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Deconstruction of Malaysian Agro-Wastes with Inexpensive and Bifunctional Triethylammonium Hydrogen Sulfate Ionic Liquid

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Abstract. Ionic liquids (ILs) are known to be very effective at deconstructing biomass, but, they are typically 5-20 times more expensive than molecular solvents; this is a major impediment to the utilisation of ILs in biorefinery applications. In view of this, this paper is the first to report a preliminary study on the use of inexpensive and bifunctional triethylammonium hydrogen sulfate ionic liquid, $[N_{2220}][HSO_4]$ IL, in deconstructing two Malaysian agro-wastes, oil palm empty fruit bunches (OPEFB) and coconut husk. The $[N_{2220}][HSO_4]$ IL was synthesised *via* simple acid-base neutralisation route between two inexpensive precursors: sulfuric acid, H_2SO_4, and triethylamine, N_{222}. The results of deconstruction of OPEFB and coconut husk under the applied conditions, IL/H_2O (80/20 wt/wt) at 120 °C for 2 h, proved that the IL provided bifunctional action as: a Brønsted acid catalyst that hydrolysed chemical bonds linking carbohydrate-rich-material (cellulose and hemicellulose) and lignin fractions, and; a delignification agent that dissolved lignin, separating the biopolymer from the carbohydrate-rich-material. The outcomes of this study indicate that the deconstruction of Malaysian agro-wastes for isolating valuable biopolymers can be performed in a more economical and effective way using the $[N_{2220}][HSO_4]$ IL.

INTRODUCTION

Oil palm empty fruit bunches (OPEFB) and coconut husk are two examples of wastes produced in substantial quantities by the agriculture industry in Malaysia. These agro-wastes are typically disposed through conventional technologies, like incineration and composting. However, such technologies produce a wide range of toxic pollutants emitted into the air, land and water. Interestingly, the agro-wastes could be reused in a more innovative way by valorising its biopolymer constituents, cellulose, hemicellulose and lignin, into valuable products, like bioplastics and coating materials. The biopolymers can be extracted through the so called ‘deconstruction process’.

A number of deconstruction processes are available. The ideal process removes lignin to a greater extent, yielding a pulp with a high cellulose content (>90%). The bisulfite process was previously employed, where OPEFB was treated with 6% sodium bisulfite ($NaHSO_3$) solution at 180 °C for 30 min [1]. Unfortunately, the process produced cellulose-pulps with 70% unremoved-lignin [1]. Ionic liquids (ILs) have been actively employed in a number of biomass deconstruction experiments, and this is due to their remarkable properties: negligible vapour pressure, high

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thermal stability, and tuneable chemical properties [2]. Deconstruction of biomass by using ILs can be performed *via* two distinct strategies: 'dissolution' and '*IonoSolv*' [3].

The dissolution disrupts biomass composite that evolved directly from cellulose dissolution [3]. An example of IL that does such an action is 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][CH_3CO_2]$. A study by Rahman *et al.* is amongst the first to employ the $[C_2C_1im][CH_3CO_2]$ IL in deconstructing 5 wt% of OPEFB at 100 °C for 16 h [4]. Despite achieving complete dissolution of OPEFB in the IL, the resultant cellulose pulp still contained ca. 65% unremoved lignin even after such a long period of incubation [4]. It is worth highlighting that the $[C_2C_1im][CH_3CO_2]$ IL is an expensive solvent, costing RM5225/kg at the time of writing (Sigma Aldrich, CAS number: 284049-75-8). Taking into account the aforementioned drawbacks, the utilisation of the $[C_2C_1im][CH_3CO_2]$ IL for large-scale deconstruction of the agro-wastes might not be viable, particularly in the present economic climate.

The *IonoSolv* process dissolves lignin and hemicellulose, leaving cellulose as an intact solid. Protic ILs do this action, and the one currently receiving significant attention in chemical literature is triethylammonium hydrogen sulfate, $[N_{2220}][HSO_4]$. The IL can be made available at bulk scale for \$1.24 kg^{-1} [2], a major boost to economic viability of the *IonoSolv* process. The first study utilising the $[N_{2220}][HSO_4]$ IL to deconstruct *Switchgrass* was reported [2]. Interestingly, the IL displayed substantial lignin removal, far outweighing the lignin removal by the $[C_2C_1im][CH_3CO_2]$ IL. The process was then applied to *Miscanthus and Willow* with great outcomes [5]. As reported by Brandt *et al.*, deconstruction of 9 wt% of *Miscanthus* with the $[N_{2220}][HSO_4]$ IL with 20% water at 120 °C for 4 h resulted in ca. 85% lignin removal [6].

To our knowledge, we are the first to report a preliminary study of deconstruction of OPEFB and coconut husk with the $[N_{2220}][HSO_4]$ IL in Malaysia. First, we show step-by-step synthesis of $[N_{2220}][HSO_4]$ IL through facile neutralisation of triethylamine, N_{222}, and sulfuric acid, H_2SO_4. The results of ^{1}H-NMR and TGA are presented, confirming the IL's chemical structure and thermal stability, respectively. Then, we demonstrate the deconstruction of OPEFB and coconut husk with the $[N_{2220}][HSO_4]$ IL using a detailed flowchart and present some preliminary outcomes.

METHODOLOGY

Materials

Sulfuric acid, H_2SO_4, (95-98%), triethylamine, N_{222}, and absolute EtOH were purchased from Sigma-Aldrich and used as received without further purification. OPEFB as pellets were donated by a local palm mill in Felda Semanchu, Kota Tinggi, Johor, Malaysia, while coconut husk was collected from Jasin, Melaka, Malaysia. After drying in the sun for several days, both biomass samples were ground and sieved, yielding particles with the nominal sizes of 250-500 μm. Using a published protocol, the moisture contents of OPEFB and coconut husk particles were determined to be 6.05 wt% and 9.17 wt%, respectively [7].

Synthesis of $[N_{2220}][HSO_4]$ IL

Referring to a procedure by George *et al.* [2], 10 M of H_2SO_4 (508 g, 5.0 moles) was added dropwise to a mixture of N_{222} (512 g, 5.0 moles) and de-ionised water (500 mL) with vigorous stirring, at room temperature and in an ice bath. After removing excess water by rotary evaporator, the resultant IL was characterised by the following analytical instruments: Proton-Nuclear Magnetic Resonance (^{1}H-NMR) and Thermogravimetric Analysis (TGA).

Deconstruction of Biomass with $[N_{2220}][HSO_4]$ IL

Similar to the protocol used by S. Zahari [7], OPEFB or coconut husk particles (oven-dried weight) was mixed with a $[N_{2220}][HSO_4]/H_2O$ mixture (80/20 wt/wt), giving a total biomass loading of 9 wt%. The resultant sample was incubated in an oven without stirring at 120 °C for 2 h. Upon completion of the incubation, the sample was cooled to room temperature, diluted with EtOH (10 mL), and then filtered through a 542-Whatman filer paper in a Büchner funnel. The filtration step obtained a solid fraction labelled as 'cellulose-rich-material' (CRM) and an EtOH-filtrate. The recovered CRM was repeatedly rinsed with EtOH and later dried at room temperature.

Meanwhile, the excess EtOH was removed from the EtOH-filtrate by rotary evaporation under reduced pressure, yielding a black liquor. De-ionised water was then added to the liquor, whereupon, a black precipitate developed instantaneously. The black precipitate was separated from the liquid by centrifugation at a speed of 6000 r.p.m for

30 minutes. After discarding the liquid, the resultant solid, labelled as 'acid-soluble-lignin' (ASL), was dried in an oven at 50 °C overnight. Equation 1 was applied to determine the recovery of either CRM or ASL.
Recovery of product,

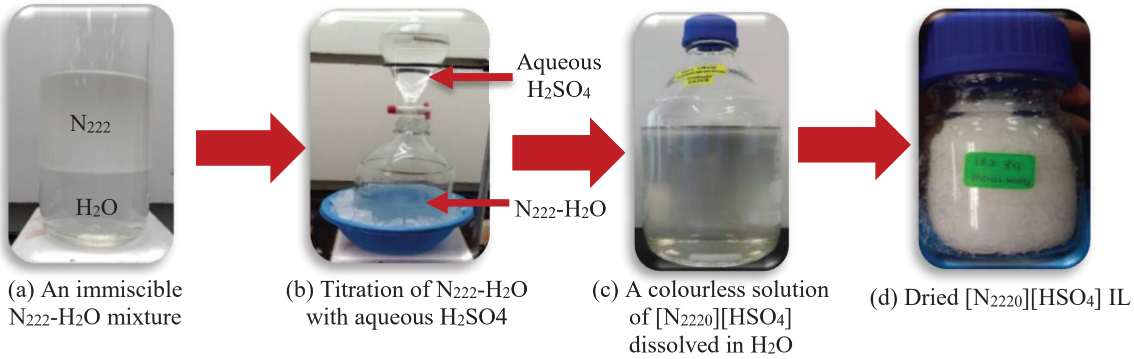
$$\%\text{ (CRM or ASL)} = \frac{m_a}{m_b} \times 100 \tag{1}$$

Where,
m_a = Mass of product (CRM or ASL)
m_b = Mass of pristine biomass particles (OPEFB or coconut husk)

RESULTS AND DISCUSSION

Synthesis and Characterisation of $[N_{2220}][HSO_4]$ IL

FIGURE 1 summarises the overall synthesis procedure of the $[N_{2220}][HSO_4]$ IL that followed an acid-base neutralisation route.



(a) An immiscible N_{222}-H_2O mixture (b) Titration of N_{222}-H_2O with aqueous H2SO4 (c) A colourless solution of $[N_{2220}][HSO_4]$ dissolved in H_2O (d) Dried $[N_{2220}][HSO_4]$ IL

FIGURE 1. Synthesis of the $[N_{2220}][HSO_4]$ IL

Shortly after the N_{222}-H_2O mixture was titrated against the diluted H_2SO_4 (FIGURE 1 (b)), the resultant mixture became warm; an indicative of the formation of new chemical bonds. Upon completion of the H_2SO_4 addition, the immiscible N_{222}-H_2O (FIGURE 1 (a)) turned into a clear solution (FIGURE 1 (c)), which later formed a colourless salt following the evaporation of excess water under reduced pressure (FIGURE 1 (d)). This implies that the reaction products interacted with water molecules most likely *via* intermolecular interactions. Based on the highlighted observations, the synthesis was believed to occur via the proposed mechanism in FIGURE 2.

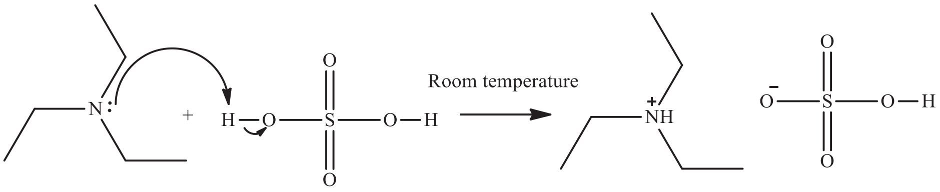


FIGURE 2. The synthesis of the $[N_{2220}][HSO_4]$ IL

The $[N_{2220}][HSO_4]$ IL was firstly characterised by ^{1}H-NMR, and its spectrum is illustrated in FIGURE 3. Expectedly, the δ values of the IL moved downfield (FIGURE 3 (b)), relative to those of the N_{222} reagent (FIGURE 3 (a)). This is a typical pattern when proton nuclei is more deshielded as a consequence of the enhanced inductive effect. As regards to this study, the enhanced inductive effect was most likely to be linked to the formation of N^+ by the protonation of $\underline{N}H$ in N_{222} by $\underline{H}O$ in H_2SO_4, as proposed in FIGURE 2. The N^+, an electron-deficiency species, pulls the electron density around the proton nuclei on C_α and C_β. As a result, the proton nuclei experiences greater effective magnetic field, as reflected by higher frequency absorbed (FIGURE 3 (b)).

The $[N_{2220}][HSO_4]$ IL was then subjected to TGA analysis, and the recorded profile is shown in FIGURE 3 (c). If N_{222} remains unreacted, the resultant TGA profile must have exhibited a rapid mass loss below 100 °C simply because the compound is fairly volatile. Instead, the IL decomposed starting at 280 °C (T_{onset}) (FIGURE 3 (c)); such high-temperature stability was believed to be caused by ionic interactions between $[N_{2220}]^+$ cation and $[HSO_4]^-$ anion.

In summary, both ^{1}H-NMR and TGA analyses (FIGURE 3) strongly suggest that the reaction between N_{222} and H_2SO_4 involved complete proton transfer, yielding $[N_{2220}]^+$ cation and $[HSO_4]^-$ anion, as proposed in FIGURE 2. As reported previously, complete proton transfer would be achieved when the difference of the standard pK_a values for a base and an acid is larger than 10 ($\Delta pK_a > 10$) [7]. The pK_a for N_{222} is ca. 18 while H_2SO_4 has a pK_a value of ca. -3; this seems sufficiently large to enable complete proton transfer.

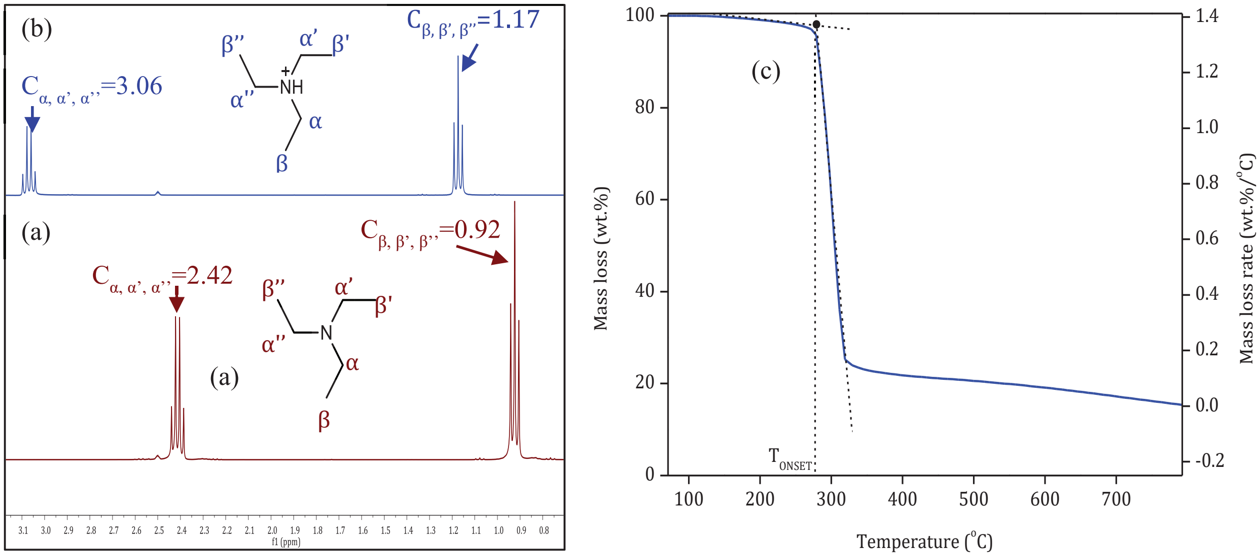


FIGURE 3. ^{1}H-NMR (400 MHz, DMSO) spectra of (a) fresh N_{222}, and; (b) $[N_{2220}][HSO_4]$ IL. (c) TGA profile of $[N_{2220}][HSO_4]$ IL (10 °Cmin^{-1} with N_2 flow rate of 10 mLmin^{-1})

Deconstruction of Biomass with $[N_{2220}][HSO_4]$ IL

FIGURE 4 depicts the overall deconstruction process. The incubation step resulted in a dark mixture (FIGURE 4 (c)); indirect evidence of IL successfully dissolving lignin. This is a typical observation for biomass deconstruction using an ionic liquid comprising $[HSO_4]^-$ anion, as previously observed by Li [9]. After diluting with EtOH, the dark mixture was filtered, yielding two products: (1) a CRM solid likely containing cellulose and hemicellulose (FIGURE 4 (d)), and (2) a dark EtOH-filtrate (FIGURE 4 (e)). Water is an anti-solvent for lignin; thus, development of a black precipitate after adding water to the concentrated filtrate (FIGURE 4 (f)) confirmed that lignin had dissolved in the IL during the course of incubation process. In short, the outcomes of the deconstruction process (FIGURE 4) strongly reflect the $[N_{2220}][HSO_4]$ IL performed two actions concurrently as: (1) a Brønsted acid catalyst, through $[HSO_4]^-$ anion, that hydrolysed chemical bonds, which link CRM and lignin, and; (2) a delignification agent that dissolved lignin, separating lignin from CRM.

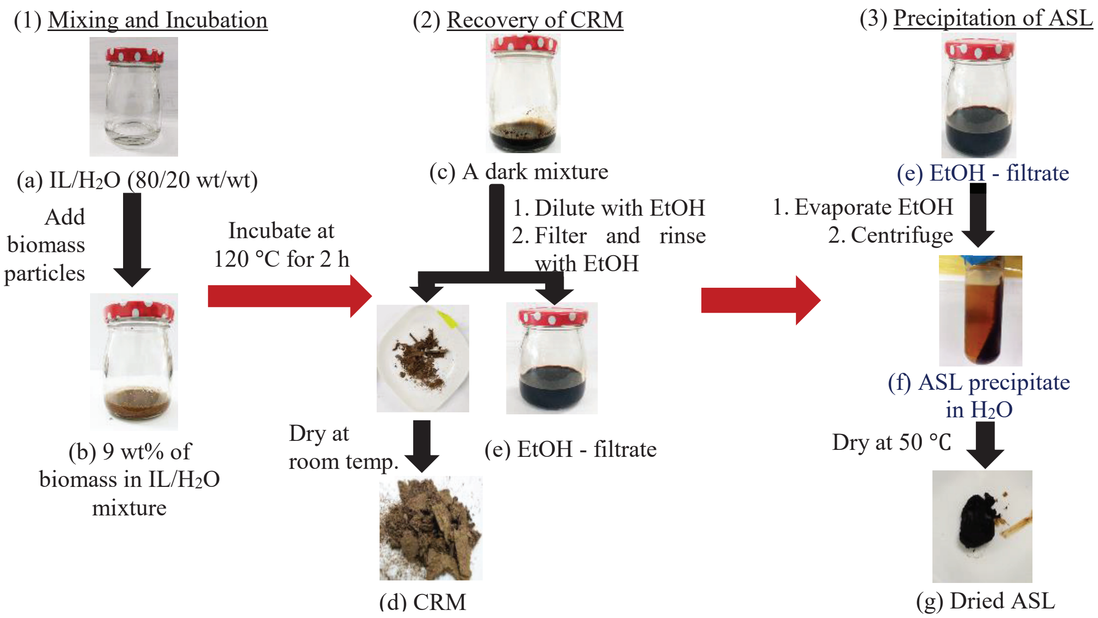


FIGURE 4. Deconstruction of biomass with a $[N_{2220}][HSO_4]/H_2O$ mixture

The results of the deconstruction of OPEFB and coconut husk under the deconstruction conditions, a $[N_{2220}][HSO_4]/H_2O$ (80/20 wt/wt) mixture at 120°C for 2 h, are displayed in FIGURE 5. The typical composition of biopolymers of untreated OPEFB and coconut husk is summarised in TABLE 1. The deconstruction of OPEFB (FIGURE 5 (left)) removed almost the entire lignin from the biomass (relative to the composition of untreated OPEFB in TABLE 1). However, a substantial mass loss was recorded; a plausible sign of most hemicellulose (and cellulose to a lesser extent) severely degraded, yielding undesirable HMF and furfural compounds. These compounds were believed to be dissolved in the reddish-brown solution, obtained following the recovery of ASL precipitate by centrifugation (FIGURE 4 (f)). The severe hemicellulose degradation is likely to be caused by the Brønsted acidity possessed by the $\underline{H}O$ in $[HSO_4]^-$ anion which in turn encourages degradation of hexose and pentose monomers of hemicellulose, as suggested by Shahrul [7]. Unlike OPEFB, the removal of lignin from coconut husk was noticeably modest (FIGURE 5 (right)), relative to the composition of untreated coconut husk in TABLE 1. As reported by Brandt *et al.,* the more the lignin is present in biomass, the longer the incubation period required [10]. Therefore, it could be said that the deconstruction period of 2 h might be insufficient to achieve maximum lignin removal for coconut husk, which contains 1.6 times more lignin compared to OPEFB (TABLE 1).

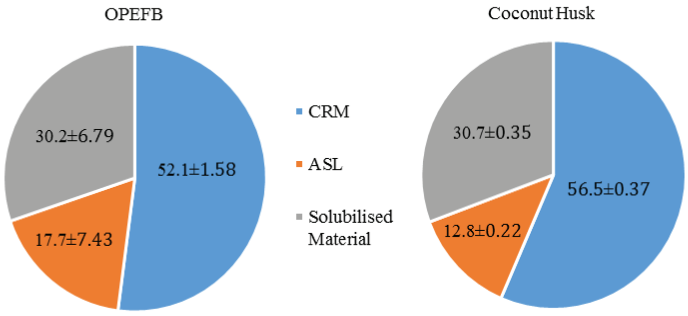


FIGURE 5. Recovery of biopolymers from deconstruction of OPEFB (left) and coconut husk (right) in a $[N_{2220}][HSO_4]/H_2O$ mixture at 120 °C for 2 h. Recovered biopolymer (wt%) is expressed as the quantity of recovered biopolymer after deconstruction (g) per the amount of untreated OPEFB (or coconut husk) particles used (g). Error values are standard deviations of triplicate trials

TABLE 1. Typical composition of biopolymers of OPEFB and coconut husk

	CRM (wt%)	**Lignin (wt%)**	**Reference**
Untreated OPEFB	72.9 (43.7 wt% of cellulose and 25.6 wt% of hemicellulose)	19.9	[4]
Untreated Coconut husk	66 (28 wt% of cellulose and 38 wt% of hemicellulose)	32.8	[11]

Economic and Environmental Benefits

The deconstruction of agro-wastes utilising the [N_{2220}][HSO_4] IL could potentially be a commercially viable process for the biorefinery industry in Malaysia based on several reasons. First, the IL is very easy to synthesise (two simple steps: mixing and drying, FIGURE 1) using inexpensive chemicals, guarantying 100% yield with water as the only waste generated. At the time of writing, it is estimated that (through Sigma Aldrich' price check) purchasing the required chemicals to prepare ca. 2 kg of the IL would cost RM1010 (N_{222}, CAS Number 121-44-8 = RM 575/L, while 95-98% H_2SO_4, CAS Number 7664-93-9 = RM 435/L). The estimated cost is far cheaper than purchasing the intensively studied IL 1-butyl-3-methylimidazolium acetate, [C_4C_1im][CH_3CO_2] (CAS Number 284049-75-8 = RM 5,225/kg). Second, the [N_{2220}][HSO_4] IL is thermally stable at elevated temperatures (TGA result, FIGURE 3 (c)), unlike the [C_4C_1im][CH_3CO_2] IL that decomposed when heated at 120 °C and above [7]. This is crucial as most effective deconstruction utilising IL occurs at 150 °C. Third, using the [N_{2220}][HSO_4] IL, the steps for recovering biopolymers are much simpler than employing a biomass-dissolving IL, such as [C_4C_1im][CH_3CO_2].

If the environmental aspect is to be concerned, the deconstruction utilising the [N_{2220}][HSO_4] IL seems to be a process that is more eco-friendly than its competitors, such as the incineration. A typical characteristic of ILs is to have a negligible vapour pressure, meaning that the ILs will not evaporate with increasing temperature. Additionally, the high thermal stability possessed by the [N_{2220}][HSO_4] IL (TGA result, FIGURE 3 (c)) implies that the IL will not decompose during the course of deconstruction (temperature of 120 °C for 2 h). This is important as the decomposition of ILs can produce toxic and volatile fragments.

CONCLUSIONS

Inexpensive [N_{2220}][HSO_4] IL was successfully synthesised through a simple acid-base-neutralisation reaction between inexpensive N_{222} and H_2SO_4 precursors. ^{1}H-NMR analysis indicated that the synthesis involved protonation of $\underline{N}$H in N_{222} by the strongest acidic proton $\underline{H}$O in H_2SO_4, yielding a salt constituting of [N_{2220}]$^+$ cation and [HSO_4]$^-$ anion that is remarkably stable up to 280 °C, as displayed by TGA profile. The [N_{2220}][HSO_4] IL was proven to provide bifunctional action towards deconstruction of OPEFB and coconut husk under the studied conditions, a mixture IL-H_2O (IL/H_2O of 80/20 wt/wt) at 120 °C for 2 h. It served not only as a Brønsted acid catalyst but also a delignification agent, as evidenced by the recovery of CRM and ASL as two individual products.

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