, and related processing steps: A review. *Bioresources* **2019**, *14*, 2300–2351. [CrossRef]
2. Wallmo, H.; Richards, T.; Theliander, H. Lignin precipitation from kraft black liquors: Kinetics and carbon dioxide absorption. *Pap. Ja Puu Pap. Timber* **2007**, *89*, 436–442.
3. Hu, Z.; Du, X.; Liu, J.; Chang, H.-M.; Jameel, H. Structural Characterization of Pine Kraft Lignin: BioChoice Lignin vs Indulin AT. *J. Wood Chem. Technol.* **2016**, *36*, 432–446. [CrossRef]
4. Öhman, F.; Wallmo, H.; Theliander, H. A novel method for washing lignin precipitated from kraft black liquor–Laboratory trials. *Nord. Pulp Pap. Res. J.* **2007**, *22*, 9–16. [CrossRef]
5. Ragnar, M.; Lindgren, C.T.; Nilvebrant, N.-O. pKa-Values of Guaiacyl and Syringyl Phenols Related to Lignin. *J. Wood Chem. Technol.* **2000**, *20*, 277–305. [CrossRef]
6. Wallmo, H.; Littorin, A.; Karlsson, H.; Lindholm, K.; Stern, R.; Christiansen, G. The Evolution of LignoBoost Technology and the Lignin BioProducts Market, Part 2. In Proceedings of the 2016 International Bioenergy and Bioproducts Conference Proceedings, Jacksonville, FL, USA, 28–30 September 2016.
7. Tomani, P. The lignoboost process. *Cellul. Chem. Technol.* **2010**, *44*, 53–58.
8. Fengel, D.; Gerd, W. *Wood: Chemistry, Ultrastructure, Reactions*; Walter de Gruyter: Berlin, Germany, 1984; ISBN 978-3-11-008481-8.
9. Alén, R. Structure and chemical composition of wood. In *Forest Products Chemistry*; Stenius, P., Ed.; Fapet Oy: Helsinki, Finland, 2000; pp. 11–57.

10. Schlee, P.; Hosseinaei, O.; Baker, D.; Landmér, A.; Tomani, P.; Mostazo-López, M.J.; Cazorla-Amorós, D.; Herou, S.; Titirici, M.-M. From Waste to Wealth: From Kraft Lignin to Free-standing Supercapacitors. *Carbon* **2019**, *145*, 470–480. [CrossRef]

11. Akiyama, T.; Goto, H.; Nawawi, D.S.; Syafii, W.; Matsumoto, Y.; Meshitsuka, G. Erythro/threo ratio of β-O-4-5 structures as an important structural characteristic of lignin. Part 4: Variation in the erythro/threo ratio in softwood and hardwood lignins and its relation to syringyl/guaiacyl ratio. *Holzforschung* **2005**, *59*, 276–281. [CrossRef]

12. Sarkanen, K.V.; Chang, H.M.; Allan, G.G. Species variation in lignins III. *TAPPI J.* **1967**, *50*, 587.

13. Santos, R.B.; Capanema, E.A.; Balakshin, M.Y.; Chang, H.-M.; Jameel, H. Lignin Structural Variation in Hardwood Species. *J. Agric. Food Chem.* **2012**, *60*, 4923–4930. [CrossRef]

14. Jardim, J.M.; Hart, P.W.; Lucia, L.; Jameel, H.; Chang, H. A quantitative comparison of the precipitation behavior of lignin from sweetgum and pine kraft black liquors. *Bioresources* **2020**, *15*, 1–18. [CrossRef]

15. Chen, C.L. Nitrobenzene and cupric oxide oxidations. In *Methods in Lignin Chemistry*; Springer: Berlin/Heidelberg, Germany, 1992; pp. 301–321.

16. Min, D.; Xiang, Z.; Liu, J.; Jameel, H.; Chiang, V.; Jin, Y.; Chang, H.-M. Improved Protocol for Alkaline Nitrobenzene Oxidation of Woody and Non-Woody Biomass. *J. Wood Chem. Technol.* **2014**, *35*, 52–61. [CrossRef]

17. Marton, J. Reactions in alkaline pulping. In *Lignins: Occurrence, Formation, Structure and Reactions*; Sarkanen, K.V., Ludwig, C., Eds.; Wiley Interscience: New York, NY, USA, 1971; pp. 639–694.

18. Santos, R.B.; Capanema, E.A.; Balakshin, M.K.; Chang, H.; Jameel, H. Effect of hardwoods characteristics on kraft pulping process: Emphasis on lignin structure. *BioResources* **2011**, *6*, 3623–3637.

19. Almeida, D.; Santos, R.B.; Hart, P.W.; Jameel, H. Hardwood pulping kinetics of bulk and residual phases. *TAPPI J.* **2015**, *14*, 652–662. [CrossRef]

20. Santos, R.B.; Hart, P.; Jameel, H.; Chang, H.-M. Wood Based Lignin Reactions Important to the Biorefinery and Pulp and Paper Industries. *Bioresources* **2012**, *8*, 1456–1477. [CrossRef]

21. Santos, R.B.; Jameel, H.; Chang, H.-M.; Hart, P.W. Impact of lignin and carbohydrate chemical structures on kraft pulping processes and biofuel production. *TAPPI J.* **2013**, *12*, 23–31. [CrossRef]

22. Theliander, H. Recovery of Cooking Chemicals: The Treatment and Burning of Black Liquor. In *Pulping Chemistry and Technology*; Volume 2; Ek, M., Gellerstedt, G., Henriksson, G., Eds.; Walter de Gruyter: Berlin, Germany, 2009; pp. 297–334, ISBN 9783110213416.

23. Magaton, A.S.; Colodette, J.L.; Piló-Veloso, D.; Gomide, J.L. Behavior of Eucalyptus Wood Xylans across Kraft Cooking. *J. Wood Chem. Technol.* **2011**, *31*, 58–72. [CrossRef]

24. Helander, M.; Mattsson, T.; Theliander, H.; Lindström, M.E. Parameters Affecting the Cross-Flow Filtration of Dissolved LignoBoost Kraft Lignin. *J. Wood Chem. Technol.* **2015**, *36*, 1–8. [CrossRef]

25. Jardim, J.M.; Hart, P.W.; Lucia, L.; Jameel, H. Probing the molecular weights of sweetgum and pine kraft lignin fractions. *TAPPI J.* **2021**, *20*, 381–391. [CrossRef]

26. Aminzadeh, S.; Zhang, L.; Henriksson, G. A possible explanation for the structural inhomogeneity of lignin in LCC networks. *Wood Sci. Technol.* **2017**, *51*, 1365–1376. [CrossRef]

27. Lawoko, M.; Henriksson, A.G.; Gellerstedt, G. Structural Differences between the Lignin−Carbohydrate Complexes Present in Wood and in Chemical Pulps. *Biomacromolecules* **2005**, *6*, 3467–3473. [CrossRef] [PubMed]

28. Kang, X.; Kirui, A.; Widanage, M.C.D.; Mentink-Vigier, F.; Cosgrove, D.J.; Wang, T. Lignin-polysaccharide interactions in plant secondary cell walls revealed by solid-state NMR. *Nat. Commun.* **2019**, *10*, 347. [CrossRef]

29. Min, D.-Y.; Yang, C.; Chiang, V.; Jameel, H.; Chang, H.-M. The influence of lignin–carbohydrate complexes on the cellulase-mediated saccharification II: Transgenic hybrid poplars (*Populus nigra* L. and *Populus maximowiczii A.*). *Fuel* **2014**, *116*, 56–62. [CrossRef]

30. Giummarella, N.; Pu, Y.; Ragauskas, A.J.; Lawoko, M. A critical review on the analysis of lignin carbohydrate bonds. *Green Chem.* **2019**, *21*, 1573–1595. [CrossRef]

31. Zhang, Y.; Wang, S.; Xu, W.; Cheng, F.; Pranovich, A.; Smeds, A.I.; Willför, S.M.; Xu, C. Valorization of Lignin–Carbohydrate Complexes from Hydrolysates of Norway Spruce: Efficient Separation, Structural Characterization, and Antioxidant Activity. *ACS Sustain. Chem. Eng.* **2019**, *7*, 1447–1456. [CrossRef]

32. Sakagami, H.; Hashimoto, K.; Suzuki, F.; Ogiwara, T.; Satoh, K.; Ito, H.; Hatano, T.; Takashi, Y.; Fujisawa, S.-I. Molecular requirements of lignin–carbohydrate complexes for expression of unique biological activities. *Phytochemistry* **2005**, *66*, 2108–2120. [CrossRef]

33. De Carvalho, D.M.; Lahtinen, M.H.; Lawoko, M.; Mikkonen, K. Enrichment and Identification of Lignin–Carbohydrate Complexes in Softwood Extract. *ACS Sustain. Chem. Eng.* **2020**, *8*, 11795–11804. [CrossRef]