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Biorefinery Lignosulfonates from Sulfite-Pretreated Softwoods as Dispersant for Graphite

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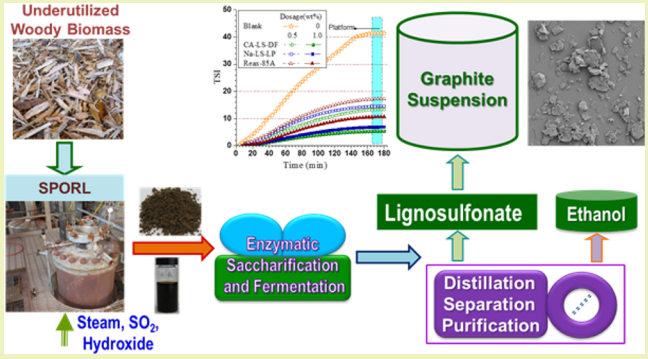
Supporting Information

ABSTRACT: Two biorefinery lignosulfonates (LSs), Ca-LS-DF and Na-LS-LP, were, respectively, isolated from pilot-scale sulfite-pretreated spent liquor of lodgepole pine and fermentation residue of Douglas-fir harvest forest residue. The molecular weights of Na-LS-LP and Ca-LS-DF were approximately 9 000 and 11 000 Da, respectively. The two LSs were applied as dispersant for graphite in aqueous suspensions. The dispersion stability was evaluated by a scanning electron microscope and Turbiscan Lab Expert. LS performance in modifying graphite was better than that of a commercial dispersant Reax-85A as indicated by the Turbiscan TSI values, zeta potential of suspension particles, and SEM imaging. The practical importance of this study lies in the fact that the pilot-scale sulfite pretreatments that produced the two LSs also produced excellent bioethanol yields at high titer without detoxification and washing, suggesting the LSs are a true value-added coproduct for high yield biofuel production.



KEYWORDS: *Lignosulfonate, Graphite, Dispersion stability, Lignin-coproducts, Biorefinery*

INTRODUCTION

Graphene is a class of two-dimensional carbon nanostructured materials with a honeycomb hexagonal lattice.[1] It has been used commercially as a graphene-infused 3-D printer powder. It also attracted great research interest recently because of its unique mechanical structural, electrical, and thermal properties,[2−4] for a variety of potential technological applications.[5] Graphene is not soluble in water. The strong $\pi-\pi$ stacking and van der Waals interactions between single graphene layer often result in irreversible agglomeration and precipitation.[6] A stable aqueous graphene dispersion system is required for many graphene processing applications, such as electrically conductive coatings,[7,8] supercapacitors,[9,10] and fabrication of lithium-ion battery, etc. Currently, stable aqueous graphene dispersions are obtained by adsorption of water-soluble anionic polymers onto the graphene surface to modify solid graphene surface hydrophobicity.[11] These water-soluble anionic polymers included sodium 4-styrenesulfonate, naphthalene diimide surfactants, sodium carboxymethyl cellulose, and anionic urethane acrylate are expensive. The rationale of the present study is to find renewable and low cost dispersants for dispersing graphene in suspension.

Lignosulfonate (LS) as an amphiphilic biopolymer with an anionic group was often widely used as a dispersant,[12] including for formulating stable aqueous graphene suspensions.[1,13,14] LS is renewable and commercially available from commercial sulfite pulping. LS is relatively low cost compared with aforementioned dispersants. However, with the gradual closure of sulfite pulping mills throughout the world, LS becomes scarce. Fortunately LS can also be produced from biorefinery operations using sulfite chemistry such as sulfite pretreatment to overcome the recalcitrance of lignocelluloses (SPORL).[15−18] LS from biorefineries may have different properties from those from sulfite pulping due to the differences in sulfite reaction conditions and delignification chemistry. The objective of the present study is to evaluate the potential of biorefinery LSs for dispersing graphene suspensions. This also provides needed opportunities for valorization of biorefinery lignin to improve biorefinery economics for commercialization. Two biorefinery LSs, Na-LS-LP and Ca-LS-DF, were compared with a commercial LS for dispersing graphene in aqueous suspensions.

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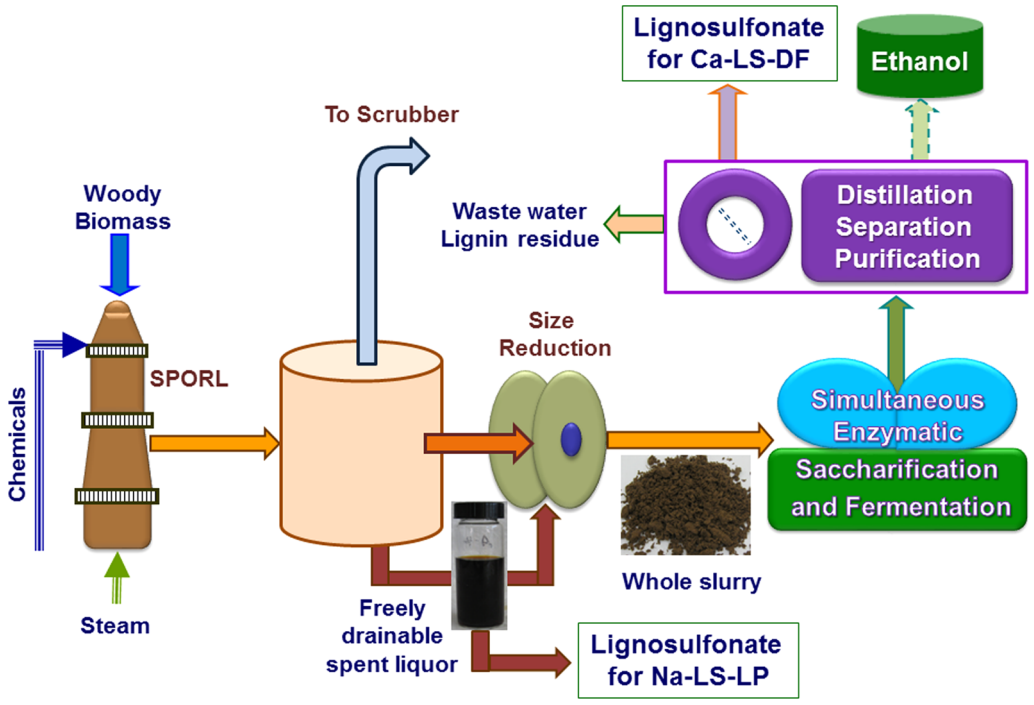

Figure 1. Schematic diagram shows where the two biorefinery lignosulfoantes originated in a pilot-scale forest biorefinery operation.

The Na-LS-LP was from the SPORL spent liquor of lodgepole pine,[19] and Ca-LS-DF was isolated from the fermentation broth of the whole slurry of SPORL pretreated Douglas-fir forest residue.[20] Very high ethanol yields were produced at high titers under the conditions which produced the two biorefinery LSs.[19,20] Therefore, this study has practical relevance for increasing revenue streams to improve process economics for sustainable forest biorefinery operations.

MATERIALS AND METHODS

Materials. Ca-LS-DF was separated from the residue of enzymatic saccharification and fermentation of the whole slurry of a Douglas-fir forest residue (FS-10) pretreated by SPORL at a pilot-scale facility[20] as shown schematically in Figure 1. The whole slurry was produced by disk milling collected SPORL pretreated solids together with the collected spent liquor. Detailed description of the FS-10, the pretreatment by SPORL, enzymatic saccharification, and fermentation along with all process mass balance data can be found in two previous studies.[17,20] Table 1 briefly listed the process conditions for SPORL and enzymatic saccharification and fermentation. Excellent ethanol yield of 284 L/tonne residue was achieved at a moderate cellulase (CTec3) loading.[20] The fermentation residue contained solubilized LS, sulfonated solid lignin, and a small amount of unhydrolyzed polysaccharides. The fermentation residue was filtered. The decanted solid residue was washed with distilled water at ambient temperature. The supernatant containing primarily soluble LS was dried at 50 °C for 60 h until no further weight loss was observed after centrifuging at 10 000 rpm for 30 min. The final dried LS was labeled as Ca-LS-DF.

Another biorefinery sodium LS (Na-LS-LP) was directly separated from the freely drainable spent liquors (Figure 1) of SPORL pretreated mountain pine beetle killed lodgepole pine (BKLP) through dialysis as described previously.[21] The liquors were first centrifuged at 4000 rpm for 20 min to remove solids. Two membranes ES404 and FP200 (Xylem PCI Membranes, Kostrzyn, Poland) with cutoff molecular weight of 4 and 200 kDa, respectively, were used to remove low molecular weight impurities such as sugars and sugar degradation products (furans and organic acids, etc.) and very fine particular matters.

Table 1. Feedstock and Pretreatment Conditions Used for the Production of the Two Biorefinery LSs along with LS and Ethanol Yields

	Ca-LS-DF[20]	Na-LS-LP[19]
feedstock[a]	FS-10	BKLP
Pretreatment Conditions		
T and time	145 °C for 4 h	165 °C for 60 min
chemical loadings on wood	2.4 wt % free SO_2	2.2 wt % H_2SO_4
	6.5 wt % $Ca(HSO_3)_2$	8.0 wt % $NaHSO_3$
liquor to wood ratio	3.55	3.00
cellulase (CTec3) loading	35 mL/kg untreated wood	35 mL/kg untreated wood
fermentation total solids	16.7 wt %	20.0 wt %
ethanol yield and titer	284 (L/tonne); 41.9 g/L	288 (L/tonne); 52.2 g/L
LS yield[b]	130 kg/tonne	68 kg/tonne

[a]FS-10, Douglas-fir forest residue; BKLP, mountain pine beetle killed lodgepole pine. [b]As Klasson lignin based on mass balance.

Reax-8A, a commercial sodium LS, commonly used as a dispersant for dyes, pesticides, graphite, and carbon nanofibers[22] was from WestRock Corporation (Richmond, VA, USA),

Graphite was purchased from Aladdin Company (Shanghai, China). The surface area of the graphite sample was 4.16 m^2/g measured by BET method using a commercial instrument (TRISTAR II3020, Mircromeritics Instrument Co., Norcross, GA, USA).

Fourier Transform Infrared and Hydrogen Nuclear Magnetic Resonance Spectra. The three LS samples were analyzed by Fourier transform infrared (FTIR) spectroscopy using a NicoLet 380 FT-IR spectrometer (Thermo Scientific Nicolet, Waltham, MA). Spectra were obtained on a potassium bromide pellet containing 1% dried sample. The spectra resolution was 4 cm^{-1} in a frequency range of 500−4000 cm^{-1}, and the results were averages of 64 scans.

Molecular Weight. The molecular weight distributions of the LS samples were determined by aqueous gel-permeation chromatography (GPC) using Ultrahydrogel 120 and Ultrahydrogel 250 columns and UV detection at 280 nm (Waters 2487, Waters Co., MA). Sodium

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nitrate was used as the mobile phase at a flow rate of 0.50 mL/min. Sodium polystyrenesulfonates were used as a standard for calibration.

LS Functional Groups Content. The low molecular weight organic acids, inorganic salts, and other impurities of all samples were first removed by anion and cation exchange resins before determining functional groups content. The sulfur content of LS was determined by elemental analyses (model 3000, Eurovector, Milan, Italy). The sulfonic acid groups content was calculated assuming all measured sulfur was associated with sulfonic acid groups.

The carboxyl groups content of a LS was determined by nonaqueous conductometric titration[23] using an automatic potentiometric titrator (809 Titrando, Metrohm Corp., Switzerland). The p-hydroxybenzoic acid was used as the internal standard and the tetrabutyl aqueous ammonia standard solution was used as the titrant to measure carboxyl groups content.

The phenolic hydroxyl groups content was measured using the FC-reagent method.[24] Dried LS of 50 mg was dissolved in 100 mL of distilled water in a flask. An aliquot of 15 mL of the LS solution was mixed thoroughly with 1.5 mL of the FC-reagent and then added 5 mL of 200 g/L Na_2CO_3 solution and adjusted the volume to 25 mL with distilled water. The mixture was kept stirring for 2 h at 30 °C, and its absorption at 760 nm was measured by a spectrophotometer (UV-2450, Shimadzu, Kyoto, Japan). Vanillin solutions were used for calibration.

Determination of Surface Tension of LS Solutions. LS aqueous solutions at concentrations of 0, 1.0, 2.5, 5.0, 10.0, 20.0, 50.0 g/L were prepared at pH 7.0. All LS solutions were kept stable for 24 h at 25 °C before measurements using a Wilhelmy plate with a Dynamic Contact Angle Meter (Dataphysics Instruments Co. Ltd., Filderstadt, Germany). The experimental error was <0.03 mN/m.

Determination of Zeta Potential of Graphite Particles. The zeta potential of graphite particles was measured using a ZetaPALS analyzer (Brookhaven Instruments, Holtsville, NY). Graphite aqueous solutions of mass concentration 3.0 wt % with different dispersant concentrations were prepared. The pH of all samples were adjusted to 7.0. After shaking at 200 rpm for 3 h at 25 °C, five replicate samples were taken and analyzed. The averages were reported.

Scanning Electron Microscope (SEM). The SEM images of dispersant-dye suspension were recorded with a Nova Nano SEM instrument (Zeiss Netherlands BV, Sliedrecht, The Netherlands). The samples were prepared by dropping diluted graphite aqueous solutions with dispersant onto the silicon wafer graphite.

Turbiscan Lab Expert Stability Analyses. Graphite was ground by a planetary mill for 60 min and sieved to obtain graphite particles with mean diameter of 100 nm for dispersion experiments. A graphite aqueous suspension of 20 g was prepared using 0.6 g of the ground and sieved graphite (3 wt %) with a dispersant dosage of 0.5 wt % based on graphite. The prepared graphite suspension was adjusted to pH 7.0 before being placed into cylindrical glass tubes for analysis by a Turbiscan Lab analyzer (Formulaction Co., L'Union, France) to evaluated dispersion stability. The stability index (TSI value) of an aqueous graphite suspension was calculated based on the measured incident and back scattered light intensities in the entire height (40 mm) of aqueous graphite suspension in 3 h.[14,25]

RESULTS AND DISCUSSION

FTIR Spectra of LS. The FTIR spectra of the three LSs, Ca-LS-DF, Na-LS-LP, and Reax-85A are shown in Figure 2. The chemical shift assignments are provided in the Supporting Information (Table S1). The FTIR spectra showed some differences in the COO-vibration (~1610 and 1422 cm^{-1}), specifically, Reax-85A had a slightly broader dip at ~1610 cm^{-1} and a lower absorption intensity at 1422 cm^{-1} than the corresponding band for Ca-LS-DF and Na-LS-LP, suggesting that Reax-85A had more carboxyl groups content. C−O−C (635−638 cm^{-1}) stretching vibration also showed some differences. For example, Ca-LS-DF has lower activities in C−O−C stretching than the other two LSs. The bands of

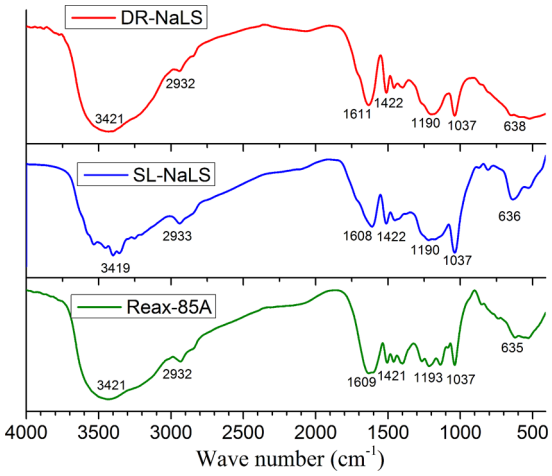

Figure 2. FTIR spectra of the three LSs evaluated.

asymmetric and S═O stretching vibration of SO_3^{2-} (1190 and 1037 cm^{-1}) were broader for the biorefinery LSs, Ca-LS-DF, and Na-LS-LP, than Reax-85A, indicating biorefinery LSs had higher sulfonic groups content. These qualitative analyses agreed with quantitative analyses in the following discussions. The 1H-NMR spectra of three LSs were also recorded and showed no difference (not shown).

Molecular Weight and the Functional Groups. Dispersion performance of LS in aqueous solution systems are primarily dictated by its molecular weight and the contents of functional groups such as sulfonic acid, phenolic hydroxyl, and carboxyl groups.[12,14] The weight-averaged molecular M_w of Ca-LS-DF and Na-LS-LP was 10 650 and 8 870 Da, respectively, higher than that of Reax-85A. Also, both Na-LS-LP and Ca-LS-DF had a slightly broader distribution (Figure 3).

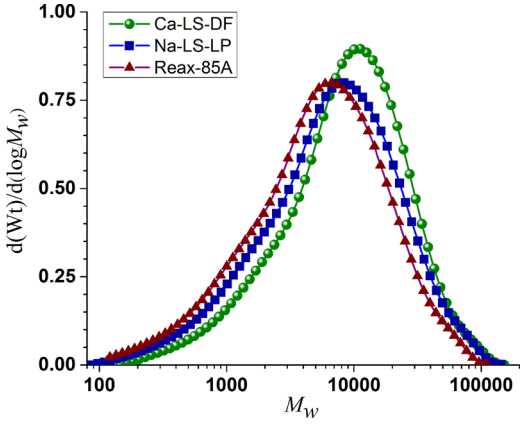

Figure 3. Molecular weight distribution of the three LSs.

As listed in Table 2, Reax-85A had less sulfonic acid groups content but had higher carboxyl groups content than Na-LS-LP and Ca-LS-DF. Phenolic hydroxyl groups contents of the 3 LSs were not substantially different at approximately 1.75 mmol/g. The Ca-LS-DF has a slightly lower sulfonic and higher phenolic hydroxyl group content than Na-LS-LP.

Surface Tension of LS in Aqueous Solution. The graphite particles were dispersed in solutions by adsorbing a dispersant to increase the wettability of graphite particle surfaces and reduce spontaneous aggregation. Hence, solutions

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Table 2. Functional Group Contents and Molecular Weights of Three LSs

	functional group content (mmol/g)			molecular weight		
sample	sulfonic	phenolic hydroxyl	carboxyl	M_w	M_n	M_w/M_n
Ca-LS-LF	1.35	1.75	0.84	10650	3730	2.86
Na-LS-LP	1.47	1.76	0.73	8870	3120	2.84
Reax-85A	1.23	1.75	0.90	8020	3240	2.47

with low surface tension can facilitate wetting solid particles for dispersion.[26] The surface tensions of three LS solutions at different concentrations are presented in Figure 4. With the

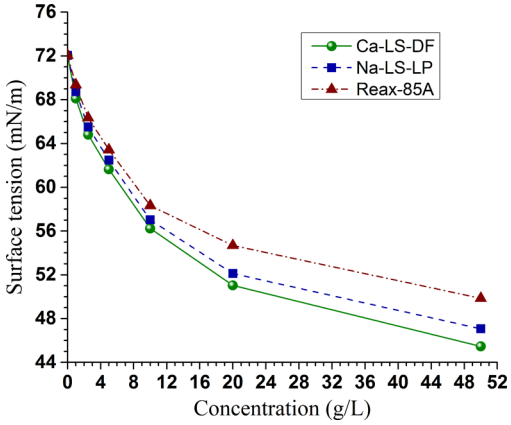

Figure 4. Surface tension of LS solutions at 25 °C.

increase in LS concentration, the surface tension of the LS solution decreased continuously. No critical aggregation concentration (CAC) was observed for the three LS samples. It appears that dispersant with a higher molecular weight (Table 2) resulted in a lower surface tension of the solution, in agreement with previous studies.[27,28] The hydrophobic skeleton of LS with higher M_w appears as random spheres in shape, so it cannot form a regular arrangement at the interfacial phase.[27] Ca-LS-LF with a higher molecular weight had higher surface activities in an aqueous solution and much stronger hydrophobicity than Na-LS-LP and Reax-85A each with a lower molecular weight.

Zeta Potential of Graphite Particles in Aqueous Solution. Zeta potential was commonly used to characterize interfacial electrostatic interactions. The adsorption between LS and graphite particle surfaces were mainly through hydrogen bonding, electrostatic, hydrophobic interactions, and van der Waals.[1,29] Sulfonic acid, phenolic hydroxyl, and carboxyl groups of LS can interact with graphite particles and affect its dispersion. Zeta potential of graphite particles was approximately −10 mV without dispersants and was increased (absolute value) continuously with dispersant application dosage (Figure 5). However, the increase in zeta potential diminishes as LS dosage over 1.0 wt % of graphite. Application of Na-LS-LP resulted in slightly higher graphite particle zeta-potential than Ca-LS-DF and Reax-85A due to its more negatively surface charged groups (sulfonic acid, phenolic hydroxyl, and carbonyl groups).

Dispersion Stability of LS on Graphite. SEM images revealed substantial graphite particle aggregations in an aqueous suspension without dispersant (Figure 6a). Typical sizes of aggregates were approximately 2−4 μm; however, very large

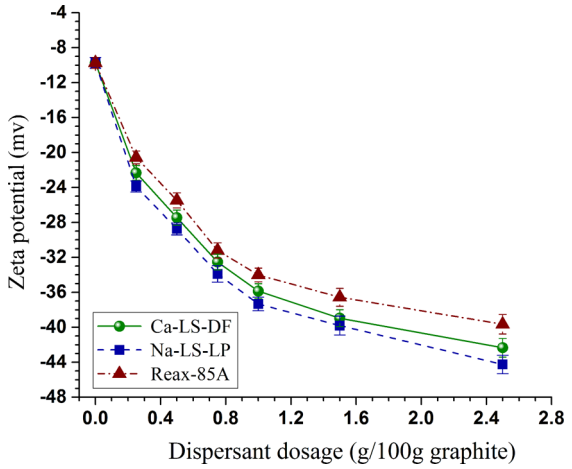

Figure 5. Zeta potential of graphite particles at different LS loadings.

aggregates were also observed. With the application of the two biorefinery LSs, aggregation was substantially reduced (Figure 6b,c), especially the application of Na-LS-LP with typical aggregate size of approximately 1 μm (Figure 6c). The application of Reax-85A improved dispersion but only had minor improvement in reducing aggregation (Figure 6d).

The Turbiscan Stability Index (TSI) was used to measure the dispersion stability of graphite aqueous suspensions with and without LS. TSI not only can measure the long-term stability of opaque and concentrated dispersions with a single instrument but also can more easily and accurately detect dispersion instability than naked eyes.[30] TSI accounts all processes such as sedimentation and settling and can be used for estimating the suspension stability.[14,31] The reported TSI value was a statistical factor related to the variation rate of transmission and backscattering light intensity of a dispersion. An increase in TSI means that particle sedimentation was fast and the thickness of sediment was increased. Therefore, a high TSI value means that a suspension had a low stability.[14,21,31] The TSI of a blank graphite suspension (without dispersant) increased rapidly with time to approximately 40 after 140 min (Figure 7). The very high TSI value of the blank suspension suggests graphite particles were unstable and rapid sedimentation took place due to aggregation (Figure 6a). The TSI values of a graphite suspension decreased with the application of LS and increasing LS concentrations.

The graphite suspensions applied with Ca-LS-DF resulted in the lowest TSI of approximately 13 and 6 at both application dosages of 0.5 and 1.0 wt %, respectively (Figure 7). The higher M_w of Ca-LS-DF may have improved the wettability and surface activity to increase steric hindrance. However, the difference in TSI between the applications of the two biorefinery LSs, Ca-LS-DF and Na-LS-LP, was small of approximately 1 unit or 10% (Figure 7), comparing with the differences of 4 units or 35−40% between applying these two biorefinery LSs with that of applying Reax-85A.

CONCLUSIONS

High value utilization of biorefinery lignin with minimal processing is critical to improve the commercial viability of biofuel production. This study demonstrated two biorefinery lignosulfonates isolated from the spent liquors and fermentation residue of SPORL pretreated softwoods as dispersants for graphite. Both biorefinery LSs showed better performance in

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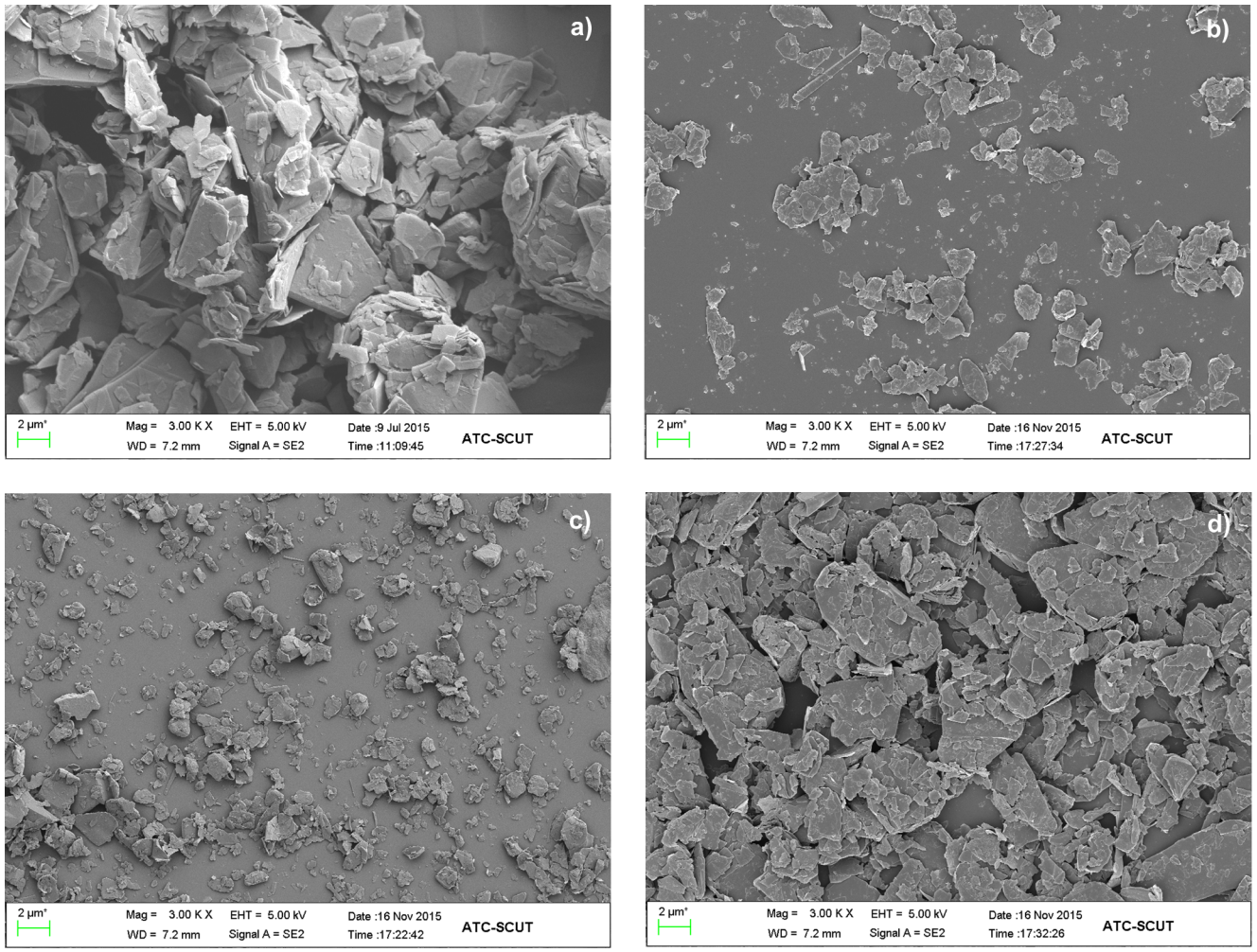

Figure 6. SEM images of graphite (a) control sample (no dispersant); (b) graphite aqueous solution with Ca-LS-DF; (c) graphite aqueous solution with Na-LS-LP; and (d) graphite aqueous solution with Reax-85A.

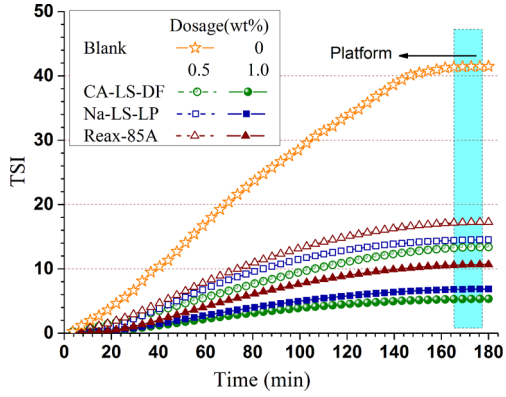

Figure 7. Effects of dispersant dosage on the Turbiscan Stability Index (TSI) of graphite suspension. Data are reported as a function of time (0–3 h).

dispersing graphite suspension than a commercial dispersant Reax-85A. Since, the SPORL conditions under which the two biorefinery LSs produced also resulted in excellent sugar and biofuel yields at high titer without detoxification and solid washing, this study has practical significance for sustainable biofuel production from woody biomass. The study also provided a low cost and sustainable solution for dispersing graphite in a variety of promising applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b01664.

Table of the assignments of lignin IR and ^{1}H NMR spectral bands (PDF)

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Notes

The authors declare the following competing financial interest(s): Zhu is a co-inventor of the SPORL pretreatment process.

This work is conducted on official government time of Zhu while Qin and Wu were visiting scientists at the USDA Forest Products Lab.

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