Efficient and Green Approach for the Esterification of Lignin with Oleic Acid Using Surfactant-combined Microreactors in Water

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A green, effective, and feasible reaction for esterification of lignin with oleic acid in water at room temperature was investigated. A surfactantcombined system (p-toluenesulfonic acid/4-dodecylbenzenesulfonic acid) was designed to simultaneously solubilize kraft lignin and disperse the oleic acid, producing microreactors for esterification. Esterification using a higher 4-dodecylbenzenesulfonic acid dosage at room temperature was found to be a good option, and an increasing oleic acid dosage had no effect on improving the degree of esterification. Structural characterization analyses confirmed the successful esterification of lignin with oleic acid, indicating the effectiveness and feasibility of esterification of macromolecules in water. Due to the introduction of a long flexible aliphatic chain, the lignin ester showed a noticeable decrease in glass transition temperature, an obvious increase in contact angle, and exhibited excellent thermoplasticity, processability, and hydrophobicity. Additionally, ligninester nanoparticles were prepared through the micellization of ptoluenesulfonic acid. Therefore, the method of esterification using surfactant-combined microreactors in water is promising for high valueadded utilization of lignin.

Keywords: Green reaction; Water; Lignin esterification; Surfactant; Microreactors

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INTRODUCTION

Ever-increasing rates of petroleum usage, depletion of reserves, and environmental concerns regarding the use of fossil fuels have prompted a need to find alternative renewable resources (Van Dam *et al.* 2005). Lignocellulose has gained significant attention due to its renewability, wide availability, and lack of competition with food production (Schutyser *et al.* 2018). Lignocellulosic biomass is primarily composed of cellulose, hemicellulose, and lignin. After cellulose, lignin is the second most abundant natural polymer in the plant kingdom and is the primary renewable source of aromatic structures on Earth. Lignin is an amorphous polymer, composed of three types of phenylpropane units (ρ -coumaryl, coniferyl, and sinapyl alcohols) linked *via* ether and C-C bonds (Wang *et al.* 2019). Its high energy, high volume, and attractive structure give it great potential for use

in bio-based materials. However, currently < 2% of lignin is commercialized due to several obstacles that require further investigation (Kai *et al.* 2016).

Chemically, lignin is composed of a variety of functional groups, including hydroxyls (phenolic and aliphatic hydroxyls), methoxyls, carbonyls, and carboxyls (Zhou *et al.* 2012). The hydroxyl groups, lignin's most characteristic functional groups, possess properties of high reactivity and functional modification flexibility, providing promising polymer preparation potential (Ten *et al.* 2015).

Esterification of lignin's hydroxyl groups can improve its organic solubility, thermoplasticity, and hydrophobicity (Thielemans and Wool 2005). Hydroxyl esterification leads to decreased hydrogen bonding and increased chain flexibility, which lowers the glass transition point of lignin and improves its processability. Possessing these excellent qualities, esterified lignin has been utilized for various applications (Wang *et al.* 2016). Its use in polymer blends has been demonstrated by Zhao *et al.* (2019), in which 15% lignin ester was blended with poly(vinyl chloride) (PVC) plates and improved the thermal stabilities and mechanical properties of the plates. Luo *et al.* (2017) reported the synthesis of eight lignin esters that were blended with poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) or polypropylene (PP), and found that lignin hexanoate showed high thermoplasticity. Further studies have reported lignin ester miscibility with polyethylene (PE) (Dehne *et al.* 2016), polystyrene (PS) (Pawar *et al.* 2016), and poly(ε -caprolactone) (PCL) (Teramoto *et al.* 2009) with improved blend qualities.

Fatty acid esterified lignin has been shown to have remarkably increased non-polar solubility, a considerably reduced glass transition temperature (T_g), and highly increased hydrophobicity (Lewis *et al.* 1943; Pawar *et al.* 2016). Hult *et al.* (2013) reported that lignin palmitate and laurate derivatives have high potentials as water vapor and oxygen barrier coatings in fiber-based packaging. Gordobil *et al.* (2017) modified lignin with dodecanoyl chloride, producing a hydrophobic lignin ester for use as a protective agent for wood products. In general, esterification methods are not eco-friendly, using large amounts of organic solvents and hazardous acid anhydride/acyl chloride reagents (Hulin *et al.* 2015).

Water, as a reaction solvent, has received considerable attention in synthetic organic chemistry due to being low-cost and green. Although an excess of water has been shown to have detrimental effects on the equilibrium of esterification reactions (Manabe and Kobayashi 2002a), a few esterification studies using water have been reported. Baile *et al.* reported the direct polyesterification of 1,10-decanediol and nonanedioic acid in water using 4-dodecylbenzenesulfonic acid (DBSA) and sodium dodecylbenzenesulfonate catalysts (Baile *et al.* 1990). Manabe *et al.* (2002b) also reported a DBSA-catalyzed esterification of lauric acid and 3-phenyl-1-propanol in water. The DBSA acts as a surfactant catalyst, forming emulsion droplets with substrates. The hydrophobic interiors of the droplets exclude water molecules during the reaction. Using this method, a maximum esterification yield of 84% was obtained. Despite these examples, methods for esterification in water are limited in terms of substrate and reaction applicability. Furthermore, few reports of macromolecular esterification in water exist.

The current work involves the development of surfactant-combined microreactors for the esterification of lignin and oleic acid in water at room temperature. *p*toluenesulfonic acid (TsOH) and DBSA are used as catalysts for the solubilization and dispersion of lignin and oleic acid, respectively, with the formation of emulsion droplets between the surfactants (TsOH/DBSA) and substrates (lignin/oleic acid). The droplet interiors serve as stable microreactors, whose hydrophobicity excludes water molecules produced during the reaction. The effects of oleic acid dosage, DBSA dosage, and reaction temperature on the esterification are discussed. The lignin esters were characterized by gel permeation chromatography (GPC), Fourier-transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance spectroscopy (¹H-NMR), particle size analyzer (PSA), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and contact angle analysis. Additionally, optical microscopy was used to find evidence related to the hypothetical mechanism of surfactant-combined microreactors formation and the feasibility of esterification in water.

EXPERIMENTAL

Materials

Kraft lignin, produced by the kraft pulping of a mixture of various Southeast Asian hardwood chips, was kindly provided by Moorim Pulp & Paper Co., Ltd. (Ulsan, South Korea). The *p*-toluenesulfonic acid (99%), 4-dodecylbenzenesulfonic acid (95%), and oleic acid (90%), all analytical grade, were used as received from Sigma-Aldrich (Darmstadt, Germany).

Methods

Lignin esterification

A combined-surfactant solution, composed of 40% TsOH and a certain amount of DBSA (0.1 g or 0.5 g), was prepared in a 250-mL flat-bottomed flask equipped with a magnetic stir bar. Kraft lignin (1 g) was dissolved in 50 mL of the solution, followed by dispersal of a certain amount of oleic acid (1 g or 2 g), to form an emulsion. The reaction mixture was stirred at reaction temperature for 48 h at 300 rpm. The detailed reaction parameters are shown in Table 1. After the reaction, the mixture was poured into distilled water to precipitate the lignin ester, and purified by dialysis (Cellu-Sep H1, MWCO: 1000; Membrane Filtration Products, Inc., Seguin, TX, USA) to remove excess surfactant and unreacted oleic acid. The waste liquor was concentrated to recycle TsOH (Fig. 1). After that, the lignin ester was washed with diethyl ether and then dried at 40 °C for 48 h.



Fig. 1. Schematic flow diagram for esterification of lignin and oleic acid using combined surfactants

Lignin characterization

FT-IR spectroscopy was conducted using a spectrophotometer (PerkinElmer Frontier, Waltham, MA, USA) with an attenuated total reflectance (ATR) attachment.

Instrument resolution was 4 cm⁻¹, and a spectrum region of 450 to 4000 cm⁻¹ was used. The FT-IR spectra were obtained directly for lignin samples that had been oven-dried at 40 °C for two days.

The ¹H-NMR spectra were measured using a 600 MHz FT-NMR (Bruker Avance Neo 600; Bruker Corporation, Karlsruhe, Germany). Samples were prepared using 20 mg of lignin dissolved in 0.7 mL of DMSO- d_6 . Measurements were taken at room temperature using a setting of 128 scans (Wu *et al.* 2013).

The GPC (Shimadzu-20A; Shimadzu Corporation, Kyoto, Japan), using PLgel columns (PLgel 5-µm mixed-C and -D, and PLgel 3-µm mixed-E), was employed to analyze the average molecular weights of the lignin samples using a previously reported procedure (Seo *et al.* 2019).

The TGA was performed using an SDT Q600 instrument (TA Instruments, New Castle, DE, USA). A sample heating rate of 20 °C/min from 20 to 650 °C was employed. The sample carrier gas used was N₂. The T_g values of the lignin samples were determined using a DSC Q2000 instrument (TA Instruments, New Castle, DE, USA). Approximately 5 to 10 mg lignin samples were used for determination under N₂ atmosphere. The temperature program was performed as follows: (1) raise temperature to 105 °C at a rate of 10 °C/min, hold for 5 min to remove moisture, then cool to 20 °C at a rate of 10 °C/min; (2) raise the temperature to 180 °C at a rate of 10 °C/min; then cool to 20 °C at a rate of 10 °C/min; (3) raise the temperature to 180 °C at a rate of 10 °C/min. The T_g values of the lignin samples were calculated based on the second measurement cycle (Pawar *et al.* 2016).

Batches of emulsions containing surfactants (TsOH/DBSA) and reactants (lignin/ oleic acid), with the formula: 40% TsOH, 1% DBSA, 2% lignin, and 2% oleic acid, were prepared. A second emulsion, with all compounds except oleic acid, was prepared as a control. Samples were then analyzed by optical microscopy (Olympus CKX53; Olympus Corporation, Tokyo, Japan) to determine the mechanism of formation of the surfactantcombined microreactors.

The particle size of the lignin ester was determined using a Malvern Mastersizer 3000 instrument (Malvern Instruments, Ltd., Worcestershire, England). Samples were prepared using the lignin esterification method described earlier, with the dialysis suspension analyzed directly for determination of particle size.

The contact angles of the lignin samples were determined using a contact angle analyzer (Pocket Goniometer, FIBRO System AB; FIBRO Precision Products Co., Ltd., Tranås, Sweden). Lignin samples were prepared by a pressed disc method. Paper tape, with 1 cm² of double-sided adhesive, was used as the base of the lignin disc. Lignin powder (60 mg) was spread flat onto the adhesive, and the lignin disc was pressed to obtain a flat plane. The contact angle was then directly measured from the lignin disc created.

RESULTS AND DISCUSSION

Formation of Surfactant-combined Microreactors

In general, for esterification in water to occur, surfactant-type catalysts and substrates need to form emulsion (oil-in-water) droplets. These droplets are stable, and their interiors are hydrophobic, due to the physical interactions of surfactants. During the reaction, carboxylic acids and alcohols undergo esterification in the microreactors formed by the surfactants. Water generated during the reaction is excluded from the droplets, which

shifts the equilibrium towards products, leading to good yields, despite using water as a solvent (Manabe *et al.* 2002b).

Although this model is suitable for most low molecular weight carboxylic acids and alcohols, for macromolecules, such as lignin, which have large numbers of reactive hydroxyl groups, dispersion by the same mechanism is difficult. Therefore, a surfactant-combined system (TsOH/DBSA) was designed to form stable emulsion droplets as microreactors for esterification of lignin and oleic acid. First, a high concentration of TsOH was used to solubilize lignin in water. As shown in Fig. 2a, TsOH is a hydrotrope, relying on aggregation for the solubilization of lignin, and can facilitate dissolution of lignin in water to form a clear solution. Optical microscopy showed that lignin was dispersed in the water solution with the aid of TsOH micelles. Chen *et al.* (2017) also reported a similar phenomenon for wood lignin dissolved using TsOH micelles. Second, oleic acid was added to the micelle solution using trace amounts of DBSA. As shown in Fig. 2b, lignin and oleic acid were enclosed in the emulsion droplets created by the two surfactants (TsOH/DBSA), forming microreactors.



Fig. 2. Microscopic observation of emulsion droplets comprised by TsOH/DBSA and lignin/oleic acid

Figure 3 shows a hypothetical model for the esterification of lignin and oleic acid using surfactant-combined microreactors in water based on literature (Manabe *et al.* 2002). In the interior of the microreactors, lignin and oleic acid are in contact with one another. At the same time, TsOH catalyzes the esterification reaction by concentrating protons on the surface of the droplets. Water generated during the reaction, which is inhibitory to esterification, is excreted from the microreactors, promoting an equilibrium shift towards products. After the reaction, the concentration of TsOH is lowered below its critical micelle concentration (CMC) by adding water to the reaction mixture. This leads to a decrease in the hydrotropicity of TsOH, and consequently, lignin ester precipitation.



Microreactor

Fig. 3. Hypothetical model of esterification of lignin and oleic acid using surfactant-combined microreactors in water

Molecular Weight and Chemical Structure Analyses of the Lignin Esters

The effects of oleic acid dosage (1 g or 2 g), DBSA (0.1 g or 0.5 g), and reaction temperature (20 °C or 40 °C) on esterification were analyzed. As shown in Table 1, the yields of lignin esters were approximately one gram. This may be due to the purification process, as the lignin ester is easily washed away while removing excess oleic acid. Furthermore, using different DBSA dosages, different oleic acid dosage and increasing reaction temperature caused no clear differences in the yield of lignin esters.

Run	Lignin (g)	Solvent	Oleic acid (g)	DBSA (g)	Reaction temperature (°C)	Yield of lignin ester (g)
E1	1	50 mL, 40% TsOH	1	0.1		0.96 ± 0.22
E2			2	0.1	Room	0.81 ± 0.54
E3			1	0.5	temperature	0.94 ± 0.65
E4			2	0.5		0.89 ± 0.34
E5			1	0.5	40	0.92 ± 0.49

Table 1	Yields	of Lignin	Esters	from	Different	Reaction	Parameters
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The molecular weight distributions of the kraft lignin and lignin esters were analyzed by GPC. As shown in Fig. 4, an obvious difference was observed between the molecular weight properties of the kraft lignin and lignin esters, with the molecular weight distribution curves of the lignin esters showing a greater shift towards the high molecular weight region compared to that of the kraft lignin. Kraft lignin showed a number-average molecular weight (M_n) of 1400 g·mol⁻¹, weight-average molecular weight (M_w) of 2300 g·mol⁻¹, and polydispersity index (PDI = M_w/M_n) of 1.64. After esterification, the lignin esters' molecular weight data are shown in Table 2. As predicted, a remarkable increase in the molecular weight of the lignin esters was observed after esterification, substantiating successful esterification. From the molecular weight data and distribution curves of E1 and E2, an increasing oleic acid dosage could not improve esterification. However, E3 and E5 that were obtained by using a higher DBSA dosage showed a clearer increase in molecular weight than others. Their molecular weight data were analogous, except for E3 showing a higher weight-average molecular weight and wider polydispersity. These results indicated increasing DBSA dosage could improve esterification, but increasing reaction temperature had no effect on improving the degree of esterification, so esterification *via* using a higher DBSA dosage at room temperature is a good option.



Fig. 4. Molecular weight distribution of kraft lignin (KL) and lignin esters

Sample	Mn	Mw	PDI	Dv (50) ^a	SSA ^b	
	(g·mol⁻¹)	(g∙mol⁻¹)		(µm)	(m²/g)	
KL	1400	2300	1.64	182.0	0.17	
E1	1900	3300	1.74	-	-	
E2	2100	3400	1.62	-	-	
E3	2200	5100	2.32	2.4	3.78	
E4	2000	3500	1.75	-	-	
E5	2200	4400	2.00	-	-	
^a Dv (50) represents the particle size corresponding to the volume distribution of 50%;						
^b SSA is the abbreviation of specific surface area						

Table 1. Molecular Weight and Particle Size of Kraft Lignin and Lignin Ester

The FT-IR spectra (Fig. 5) of the kraft lignin and lignin esters were used to confirm the successful esterification *via* chemical structural analyses. The kraft lignin spectrum showed: an absorption at 3400 cm⁻¹, corresponding to O-H stretching vibrations of aliphatic and phenolic hydroxyl groups; absorptions at 2920 and 2850 cm⁻¹, assigned to C-H stretches of methyl and methylene groups; peaks at 1600, 1510, and 1425 cm⁻¹, corresponding to skeletal vibrations of aromatic rings in the lignin structure; and peaks at

1214 and 1113 cm⁻¹, assigned to C-O stretching vibrations of syringyl rings in lignin (An *et al.* 2019). After esterification, all of the lignin esters spectra showed a slight decrease in absorption of O-H (3400 cm⁻¹). Instead, a characteristic band at 1710 cm⁻¹, assigned to the C=O of the ester was clearly observed, providing convincing evidence for the successful esterification of lignin and oleic acid. Additionally, a clear increase in the absorption of C-H, from the methyl and methylene groups (2920 and 2850 cm⁻¹), was attributed to the introduction of the long-aliphatic oleyl chain.

An increased signal between 1000 and 1300 cm⁻¹, assigned to the expansion of the C-O bonds in ester groups, was observed in spectra of all of lignin esters (Ibrahim et al. 2010). Compared with other spectra, the spectra of E3 and E5 showed a more obvious increase in this region. It indicated that higher DBSA dosages led to an improved degree of esterification in comparison with other reaction conditions. This may be due to the higher DBSA dosage that caused better dispersion of oleic acid, resulting in more adequate accessibility between the two substrates. Furthermore, the spectra of E3 and E5 showed a clear peak at 680 cm⁻¹, assigned to C-H in the double bond of the oleyl chain, which also confirmed the success of esterification (Van der Weerd et al. 2005) and also that higher DBSA dosage led to a more effective esterification. Concerning different oleic acid dosages, there was no clear difference between the spectra of E1 and E2. This signified that increasing oleic acid dosage had no obvious effect on the degree of esterification. Additionally, increasing reaction temperature from room temperature to 40 °C caused no difference in esterification, as shown in the spectra of E3 and E5, indicating that esterification at room temperature is a good option. These results agreed with the analyses of GPC, which showed that esterification (E3) using a higher DBSA dosage at room temperature was a good condition.



Fig. 5. FT-IR spectra of KL and lignin esters

From the results of GPC and FT-IR, the lignin ester (E3) showed a competitive degree of esterification, so ¹H-NMR spectroscopy of E3 was performed to further confirm the successful esterification by using surfactant-combined microreactors in water. As shown in Fig. 6, the ¹H-NMR spectrum of E3 showed aromatic protons at 8.00 to 6.30 ppm, and methoxyl protons at 3.50 to 4.00 ppm. The two sharp signals at 3.35 and 2.50 ppm are related to the protons of water and DMSO- d_6 , respectively (An *et al.* 2017). After esterification, the ¹H-NMR spectrum of the E3 showed a characteristic peak at 2.18 ppm (d), assigned to the protons in the α -position of the ester linkage, which substantiated the successful esterification of lignin. Strong peaks at 5.30 ppm were assigned to the C=C protons (c) of the oleyl chain, while the protons (e) close to the double bond appeared as peaks at 1.98 ppm. The methyl (a) and methylene protons (b) of the oleyl chain give rise to signals at 0.86 and 1.25 ppm, respectively (Laurichesse *et al.* 2014; Xing *et al.* 2017). Therefore, the results of ¹H-NMR were in good accordance with the FT-IR and GPC results, confirming successful esterification of lignin and oleic acid using surfactant-combined microreactors in water.



Fig. 6. ¹H NMR spectra of KL and lignin ester (E3)

Particle Size Analyses of the Lignin Ester

Solubilization of lignin in water was achieved using a high concentration of TsOH (above its CMC). After esterification, precipitation of lignin product was facilitated by diluting the reaction liquor below the CMC of TsOH. Literature has reported using this micellization method to successfully prepare lignin nanoparticles (Chen *et al.* 2017). In the current study, the particle size of the lignin ester (E3) was determined using a particle size analyzer. After esterification, the lignin ester was precipitated by adding water to decrease

the hydrotropicity of TsOH. The particle size distribution curve (Fig. 7) illustrated a dramatic reduction in particle size for E3, with some lignin-ester particles falling in the nano-size range. The average particle size of the E3 was reduced to 2.4 μ m compared to that of the kraft lignin (182.0 μ m). Additionally, the specific surface area of E3 (3.78 m²/g), which increased noticeably with the decrease in particle size (Table 1), was higher than that of the kraft lignin (0.17 m²/g). These results suggest the possibility for lignin-ester nanoparticle preparation using surfactant-combined microreactors.



Fig. 7. Particle size distribution of kraft lignin and lignin ester (E3)

Thermal Properties of the Lignin Ester

Thermal properties of the kraft lignin and lignin ester (E3) were investigated by TGA and DSC. The TGA and derivative thermogravimetric (DTG) curves of the kraft lignin and E3 are presented in Fig. S1. The thermal properties, including the onset temperature (calculated at a weight loss of 5%, $T_{5\%}$), maximum degradation temperature (T_{max}), and amount of residual char (char %), are summarized in Table 2. The minor weight loss observed below 130 °C for both lignin samples was attributed to the gradual evaporation of water. As shown, the weight loss of E3 due to water evaporation was lower than that of the kraft lignin, confirming that the lignin ester had a lower affinity for water and higher hydrophobicity (Gordobil *et al.* 2016). These results correspond to the contact angle analyses presented in the following section. For the kraft lignin, the main weight loss stage occurred in the temperature range between 205 to 600 °C, with maximum degradation at 345 °C. The thermal parameter $T_{5\%}$ values for the kraft lignin and E3 remained almost unchanged (≈ 205 °C). However, according to the DTG curves, E3 showed a two-step degradation process, distinctly different from that of the kraft lignin. As shown in the TGA and DTG curves of the E3, the first degradation process occurred in the temperature range

between 205 to 320 °C, with maximum degradation at 250 °C, while a second degradation process occurred in the temperature range between 320 to 600 °C, with a maximum degradation at 385 °C. Previous research has confirmed that introduction of a long-oleyl chain into the lignin macromolecule creates this two-step degradation (Xing *et al.* 2017). The first degradation phase is associated with the degradation of hydrocarbon chains (mainly involving the introduced long-aliphatic chain), while the second degradation phase may present the degradation of the lignin skeleton. In addition, the value of residual char for E3 decreased to 34.8%, compared to 43.2% for the kraft lignin. Therefore, the lignin ester obtained in this work has similar thermal properties to lignin esters obtained using acyl chlorides and organic solvents (Gordobil *et al.* 2016; Xing *et al.* 2017).

Sample	<i>T</i> ₅% (°C)	T _{max} (°C)		Char (%)	T_g (°C)
Kraft lignin	205	345		43.2	124.4
E3	205	250	385	34.8	108.1

Table 2. Thermal Properties of Kraft Lignin and Lignin Ester (E3)

Differential scanning calorimetry is commonly used to define the T_g of polymers. Figure S2 shows the DSC curves of the kraft lignin and lignin ester (E3). Kraft lignin is a rigid, condensed aromatic molecule, which possesses strong hydrogen bonding intermolecular interactions caused by its hydroxyl groups. This leads to poor thermal mobility and thermoplasticity (Koivu *et al.* 2016). As shown in Table 2, the T_g of the kraft lignin was relatively high (124.4 °C), which agrees with literature data (Cui *et al.* 2013; Hulin *et al.* 2015). However, the curve of the E3 showed a clear and low T_g at 108.1 °C, which corresponds to the literature (Koivu *et al.* 2016). Thus, a considerable reduction in the T_g of E3 compared to that of the kraft lignin was observed. After esterification, hydroxyl groups were substituted with ester groups, resulting in reduced hydrogen bonding and introduction of a long, flexible aliphatic chain. This lowered the glass transition point and improved the thermoplasticity of the lignin (Dehne *et al.* 2016).

Hydrophobic Properties of the Lignin Ester

The contact angles of liquids on solid surfaces provide direct information about the wetting behaviors of the surfaces. The contact angles with water of the kraft lignin and lignin ester (E3) were measured to analyze changes in lignin hydrophobicity. A remarkable difference between the contact angle of the kraft lignin and E3 can be seen in Fig. 8. With increased time, the contact angle of the kraft lignin sharply decreased compared to that of the E3. At 2 s, the contact angle of the kraft lignin was 30.1°, which was much lower than that of E3 (109.8°). After esterification, the contact angle of E3 was higher and more stable than that of the kraft lignin. This indicated the wetting properties of the lignin ester against water were remarkably improved, and that esterification is an effective method to endue lignin with good hydrophobicity.



Fig. 8. Contact angles of KL and lignin ester (E3) (Images were recorded at 2 s)

CONCLUSIONS

- 1. A green method for esterification of kraft lignin and oleic acid in water at room temperature was successfully achieved.
- 2. Surfactant-combined microreactors were formed using TsOH/DBSA, which were able to solubilize kraft lignin and disperse oleic acid.

- 3. Increasing oleic acid dosage had no effect on improving the degree of esterification, instead, using a higher DBSA dosage at room temperature is a good option for esterification.
- 4. Structural characterization confirmed successful esterification of kraft lignin with oleic acid, and improved thermoplasticity and hydrophobicity of the lignin ester.
- 5. The PSA results suggested the possibility for preparation of lignin-ester nanoparticles using a micellization method.

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REFERENCES CITED

- An, L., Si, C., Wang, G., Sui, W., and Tao, Z. (2019). "Enhancing the solubility and antioxidant activity of high-molecular-weight lignin by moderate depolymerization *via in situ* ethanol/acid catalysis," *Industrial Crops and Products* 128, 177-185. DOI: 10.1016/j.indcrop.2018.11.009
- An, L., Wang, G., Jia, H., Liu, C., Sui, W., and Si, C. (2017). "Fractionation of enzymatic hydrolysis lignin by sequential extraction for enhancing antioxidant performance," *International Journal of Biological Macromolecules* 99, 674-681. DOI: 10.1016/j.ijbiomac.2017.03.015
- Baile, M., Chou, Y. J., and Saam, J. C. (1990). "Direct polyesterifcation in aqueous emulsion," *Polymer Bulletin* 23(3), 251-257. DOI: 10.1007/BF01032438
- Chen, L., Dou, J., Ma, Q., Li, N., Wu, R., Bian, H., Yelle, D. J., Vuorinen, T., Fu, S., Pan, X., et al. (2017). "Rapid and near-complete dissolution of wood lignin at ≤80 °C by a recyclable acid hydrotrope," Science Advances 3(9), e1701735. DOI: 10.1126/sciadv.1701735
- Cui, C., Sadeghifar, H., Sen, S., and Argyropoulos, D. S. (2013). "Toward thermoplastic lignin polymers; Part II: Thermal & polymer characteristics of kraft lignin & derivatives," *BioResources* 8(1), 864-886. DOI: 10.15376/biores.8.1.864-886
- Dehne, L., Babarro, C. V., Saake, B., and Schwarz, K. U. (2016). "Influence of lignin source and esterification on properties of lignin-polyethylene blends," *Industrial Crops and Products* 86, 320-328. DOI: 10.1016/j.indcrop.2016.04.005
- Gordobil, O., Herrera, R., Llano Ponte, R., and Labidi, J. (2017). "Esterified organosolv lignin as hydrophobic agent for use on wood products," *Progress in Organic Coatings* 103, 143-151. DOI: 10.1016/j.porgcoat.2016.10.030
- Gordobil, O., Robles, E., Egüés, I., and Labidi, J. (2016). "Lignin-ester derivatives as novel thermoplastic materials," *RSC Advances* 6(90), 86909-86917. DOI: 10.1039/C6RA20238A

Hulin, L., Husson, E., Bonnet, J. P., Stevanovic, T., and Sarazin, C. (2015). "Enzymatic transesterification of kraft lignin with long acyl chains in ionic liquids," *Molecules* 20(9), 16334-16353. DOI: 10.3390/molecules200916334

Hult, E.-L., Koivu, K., Asikkala, J., Ropponen, J., Wrigstedt, P., Sipilä, J., and Poppius-Levlin, K. (2013). "Esterified lignin coating as water vapor and oxygen barrier for fiber-based packaging," *Holzforschung* 67(8), 899-905. DOI: 10.1515/hf-2012-0214

Ibrahim, M. N. M., Ahmed Haras, M. R., Sipaut, C. S., Aboul Enein, H. Y., and Mohamed, A. A. (2010). "Preparation and characterization of a newly water soluble lignin graft copolymer from oil palm lignocellulosic waste," *Carbohydrate Polymers* 80(4), 1102-1110. DOI: 10.1016/j.carbpol.2010.01.030

Kai, D., Tan, M. J., Chee, P. L., Chua, Y. K., Yap, Y. L., and Loh, X. J. (2016).
"Towards lignin-based functional materials in a sustainable world," *Green Chemistry* 18(5), 1175-1200. DOI: 10.1039/C5GC02616D

- Koivu, K. A., Sadeghifar, H., Nousiainen, P. A., Argyropoulos, D. S., and Sipilä, J. (2016). "Effect of fatty acid esterification on the thermal properties of softwood kraft lignin," ACS Sustainable Chemistry & Engineering 4(10), 5238-5247. DOI: 10.1021/acssuschemeng.6b01048
- Laurichesse, S., Huillet, C., and Avérous, L. (2014). "Original polyols based on organosolv lignin and fatty acids: New bio-based building blocks for segmented polyurethane synthesis," *Green Chemistry* 16(8), 3958-3970. DOI: 10.1039/C4GC00596A
- Lewis, H., Brauns, F., Buchanan, M., and Brookbank, E. (1943). "Lignin esters of monoand dibasic aliphatic acids," *Industrial & Engineering Chemistry* 35(10), 1113-1117. DOI: 10.1021/ie50406a020
- Luo, S., Cao, J., and McDonald, A. G. (2017). "Esterification of industrial lignin and its effect on the resulting poly(3-hydroxybutyrate-co-3-hydroxyvalerate) or polypropylene blends," *Industrial Crops and Products* 97, 281-291. DOI: 10.1016/j.indcrop.2016.12.024
- Manabe, K., Iimura, S., Sun, X. M., and Kobayashi, S. (2002b). "Dehydration reactions in water. Brønsted acid- surfactant-combined catalyst for ester, ether, thioether, and dithioacetal formation in water," *Journal of the American Chemical Society* 124(40), 11971-11978. DOI: 10.1021/ja026241j
- Manabe, K., and Kobayashi, S. (2002a). "Dehydrative esterification of carboxylic acids with alcohols catalyzed by polymer-supported sulfonic acids in water," *Advanced Synthesis & Catalysis* 344(3-4), 270-273. DOI: 10.1002/1615-4169(200206)344:3/4<270::AID-ADSC270>3.0.CO;2-7
- Pawar, S. N., Venditti, R. A., Jameel, H., Chang, H. M., and Ayoub, A. (2016).
 "Engineering physical and chemical properties of softwood kraft lignin by fatty acid substitution," *Industrial Crops and Products* 89, 128-134. DOI: 10.1016/j.indcrop.2016.04.070
- Schutyser, W., Renders, T., Van den Bosch, S., Koelewijn, S. F., Beckham, G., and Sels, B. F. (2018). "Chemicals from lignin: An interplay of lignocellulose fractionation, depolymerisation, and upgrading," *Chemical Society Reviews* 47(3), 852-908. DOI: 10.1039/C7CS00566K
- Seo, J. H., Jeong, H., Lee, H. W., Choi, C. S., Bae, J. H., Lee, S. M., and Kim, Y. S. (2019). "Characterization of solvent-fractionated lignins from woody biomass treated via supercritical water oxidation," *Bioresource Technology* 275, 368-374. DOI: 10.1016/j.biortech.2018.12.076

Ten, E., and Wilfred V. (2015). "Recent developments in polymers derived from industrial lignin," *Journal of Applied Polymer Science* 132(24), 42069. DOI: 10.1002/app.42069

Teramoto, Y., Lee, S. H., and Endo, T. (2009). "Phase structure and mechanical property of blends of organosolv lignin alkyl esters with poly(ε-caprolactone)," *Polymer Journal* 41(3), 219. DOI: 10.1295/polymj.PJ2008301

Thielemans, W., and Wool, R. P. (2005). "Lignin esters for use in unsaturated thermosets: Lignin modification and solubility modeling," *Biomacromolecules* 6(4), 1895-1905. DOI: 10.1021/bm0500345

- Van Dam, J. E., De Klerk-Engels, B., Struik, P. C., and Rabbinge, R. (2005). "Securing renewable resource supplies for changing market demands in a bio-based economy," *Industrial Crops and Products* 21(1), 129-144. DOI: 10.1016/j.indcrop.2004.02.003
- Van der Weerd, J., Van Loon, A., and Boon, J. J. (2005). "FTIR studies of the effects of pigments on the aging of oil," *Studies in Conservation* 50(1), 3-22. DOI: 10.1179/sic.2005.50.1.3
- Wang, C., Kelley, S. S., and Venditti, R. A. (2016). "Lignin-based thermoplastic materials," *ChemSusChem* 9(8), 770-783. DOI: 10.1002/cssc.201501531
- Wang, G., Liu, X., Yang, B., Si, C., Parvez, A. M., Jang, J., and Ni, Y. (2019). "Using green γ-valerolactone/water solvent to decrease lignin heterogeneity by gradient precipitation," ACS Sustainable Chemistry & Engineering 7(11), 10112-10120. DOI: 10.1021/acssuschemeng.9b01641
- Wu, M., Pang, J., Lu, F., Zhang, X., Che, L., Xu, F., and Sun, R. (2013). "Application of new expansion pretreatment method on agricultural waste. Part I: Influence of pretreatment on the properties of lignin," *Industrial Crops and Products* 50, 887-895. DOI: 10.1016/j.indcrop.2013.08.047
- Xing, Q., Ruch, D., Dubois, P., Wu, L., and Wang, W. (2017). "Biodegradable and highperformance poly (butylene adipate-co-terephthalate)–lignin UV-blocking films," ACS Sustainable Chemistry & Engineering 5(11), 10342-10351. DOI: 10.1021/acssuschemeng.7b02370
- Zhao, X., Zhang, Y., Hu, H., Huang, Z., Qin, Y., Shen, F., Huang, A., and Feng, Z. (2019). "Effect of lignin esters on improving the thermal properties of poly(vinyl chloride)," *Journal of Applied Polymer Science* 136(11), Article ID 47176. DOI: 10.1002/app.47176
- Zhou, S., Liu, L., Wang, B., Xu, F., and Sun, R. (2012). "Microwave-enhanced extraction of lignin from birch in formic acid: Structural characterization and antioxidant activity study," *Process Biochemistry* 47(12), 1799-1806. DOI: 10.1016/j.procbio.2012.06.006

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SUPPLEMENTARY INFORMATION



Fig. S1. TGA and DTG curves of KL and lignin ester (E3)



Fig. S2. DSC curves of KL and lignin ester (E3)