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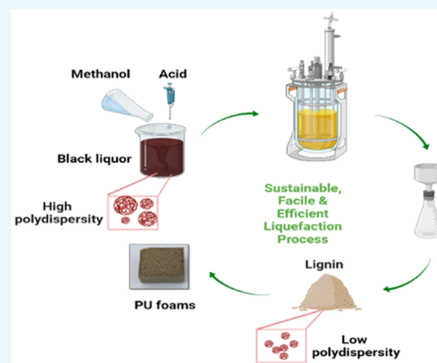
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ABSTRACT: An effective method that can produce a large amount of Kraft lignin with improved homogeneity is strongly desired for Kraft lignin's high-value applications and scientific advancements. Herein, a one-pot acid-catalyzed liquefaction method was developed to recover Kraft lignin directly from black liquor. The recovery rate and properties of the recovered lignin were affected by the reaction time, reaction temperature, moisture content (MC), pH, and acid categories. The highest lignin recovery rate of 75% was achieved when the concentrated black liquor (MC = 25%) reacted with methanol at pH = 7 and 160 °C for 10 min using acetic acid as the catalyst. Most of the recovered lignin from this method showed an average molecular weight (M_w) value less than 2000 Da and a polydispersity (PDI) value less than 2.0. Such a PDI value was lower than that of current acid precipitated lignin (around 2.2–5.4). The recovered lignin was directly used to replace 20% of the petroleum-based polyol in the formula of a flexible polyurethane (PU) foam, and it was found that the molecular weight characteristics of the lignin affected the physical and mechanical properties of the flexible PU foams. The recovered lignin with the M_w value of 1600 Da and the PDI value of 1.8 was able to maintain the major physical and mechanical properties of the flexible PU foams. This study provided a promising way to recover lignin with improved homogeneity from black liquor with the potential to customize lignin properties to meet the requirements of downstream processes.



1. INTRODUCTION

Lignin is an attractive renewable substitute for the raw materials of fossil-based products, which has been highlighted as one of the most promising solutions to mitigate global climate change caused by excessive fossil fuel usage and long-term greenhouse gas emissions.^{1–3} Lignin represents a class of aromatic polymers massively found in nature and it composes around 10–30% of plants.² In addition to the benzene rings, isolated lignin also contains plenty of hydroxyl groups and aliphatic carbons.^{4,5} As a result, lignin holds a great potential as a raw material to make biomaterials, fuels, and chemicals.^{6–8}

Globally, technical lignin is still an underutilized byproduct from the pulping process.⁹ The Kraft pulping process is one of the main pulping processes in the world, and this process uses a strong alkali aqueous solution (H_2O , Na_2S , and $NaOH$) to dissolve and isolate lignin from the cell walls of biomass at elevated temperatures, resulting in black liquor containing Kraft lignin.¹⁰ Most isolated Kraft lignin is in an ionized form and dissolved in the strong alkali black liquor.¹¹ To recover the Kraft lignin, acid precipitation methods are commonly employed in commercial techniques, such as LignoBoost, LignoForce, and sequential liquid-lignin recovery and purification (SLRP).^{12–14} Although those methods are able to recover lignin from black liquor, the precipitated lignin usually displays a wide range of molecular weight, which hinders the value-added applications of the lignin.^{15–17} This

issue has been further shown in a recent study in which the precipitated hardwood lignin possessed M_w values ranging from 15 060 to 77 450 Da and PDI values in the range of approximately 2.24–5.36.¹⁸ Such a situation necessitates developing a process to improve the molecular homogeneity of Kraft lignin.

Currently, fractionation is the major approach to narrow down the molecular weight distribution of lignin, including sequential acid precipitation, solvent extraction, and ultrafiltration technologies.^{17,19} These methods aim at separating different lignin fractions from one feedstock (lignin or black liquor). To achieve this goal, the first method requires multiple pH adjustments; the second method usually involves different solvents with variable components and ratios; the third method needs an ultrafiltration system integrated by a few membranes with specific cutoff values.^{17,19} Although some of the fractionated lignin portions presented relatively narrowed molecular weight distributions, they entail either time-

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Scheme 1. Schematic of Technical Pathways from Raw Materials to Lignin Products

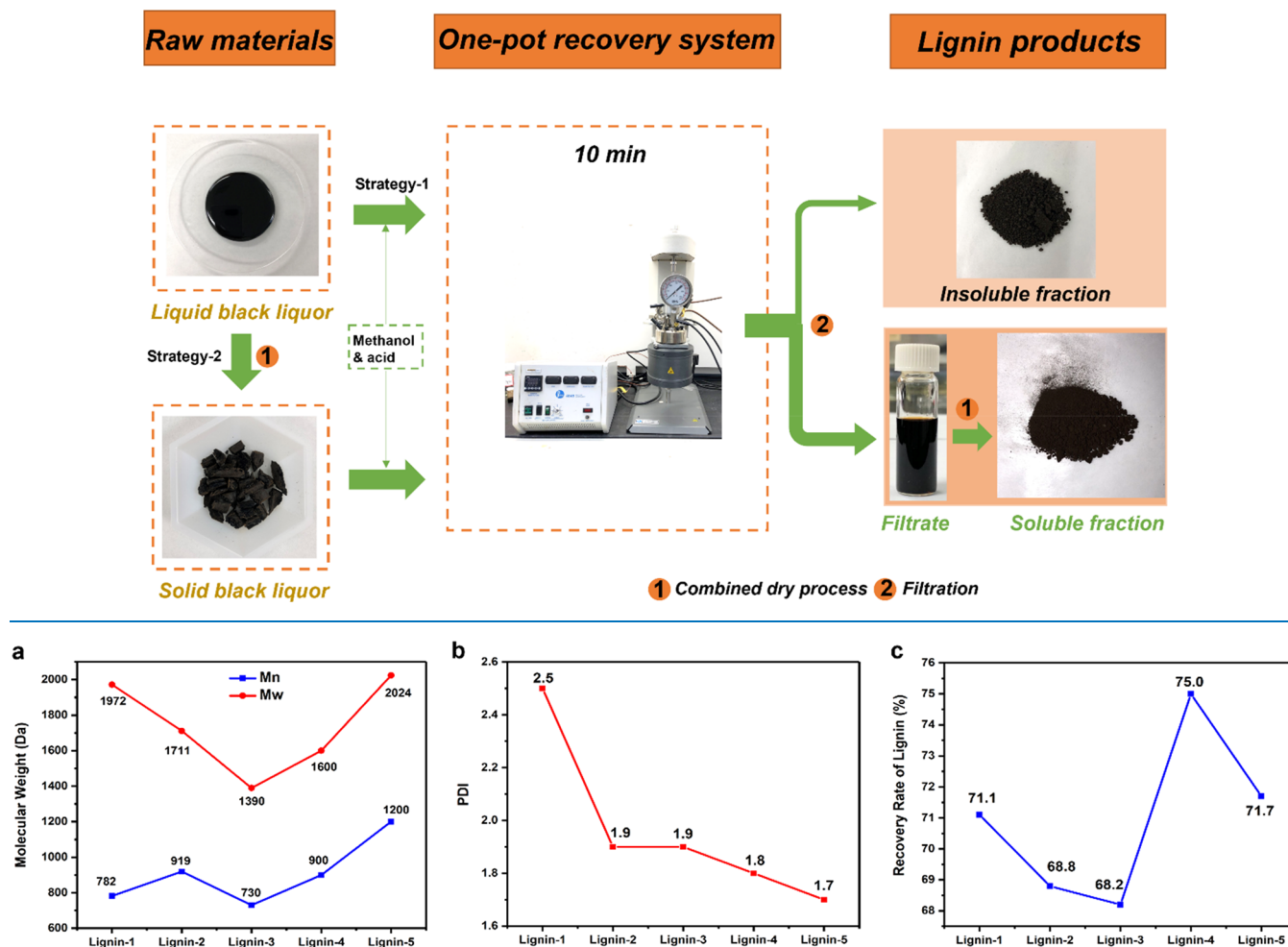


Figure 1. Plots of number average molecular weights (Mn), weight average molecular weight (Mw) (a), polydispersity (PDI) (b) and recovery rate (c) of different types of recovered lignin.

consuming operations or expensive devices, which limit their practical applications.²⁰ Thus, it is desirable to develop a simple and efficient technique to recover lignin with improved homogeneity directly from Kraft black liquor.

Liquefaction is a facile thermochemical conversion technique that has been widely employed to convert biomass to chemicals and biofuels.^{21,22} For instance, Riaz et al.²³ conducted liquefaction processes on two types of extracted lignin in supercritical ethanol/formic acid mixtures to produce bio-oil. Moreover, Xu et al.²⁴ developed a directional liquefaction coupling fractionation method to obtain platform chemicals from lignocellulosic biomass. However, there is no study of developing a liquefaction process suitable for recovering lignin directly from Kraft black liquor.

As one of the potential applications of lignin, polyurethane (PU) foams have been investigated frequently by replacing petroleum-based polyols with technical or modified lignin.^{25,26} For instance, Pan and Saddler²⁷ developed rigid PU foams by replacing petrochemical polyols with organosolv or hardwood Kraft lignin. The cellular structure, density, and compressive strength of the synthesized lignin-based PU foams exhibited high dependence on the lignin replacement ratio. Moreover, Bernardini et al.²⁸ successfully prepared lignin-based flexible PU foams with the aid of castor oil and polypropylene glycol

triol (PPG triol). This study showed that altering the formulations was able to affect the prepared flexible PU foams' apparent density, compression force deflection, and cellular structures. Recently, a study reported biobased rigid PU foams made of the Kraft lignin recovered from black liquor using the gradient acid precipitation method and related the lignin's molecular structures to the performance of the rigid PU foams.²⁹ However, the studies on how the Kraft lignin's molecular weight properties affect the performance of lignin-based flexible PU foams are still limited, and it may be due to the lack of an effective method to produce large amount of Kraft lignin with adjustable molecular weight features.

In this study, a one-pot liquefaction process was developed to recover lignin directly from the Kraft black liquor (Scheme 1). The proposed recovery method utilized subcritical methanol and acid as the recovery medium in which the lignin in black liquor was dissolved. Then, the dissolved lignin could be obtained after evaporating the recovery medium. The types of acid, the amount of water in black liquor, and the processing temperature and time were explored with respect to the recovery rate and molecular weight of lignin. Afterward, the resultant lignin without further modifications was directly used to replace 20 wt % fossil-based polyols in the formulation of flexible PU foams, and the relation between the recovered

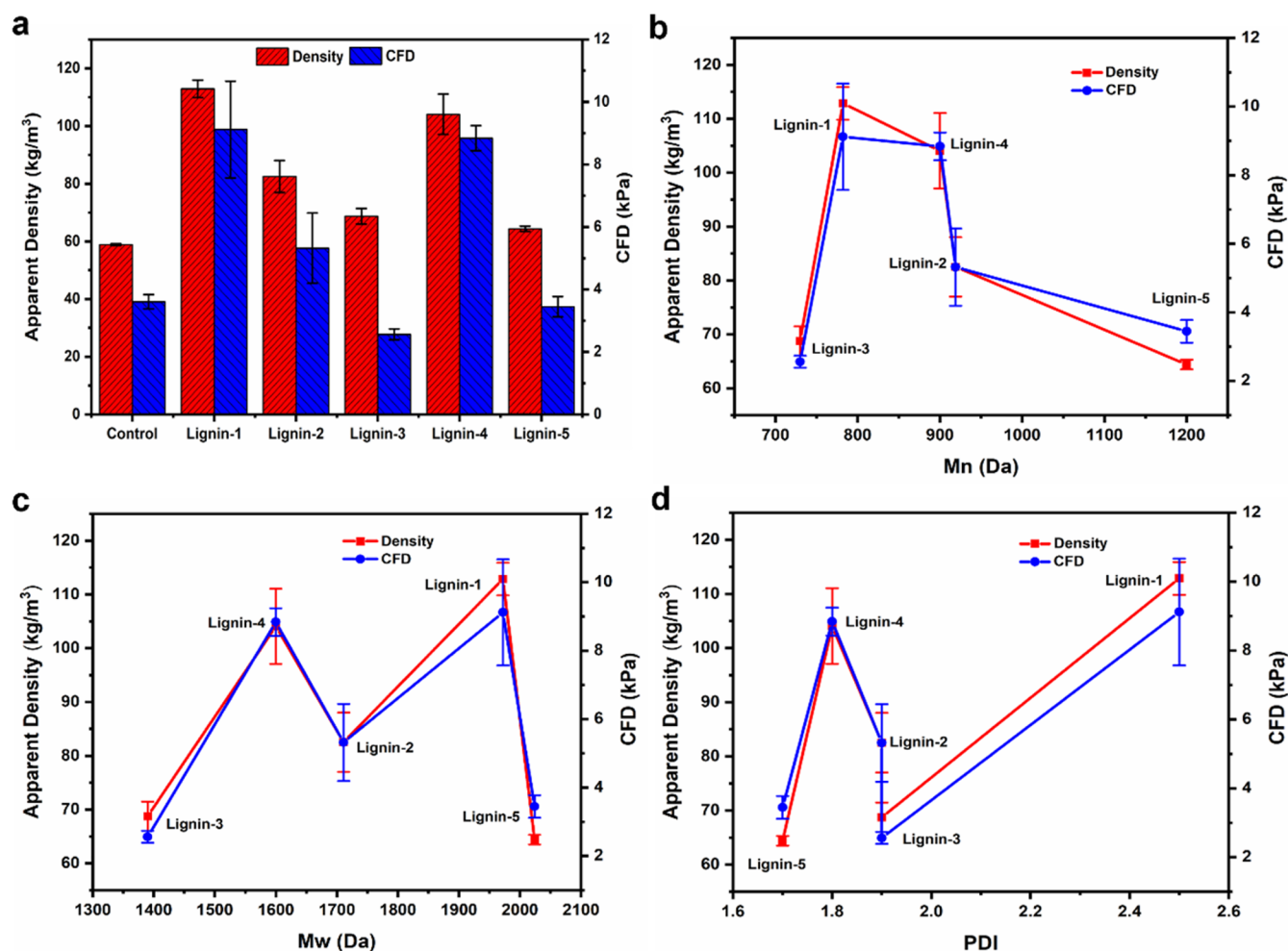


Figure 2. Apparent density and compression force deflection (CFD) of control and lignin-based PU foams (a); the lignin-based PU foams' apparent density and compression force deflection (CFD) versus the number average molecular weight (Mn) (b), the weight average molecular weight (Mw) (c), and the polydispersity (PDI) (d) of recovered lignin, respectively.

lignin's molecular weight properties and the physical/mechanical properties of the lignin-based flexible PU foams was also investigated.

2. RESULTS AND DISCUSSION

2.1. Characteristics of Recovered Lignin. The molecular weight properties and recovery rate of lignin are shown in Figure 1. The recovered lignin exhibited number average molecular weight (Mn) values in the range of around 730 to 1200 Da and weight average molecular weight (Mw) values ranging from 1390 to 2024 Da (Figure 1a). Such Mw values were lower than that of acid-precipitated lignin (around 15 000–77 000 Da) reported by a previous study employing the same Kraft black liquor source.¹⁸ A possible explanation regarding this difference is that there are condensation reactions of lignin molecules during the acid precipitation process,¹⁸ while such reactions could be reduced because of the existence of subcritical methanol during the lignin recovery processes.²⁴ Moreover, the highest polydispersity (PDI) of 2.5 was present in Lignin-1 that originated from the alkaline recovery system (pH = 12) (Figure 1b). In contrast, the lignin samples (Lignin-2, -3, -4, and -5) produced from the neutral recovery system (pH = 7) showed a lower PDI value ranging from 1.7 to 1.9 (Figure 1b). Such PDI values were lower than those generated by the acid precipitation method (PDI =

around 2.2–5.4).¹⁸ It also suggested that the recovery system neutralized by acid was able to produce more homogeneous lignin molecules. Moreover, the relatively high Mn and low Mw of Lignin-2 compared with Lignin-1 implied that the molecular weight distribution of soluble lignin could be narrowed by the neutralization using acetic acid (Figure 1b). This improved uniformity of soluble lignin might be caused by the transformation of some inhomogeneous lignin fractions dissolved in the methanol to the insoluble fractions after the addition of acid. This explanation can be verified by the slightly decreased recovery rate of Lignin-2 in comparison with Lignin-1 (Figure 1c). In contrast to Lignin-2, Lignin-3 presented lower values of both Mn and Mw but the same value of PDI (Figure 1a,b), which suggested that the heating in the given lignin recovery process was beneficial to producing smaller lignin molecules. The comparison of Mn and Mw between Lignin-3 and -4 demonstrated that introducing water into the liquefaction process might be able to dissolve lignin fractions with higher molecular weight (Figure 1a). Additionally, both Mn and Mw of Lignin-4 were lower than that of Lignin-5, while the PDI of Lignin-4 was similar to that of Lignin-5 (Figure 1a,b). This phenomenon indicated that replacing the acetic acid with sulfuric acid could boost the shift of soluble lignin from lower molecular weight to higher molecular weight,

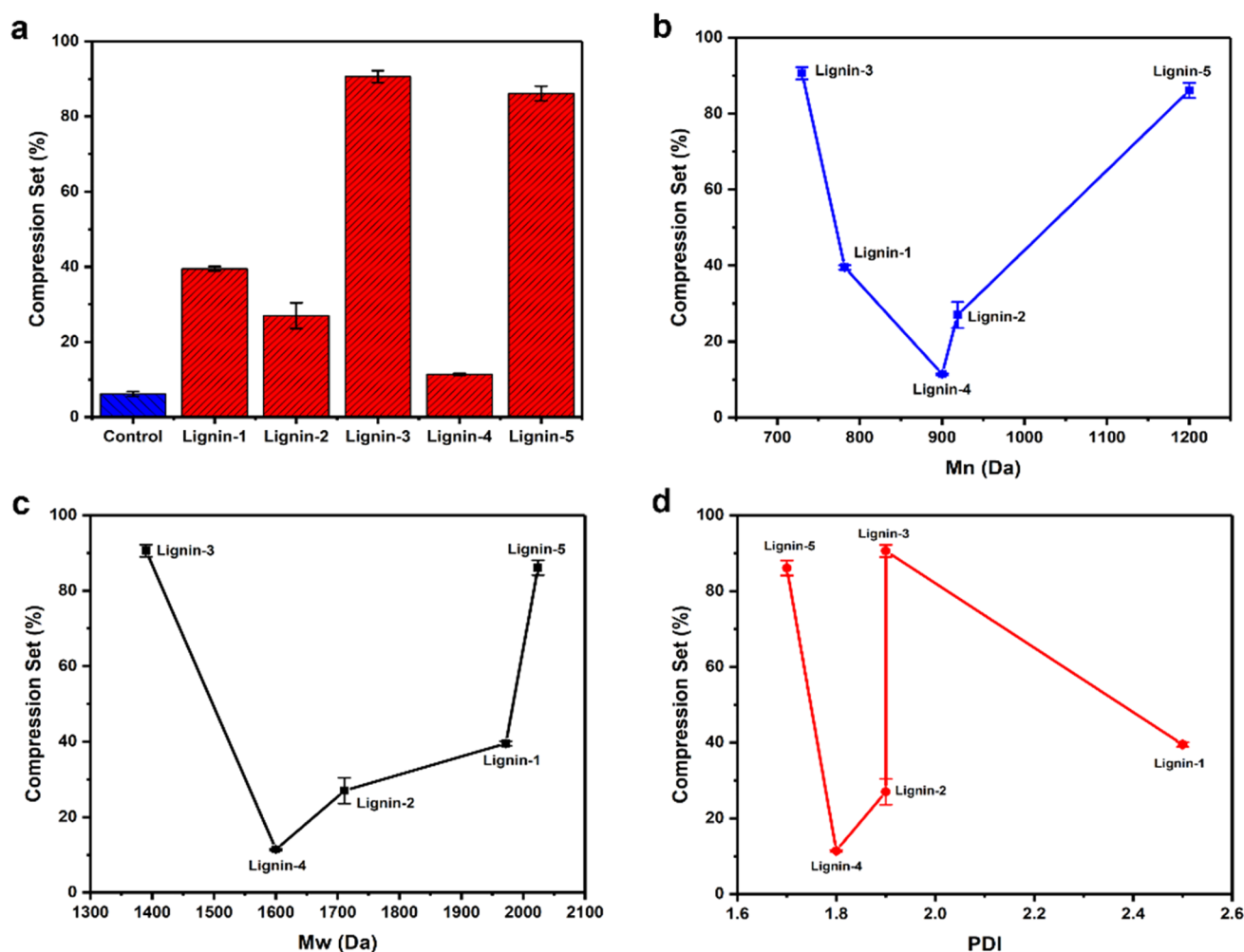


Figure 3. Compression set (CS) of control and lignin-based PU foams (a); the lignin-based PU foams' compression set (CS) versus the number average molecular weight (Mn) (b), weight average molecular weight (Mw) (c), and polydispersity (PDI) (d) of recovered lignin, respectively.

and it can be explained by the repolymerization of lignin during the liquefaction process aided by sulfuric acid.²⁴

As for the recovery rate (Figure 1c), the Lignin-4 possessed the highest value of 75.0%, while the Lignin-3 showed the lowest value of 68.2%. As mentioned before, the slightly reduced recovery rate of Lignin-2 compared with Lignin-1 was due to the partial precipitation of soluble lignin molecules triggered by adding acetic acid. It was noticeable that the recovery rate of Lignin-2 was similar to Lignin-3, which was produced from the water-free liquefaction process. The limited solubility of lignin in certain amounts of methanol may result in the similar recovery rate. Although the heat input in the liquefaction process was unable to improve the recovery rate, the dissolution process of lignin in methanol could be remarkably accelerated. More specifically, obtaining such a recovery rate of Lignin-2 involved a time-consuming dissolution process (1440 min), while the liquefaction process for the Lignin-3 only needed 10 min. Such a short duration enables the liquefaction process to be more compatible with existing industrial pulping processes. Furthermore, the introduction of water into the liquefaction process increased the recovery rate from 68.2% of Lignin-3 to 75.0% of Lignin-4. However, replacing acetic acid with sulfuric acid in the water-containing liquefaction process reduced the amount of recovered lignin (Lignin-4 vs Lignin-5). According to the

previous study, acetic acid is also an organic solvent for lignin besides its deprotonation effect, promoting the recovery rate of Lignin-4.¹⁹

2.2. Apparent Density and Compression Force Deflection of PU Foams. Apparent density is an essential parameter of PU foams since it significantly affects foams' durability and support ability. Generally, the PU foams with higher density show better durability and support ability.³⁰ The apparent densities of the lignin-based PU foams and the control are shown in Figure 2a. The control PU foam presented an average apparent density value of 59 kg/m³, while the average apparent density values of the PU foams were higher than that of the control PU foams and varied with the types of lignin in the range of approximately 64–113 kg/m³. Such a difference between most lignin-based PU foams (except Lignin-5 samples) and control PU foams in apparent density was statistically significant ($P < 0.05$). A previous study demonstrated that the lignin macromolecules comprised higher content of hydroxyl groups than the polyether-based polyols.³¹ Hence, lignin may react with more diisocyanate to form more urethane linkages, increasing the density of PU foams. The density of Lignin-1 and -2-based PU foams indicated that the Kraft lignin recovered at pH = 7 was more suitable than the Kraft lignin recovered at pH = 12 to produce the lower-density PU foams. Moreover, the comparison

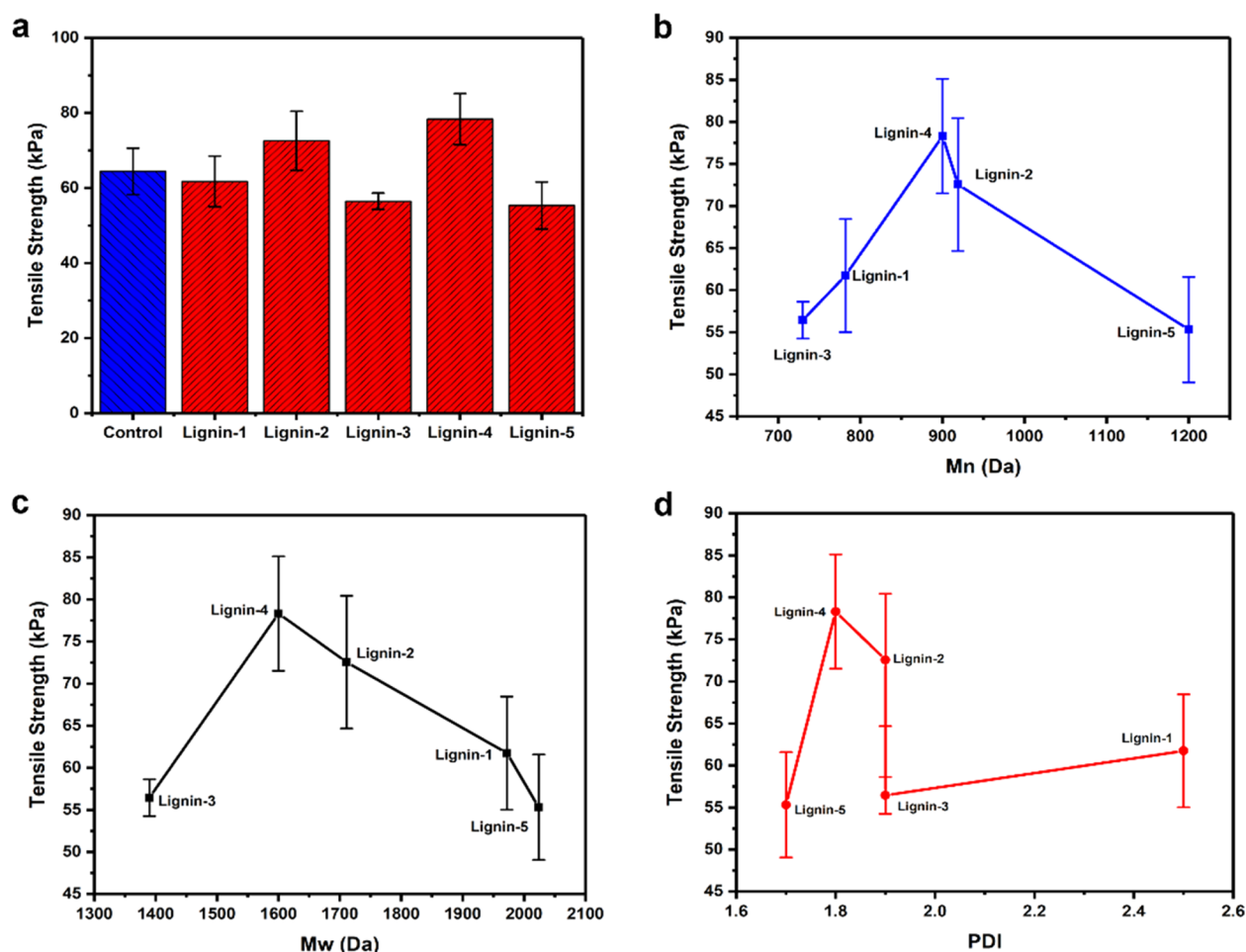


Figure 4. Tensile strength of control and lignin-based PU foams (a); the lignin-based PU foams' tensile strength versus the number average molecular weight (Mn) (b), weight average molecular weight (Mw) (c), and polydispersity (PDI) (d) of recovered lignin, respectively.

between Lignin-2 and -3 samples suggested that the density of PU foams could be further lowered when the lignin recovered from the water-free liquefaction process was used. However, the PU foams' density was reversely increased by incorporating Lignin-4, which originated from the water-containing liquefaction process. Furthermore, the higher density of Lignin-4 PU foams compared to that of Lignin-5 PU foams was associated with the different types of acid used in the liquefaction processes. The change in the density of lignin-based flexible PU foams may be associated with the molecular weight of the lignin produced from the recovery processes using different parameters since the molecular weight of lignin determines the distance between the cross-links in PU foams and thus affects the density.³² The correlation between the lignin-based PU foams' apparent density and the molecular weight properties of recovered lignin was given in Figure 2b–d. Statistically, the Mn, Mw, and PDI of the recovered lignin showed significant effect on the apparent density of lignin-based PU foams ($P < 0.05$). When the Mn of recovered lignin was increased from 730 to 1200 Da, the average apparent density value of lignin-based PU foams increased from 69 to 113 kg/m³ and then gradually decreased to 64 kg/m³ (Figure 2b), while it occurred in a fluctuating manner with respect to the Mw and PDI of recovered lignin (Figure 2c,d).

The compression force deflection (CFD) of PU foams was also shown in Figure 2a. CFD reflects the force needed to compress the foam to 50% of the original thickness. The CFD

exhibited a trend similar to the apparent density, suggesting their close correlation. The average CFD value of control PU foams was 4 kPa, while it ranged from 3 to 9 kPa and highly depended on the types of lignin. The CFD values of Lignin-1, -2, and -4 PU foams were statistically different from that of the control ($P < 0.05$). Moreover, the CFD of the lignin-based PU foams showed a trend similar to the apparent density with regard to the molecular weight features of the lignin samples (Figure 2b–d). The effect of Mn, Mw, and PDI of the recovered lignin on the CFD of the lignin-based PU foams was also statistically significant ($P < 0.05$). These results indicated that not only the apparent density but also the CFD of lignin-based PU foams could be changed by adjusting the parameters of the recovery processes.

2.3. Compression Set of PU Foams. The compression set (CS) is an indicator of the resiliency of PU foams. Generally, a lower CS value means less thickness loss and better resiliency for long-term cushioning applications.³³ As shown in Figure 3a, the average CS value of the control PU foams was less than 10%, while the lignin-based PU foams presented higher average CS values in the range of approximately 11–91%. Such a difference in the CS values between the lignin-based PU foams and the control was statistically significant ($P < 0.05$). The results indicated that partially replacing fossil-based polyols with lignin weakened the resiliency of PU foams, which may be related to an increase in cross-linking density between lignin and isocyanate.³⁴ How-

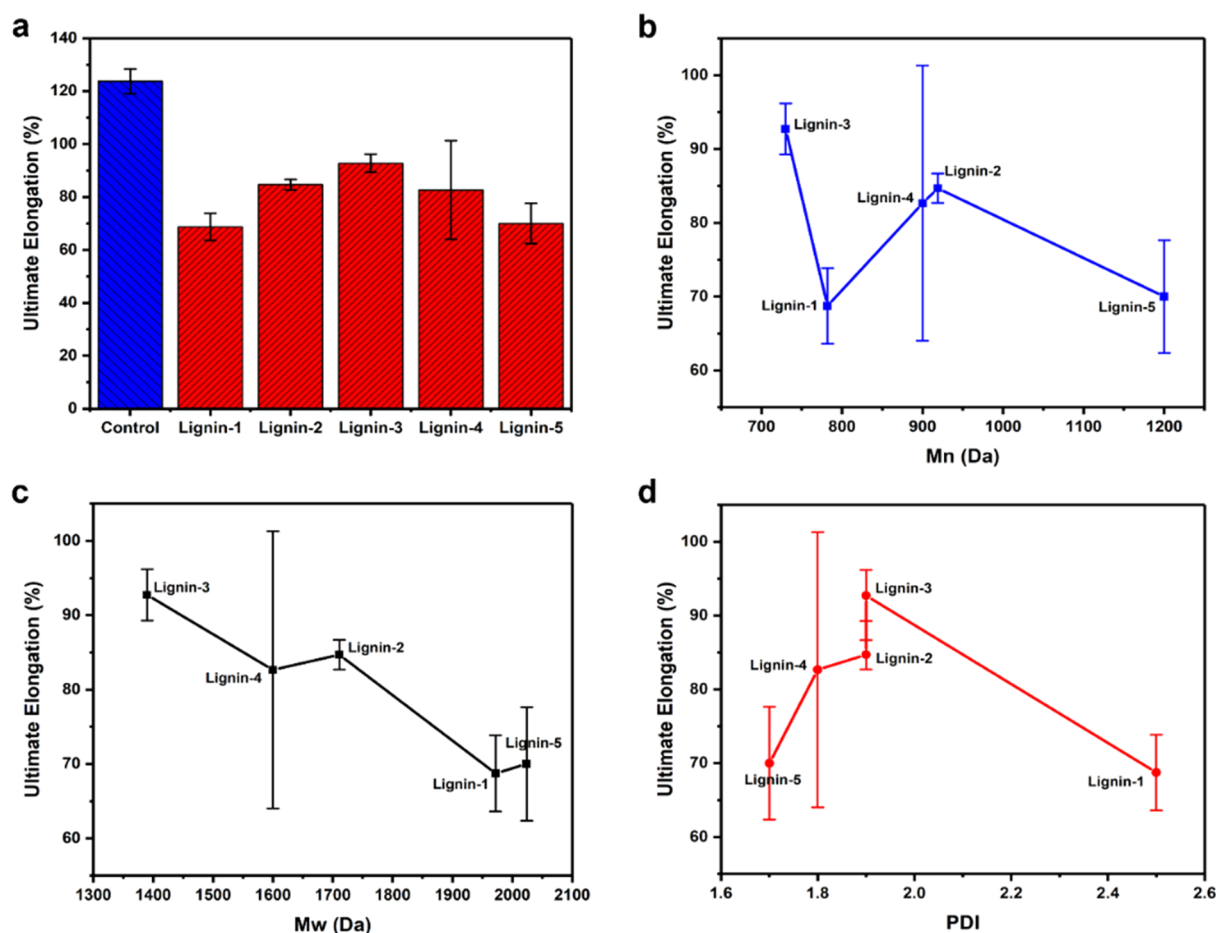


Figure 5. Ultimate elongation of control and lignin-based PU foams (a); the lignin-based PU foams' ultimate elongation versus the number average molecular weight (Mn) (b), weight average molecular weight (Mw) (c), and polydispersity (PDI) (d) of recovered lignin, respectively.

ever, the reduction in the resiliency of lignin-based PU foams varied with the types of lignin.

Furthermore, the relationship between the molecular weight nature of recovered lignin and relevant lignin-based PU foams' CS values is described in Figure 3b–d. Statistically, the Mn, Mw, and PDI of recovered lignin displayed significant effect on the CS value of lignin-based PU foams ($P < 0.05$). As shown in Figure 3b,c, the CS value of lignin-based PU foams declined first and then increased with the increase in Mn and Mw of recovered lignin, and the lowest CS value (11%) was exhibited at the samples made of Lignin-4 (Mn = 900 and Mw = 1600). Such a CS value of Lignin-4-based PU foams was similar to that of the control PU foams, and it indicated that the Lignin-4 recovered from the liquefaction process for liquid black liquor neutralized by acetic acid seems to be best for maintaining the resiliency of PU foams. In Figure 3d, it could be found that the PDI value of Lignin-4 was not the lowest, but its derived PU foams had the lowest average CS value, suggesting that the molecular weight of recovered lignin restricted in a moderate range could be preferable to reduce the loss of PU foams' resiliency.

2.4. Tensile Strength of PU Foams. The tensile strength of a PU foam is an important indicator of its ability to resist a force that tends to pull them apart in situations where the foam needs to be bent or stretched to fit the uneven surface of substrate materials.³⁵ The tensile strength results of the PU foams are presented in Figure 4a. The average tensile strength of the control PU foams was 64 kPa, and that of the lignin-

based PU foams fluctuated in the range of around 55–78 kPa. Only the tensile strength of Lignin-4 samples was statistically higher than that of the control samples ($P < 0.05$). Figure 4b–d showed the relationship between the molecular weight properties of the recovered lignin samples and the tensile strength of lignin-based PU foams. Statistically, the influence of Mn, Mw, and PDI of recovered lignin on the lignin-based PU foams' tensile strength was significant ($P < 0.05$). In contrast to the CS, the tensile strength of lignin-based PU foams displayed a reverse trend within the same range of Mn, Mw, and PDI. However, the best tensile strength (78 kPa) still existed in the PU foams made of Lignin-4 (Mn = 900, Mw = 1600, and PDI = 1.8). This result indicated that the molecular weight of recovered lignin may need to be restricted in a suitable range to enhance the tensile strength of PU foams. Moreover, although the tensile strength varied among the lignin-based PU foams, they still met the requirements for some automotive applications such as panel insulators and floor carpets.³⁶

2.5. Ultimate Elongation of PU Foams. The ultimate elongation is an indicator of the flexibility and elasticity of PU foams.³¹ As shown in Figure 5a, the control PU foams possessed an average ultimate elongation value of 124%, while the lignin-based PU foams showed relatively lower average ultimate elongation values ranging from 69% to 93%, suggesting that lignin-based PU foams had lower flexibility and elasticity than the control PU foams. Such a difference between the lignin-based PU foams and control PU foams in the ultimate elongation was statistically significant ($P < 0.05$),

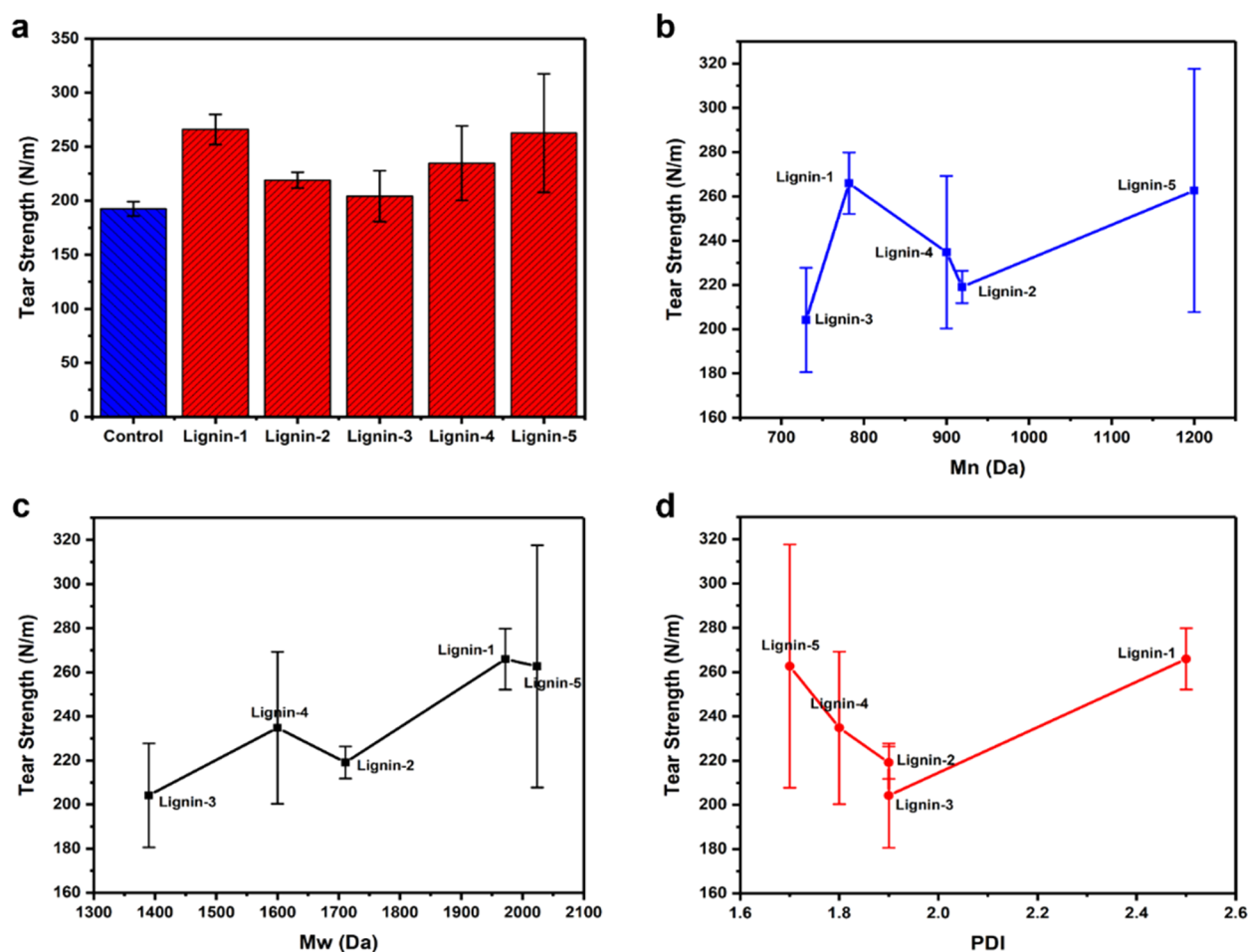


Figure 6. Tear strength of control and lignin-based PU foams (a); the lignin-based PU foams' tear strength versus the number average molecular weight (Mn) (b), weight average molecular weight (Mw) (c), and polydispersity (PDI) (d) of recovered lignin, respectively.

and it might be related to the rigid aromatic rings in the lignin macromolecules.³¹ Moreover, the ultimate elongation of lignin-based PU foams was observed to rely on the lignin categories, indicating that the flexibility and elasticity of lignin-based PU foams were indirectly affected by the lignin recovery processes.

Figure 5b–d were given to further show the influence of the recovered lignin's Mn, Mw, and PDI on the flexibility and elasticity of lignin-based PU foams. Statistically, only the effect of recovered lignin's PDI values on the ultimate elongation of lignin-based PU foams was significant ($P < 0.05$). The lignin-based PU foams' ultimate elongation fluctuated with increasing the Mn of recovered lignin, yet it tended to decline when increasing the Mw of recovered lignin. The best ultimate elongation (93%) was present in the PU foams modified by Lignin-3, whose Mn (730 Da) and Mw (1390 Da) values were the lowest (Figure 5b,c). Moreover, the ultimate elongation first gradually increased and then declined with the growth of PDI values (Figure 5d). The above results suggested that the recovered lignin with a narrow distribution in lower molecular weight could be more desirable to produce flexible and elastic lignin-based PU foams.

2.6. Tear Strength of PU Foams. The ability of PU foams to resist the crack propagation can be represented by the tear strength,³³ and the tear strength results of PU foams made in this study are presented in Figure 6a. The tear strength of PU foams appeared to follow a reverse trend to that of the ultimate elongation. The lignin-based PU foams had higher average tear

strength values (around 204–266 N/m) compared with the control PU foams (192 N/m), suggesting that the addition of recovered lignin improved the ability of PU foams to resist the crack propagation. Nevertheless, compared with the control samples, only the improvement of Lignin-1 and 5 samples in tear strength was statistically significant ($P < 0.05$). Moreover, compared with the ultimate elongation, the tear strength of the lignin-based PU foams also showed an opposite variation within the same range of Mn, Mw, and PDI of recovered lignin (Figure 6b–d), while these variations were statistically insignificant ($P > 0.05$). Among them, the PU foams made of Lignin-3 with the lowest Mn and Mw exhibited the lowest average tear strength value (204 N/m) (Figure 6b,c). Moreover, the tear strength of PU foams made of Lignin-1 with the highest PDI value displayed the highest average tear strength value, and that was followed by the PU foams made of Lignin-5 with the lowest PDI value (Figure 6d).

2.7. Support Factor of PU Foams. The weight loading capacity of PU foams is often considered in the application of floor carpets, and the effect of adding the lignin into the PU foams on the support factor was evaluated in this study.³¹ Generally, a higher value of support factor indicates a better ability of PU foams to support the weight.³¹ As shown in Figure 7a, the average support factor value of control PU foams was 3.0, and that of lignin-based PU foams ranged from 2.6 to 5.1. Among the lignin-based PU foams, only the variation of Lignin-4 and 5-based PU foams' support factor was statistically

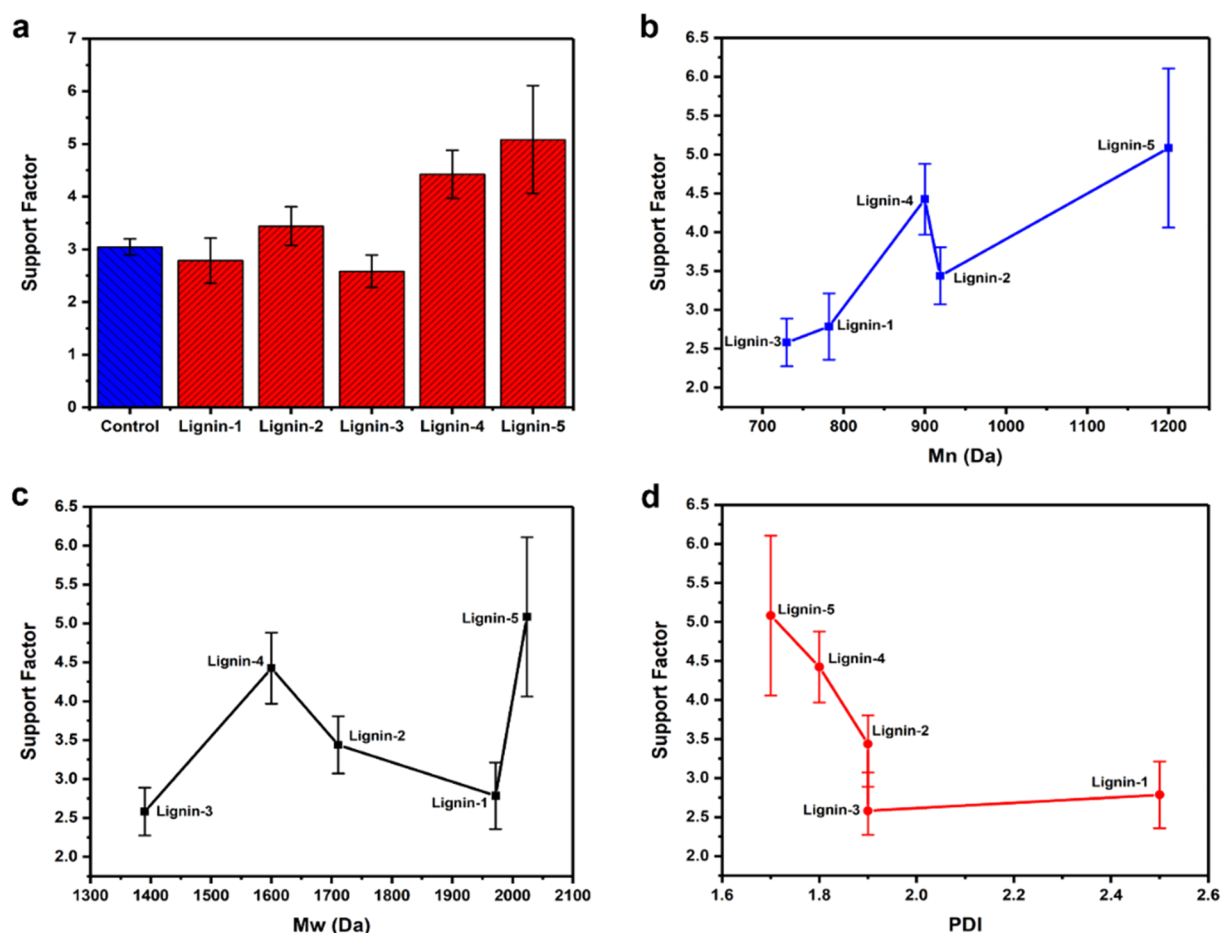


Figure 7. Support factor of control and lignin-based PU foams (a); the lignin-based PU foams' support factor versus the number average molecular weight (Mn) (b), weight average molecular weight (Mw) (c), and polydispersity (PDI) (d) of recovered lignin, respectively.

significant ($P < 0.05$) compared with the control PU foams. Furthermore, the relationship between the recovered lignin's molecular properties and the support factor of lignin-based PU foams was shown in Figure 7b–d. The influence of Mn, Mw, and PDI of recovered lignin on the support factor of lignin-based PU foams was statistically significant ($P < 0.05$). The lignin-based PU foams' support factor tended to grow while increasing the Mn of recovered lignin, but it fluctuated with the increase in Mw. Moreover, the lower PDI value of recovered lignin resulted in the higher support factor value of PU foams. Such results demonstrated that the recovered lignin with higher molecular weight in a narrow distribution may be beneficial to promoting the weight-loading ability of PU foams.

3. CONCLUSIONS

In this study, a novel one-pot acid-catalyzed liquefaction technique was developed to recover Kraft lignin directly from black liquor. Most of the recovered lignin samples had narrower molecular weight distributions ($PDI = 1.7\text{--}1.9$) compared to the acid precipitated lignin ($PDI = 2.2\text{--}5.4$). The highest recovery rate of 75% was achieved when reacting the black liquor ($MC = 25\%$) with methanol and acetic acid at $pH = 7$ and $160\text{ }^{\circ}\text{C}$ for 10 min. Moreover, the physical and mechanical properties of lignin-based flexible PU foams were found to be related to the molecular weight properties of the recovered lignin. Particularly, the recovered lignin with the Mw value of 1600 Da and the PDI value of 1.8 could maintain the

major properties of the flexible PU foams. This preliminary study demonstrated that reacting black liquor with organic solvent and acid at elevated temperatures can provide a facile method to recover Kraft lignin with improved molecular homogeneity, and the recovered lignin can be directly used to partially replace the petroleum-based polyols in flexible PU foam formulations without compromising the major physical and mechanical properties. Fine tuning of the reaction parameters to optimize the lignin properties and a techno-economic analysis will be needed in the future to qualify the technical and economic advantages of this method.

4. EXPERIMENTAL SECTION

4.1. Materials. As shown in Scheme 1, two kinds of Kraft black liquor were used in this study. The first was concentrated liquid black liquor (mixed hardwood) with an approximate 25% moisture content (MC), and it was kindly provided by Verso Corporation (Quinnesec, MI). The second was solid black liquor ($MC = 0$) derived from the liquid black liquor after a combined drying process in the lab. The combined dry process included oven drying at $80\text{ }^{\circ}\text{C}$ for 8 h followed by vacuum drying at $50\text{ }^{\circ}\text{C}$ for 24 h. The ash content in the solid of black liquor was measured as 47%. Methanol, sulfuric acid, and glacial acetic acid used in the black liquor liquefaction processing were purchased from Sigma-Aldrich. The reagents used to determine the molecular weight of lignin were tetrahydrofuran (THF), pyridine, acetic anhydride, and

hydrochloric acid purchased from Sigma-Aldrich, and polystyrene standards purchased from Agilent Technologies.

The chemicals used in the formulation of flexible PU foams included a polyether-based polyol with an OH number of 28 mg KOH/g (OH content of 0.50 mmol/g), an amine-based blowing catalyst, a polymerization catalyst, and a mixture of methylene diphenyl diisocyanate (MDI) and polymeric diphenylmethane diisocyanate (pMDI) with an isocyanate content of 28% (%NCO). Distilled water was used as the chemical blowing agent. Momentive Performance Materials Inc. provided a silicone-based surfactant. All the chemicals were used as received.

4.2. Lignin Recovery Processes. The feedstock, recovery medium, and treatment parameters of five kinds of lignin recovery processes are listed in Table 1. The purpose of entries

Table 1. Feedstock, Recovery Medium, and Treatment Parameters of Lignin Recovery Processes

entry	MC ^a (%) of black liquor	recovery medium	pH	temperature (°C)	time (min)	label of lignin
1	0	MeOH	12	25	1440	Lignin-1
2	0	MeOH and AcOH	7	25	1440	Lignin-2
3	0	MeOH and AcOH	7	160	10	Lignin-3
4	25	MeOH and AcOH	7	160	10	Lignin-4
5	25	MeOH and H ₂ SO ₄	7	160	10	Lignin-5

^aMC, moisture content.

1 and 2 was to study the effect of pH on the molecular weight, recovery rate of lignin, and the physical/mechanical properties of the resultant lignin-based PU flexible foams. Entries 2 and 3 were purposed to disclose the effect of processing temperature and time on the same properties of lignin and lignin-based PU foams. Entries 3 versus 4 and entries 4 versus 5 were aimed at exploring the effect of water content and acid categories within the liquefaction system on the investigated properties of lignin and lignin-based PU foams.

As for the operation procedures in entries 1 and 2, the solid black liquor was directly dissolved in methanol with a mass ratio of 1:10 at room temperature. Then, the pH of the mixture in entry 1 was measured as 12 using a pH meter (VWR sympHony, B10P), while the pH in entry 2 was adjusted to 7 through addition of acetic acid. To accelerate the dissolution process of the mixtures, a magnetic stir was conducted on them at 600 rpm for 24 h (1440 min). After that, the filtrate and filter cake were separated from the mixtures through vacuum

filtration, followed by a 20 mL methanol wash. The soluble fraction was collected after removing the solvent in the filtrate through the combined drying process as mentioned before. The soluble fractions obtained from entries 1 and 2 were labeled as Lignin-1 and Lignin-2 in Table 1, respectively. The filter cake was also collected as an insoluble fraction.

As shown in Scheme 1, entries 3, 4, and 5 were one-pot liquefaction processes conducted in a mini parr pressure reactor (Model No. 4560 and maximum processing capacity = 300 mL). The formulation of each entry is illustrated in Table 1. It should be noted that the mass ratio between the solid of black liquor and methanol was maintained as 1:10 regardless of the types of black liquor. Before the liquefaction processing, the solid or liquid black liquor was mixed with methanol in the reactor, and then the pH of the mixture was adjusted to 7 by adding acid. Afterward, the reactor was heated with a heating rate of 5 °C/min and then maintained at 160 °C for 10 min. At the end of the constant temperature stage, the reactor was cooled down to room temperature using cooling water. During the entire liquefaction process, a mechanical stir was continuously conducted on the mixture. The resultant products were subsequently filtered, followed by a 20 mL methanol wash. Finally, both soluble and insoluble fractions were collected after the same process as entries 1 and 2. The soluble fractions from entries 3, 4, and 5 were labeled as Lignin-3, -4, and -5 in Table 1, respectively.

4.3. Determination of Ash Content. The samples' ash content (AC) was determined using a thermogravimetric analyzer (TGAQ500, TA company). All samples were oven-dried before the ash content measurement. During a typical TGA test, a sample (~5.0 mg) was heated under airflow (flow rate = 75 mL/min) directly from room temperature to 800 °C with a heating rate of 10 °C/min and then cooled under the airflow with the same flow rate. The AC (%) was calculated on the basis of the following equation

$$AC (\%) = \frac{M_r}{M_o} \times 100 \quad (1)$$

where M_r is the mass of residue solid after the heating process, and M_o represents the original mass of a sample.

4.4. Determination of Recovery Rate of Lignin. To quantify the recovery efficiency of lignin, the recovery rate (%) is defined

$$\text{Recovery rate } (\%) = \left[1 - \frac{M_{IF} \times (1 - AC_{IF})}{M_{BL} \times (1 - AC_{BL})} \right] \times 100 \quad (2)$$

where M_{IF} represents the mass of dry insoluble fraction, AC_{IF} refers to the ash content of dry insoluble fraction, M_{BL} is the mass of dry solid in black liquor, and the AC_{BL} is the ash content of dry solid in black liquor. According to the previous study, the amount of carbohydrate in both black liquor and

Table 2. Formulations of Lignin-Based and Control PU Foams

	copolyol (g)	lignin (g)	water (g)	gelation catalyst (g)	blowing catalyst (g)	surfactant (g)	diisocyanate (g)
control	25		0.63	0.13	0.08	0.20	10.05
Lignin-1	20	5	0.63	0.13	0.08	0.20	10.05
Lignin-2	20	5	0.63	0.13	0.08	0.20	10.05
Lignin-3	20	5	0.63	0.13	0.08	0.20	10.05
Lignin-4	20	5	0.63	0.13	0.08	0.20	10.05
Lignin-5	20	5	0.63	0.13	0.08	0.20	10.05

insoluble fractions was ignored in the calculation since it was pretty low.¹⁸

4.5. Characterization for Molecular Weight of Recovered Lignin. The number average (M_n) and weight average (M_w) molecular weights of the recovered lignin were determined by a gel permeation chromatography (GPC) system (Waters Company) equipped with a refractive index detector and three 300 mm \times 7.8 mm Waters columns including 1-Styragel HR 4, 2-Styragel HR 3, and 3-Ultra-styragel in tandem. THF (tetrahydrofuran) was used as the mobile phase in the GPC system, and its flow rate was 1 mL/min. The preparation and characterization processes were conducted according to a previous report.³¹

4.6. Synthesis of PU Foams. The components of lignin-based and control PU foams are listed in Table 2. In this study, the five types of solid lignin powder, recovered from different recovery processes (Table 1), were directly used to replace 20 wt % petroleum-based polyols to prepare lignin-based flexible PU foams. More specifically, polyol was first added in a 12 oz cup, followed by the sequential addition of water, gelation catalyst, blowing catalyst, and silicone-based surfactant. Afterward, the solid lignin powder was added to the cup. The mixture was blended thoroughly for 2 min at 2000 rpm using a high-speed digital overhead stirrer to ensure homogeneous mixing. Then, isocyanate was added to the polyol component, and the solution was mixed vigorously at 2000 rpm for 4–5 s. After that, the mixture was immediately poured into a silicone mold to rise in free expansion at 60 °C for an hour and then air-dried at room temperature for 24 h to ensure complete curing before characterizations.

4.7. Characterizations of PU Foams. The characterizations of lignin-based and control PU foams in this investigation involved measuring apparent density, compression force deflection, tensile strength, ultimate elongation, tear-resistance test, compression set, and support factor, based on the previous study using ASTM 3574 standard methods.³¹

4.8. Statistical Analysis. The physical and mechanical data of PU foams were shown in average values with standard deviations, and one-way ANOVA ($\alpha = 0.05$) for these data was conducted in SPSS software.

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Notes

The authors declare no competing financial interest.

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