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A hemicellulose and lignin-first process for corn stover valorization catalyzed by aluminum sulfate in γ-butyrolactone/water co-solvent†

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A novel hemicellulose and lignin-first process for corn stover valorization catalyzed by $Al_2(SO_4)_3$ in GBL/H_2O co-solvent was developed in this study. In 25% GBL/H_2O at 160 °C, $Al_2(SO_4)_3$ assisted H_2O in breaking down intermolecular linkages of corn stover. The hydrolysis of $Al_2(SO_4)_3$ could produce H^+, $[Al(OH)_2(H_2O)_x]^+$ and SO_4^{2-}. With the solvation of GBL, the H^+ and $[Al(OH)_2(H_2O)_x]^+$ from $Al_2(SO_4)_3$ hydrolysis increased the co-conversion and dissolution of hemicellulose (96.9 wt%) and lignin (68.0 wt%), while the $AlHSO_4(OH)_2H_2O$ species formed by combining with $[Al(OH)_2(H_2O)_x]^+$ and SO_4^{2-} was found to inhibit cellulose conversion (88.7 wt% kept). Expecting for H^+ from $Al_2(SO_4)_3$ hydrolysis, the formed $AlHSO_4(OH)_2H_2O$ was found to be the catalytic active species for the cleavage of glycosidic bonds in hemicellulose to produce xylose, and also acted as a "stabilizer" to prevent the further degradation of xylose to improve its yield (87.6%, based on the weight of hemicellulose). $Al_2(SO_4)_3$ selectively promoted lignin depolymerization to lower M_w oligomers, as well as monophenols (11.20%) with high selectivity of 70.0% to VG and VP *via* C_α−OH dehydration and −C_γ(═O)−OH decarboxylation reaction. The obtained cellulose-rich residues show great potential for further use within many industrial processes. The developed process is recyclable, giving important insights to design new approaches for corn stover valorization.

1. Introduction

The over-dependence on fossil fuels for the production of fuels and chemicals has resulted in significant energy shortages and environmental issues.[1,2] As a renewable and abundant feedstock, lignocellulosic biomass is a promising candidate to replace fossil fuels.[3,4] Furthermore, lignocellulosic biomass can adsorb and use CO_2 from the atmosphere *via* photosynthesis, resulting in a nearly "closed carbon balance".[5,6] Corn stover is one of the major agricultural waste biomass in China with approximately 300 million tons produced per year, and its yield has steadily increased year after year.[7,8] Due to a lack of effective utilization modes, farmers have no other choice but to burn corn stover openly, resulting in severe air pollution

and the loss of valuable resources. Therefore, it is necessary to accelerate the effective utilization of corn stover. To compete with the current petroleum refineries, it is critical to maximize the utilization of corn stover in a cost-effective and environmentally sustainable manner.[1,3] Together with the development of sustainable green processes, it will further increase the availability of corn stover and offer considerable promise for the supply of renewable carbon.[3] However, corn stover valorization presents a significant challenge due to its inherent recalcitrance and heterogeneity.

Corn stover mainly consists of three major components: cellulose, hemicellulose, and lignin. Currently, a major challenge is the development of efficient pretreatment methods for the complete and efficient utilization of the three main components in corn stover.[9] The sustainable biorefinery encouraged a prior fractionation of biomass into its components, such as hemicellulose, cellulose and lignin, reducing the complexity of downstream processes and maximizing biomass utilization.[10] Hemicellulose is more unstable and has a lower degree of polymerization than cellulose and lignin, making it more susceptible to degradation during the pretreatment process.[11] As a result, most lignocellulosic biomass fractionations start with the removal of hemicellulose, leaving as much lignin and cellulose as possible in solid residues.[11,12] It was

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reported that a hydrothermal catalytic method could remove more than 90% hemicellulose from biomass, but the associated delignification of 10–30% was difficult to be avoided.[10] In lignocellulosic biomass, hemicellulose and lignin are cross-linked with each other by intermolecular linkages, forming a networked structure that wraps the cellulose.[13] Several studies have already been performed to show the potential of cellulose-rich solid residues for enzymatic saccharification or chemocatalytic conversion.[14,15] Recently, "lignin-first" strategy is reported to be promising to convert biomass efficiently, which refers to the fractionation and valorization of lignin prior to cellulose valorization.[16,17] It was found that hemicellulose was easily extracted with lignin. Therefore, borrowing the concept of "lignin-first" strategy, the first simultaneous removal of hemicellulose and lignin while leaving cellulose in the solid residues is noted as "hemicellulose and lignin-first" strategy, which is a promising process for the effective utilization of biomass. According to the work of Mellmer *et al.*,[18] the use of organic solvents could obtain high biomass conversion and product selectivity. In recent years, γ-valerolactone/water (GVL/H_2O) co-solvent has been used to improve the simultaneous removal of hemicellulose and lignin from biomass, since GVL is a safe, recyclable, and green biomass-derived solvent.[19,20] GBL (γ-butyrolactone), which has similar properties as GVL, can be also produced from biomass.[21–23] Zhang *et al.* discovered that GBL/H_2O co-solvent was very effective for dissolving lignin from hemicellulose-free corncob residues.[21] Furthermore, GBL has great potential as a solvent in industrial applications because it is less expensive than GVL. Therefore, GBL/H_2O as a solvent for biomass transformation is worth for further investigation.

Homogeneous metal salts are particularly interesting due to their excellent properties as Lewis/Brønsted acids and salting-in(out)agents.[6] Aluminum sulfate ($Al_2(SO_4)_3$) is an inexpensive, efficient, stable, and low toxicity metal-salt catalyst, which was found to be effective for the conversion of sugars and biomass-derived oligomers.[24–27] In these catalytic reactions, Lewis acid species $[Al(OH)_2(aq)]^+$ and Brønsted acid species $[H^+]$ from $Al_2(SO_4)_3$ hydrolysis were found to have a synergistic effect, promoting the hydrolysis, isomerization and dehydration reaction. It is worth mentioning, however, that the transformation mechanism of raw biomass was more complex than pure xylan. Previous work showed that the synergistic effects of H_2O and $Al_2(SO_4)_3$ facilitated the selective conversion of hemicellulose from corn stover to 85.1 wt% xylose, where the aluminum species $[Al(OH)_2(H_2O)_x]^+$ and H^+ from $Al_2(SO_4)_3$ hydrolysis were found to promote the conversion of hemicellulose.[28] While the function of SO_4^{2-} from $Al_2(SO_4)_3$ on the conversion of the three main components was ignored. Furthermore, the role of $Al_2(SO_4)_3$ in the organosolv fractionation of raw biomass was unknown. The use of $Al_2(SO_4)_3$ with GBL/H_2O for corn stover valorization could be an interesting route, which needed to be investigated further.

Herein a novel process for the hemicellulose-lignin first fractionation from corn stover catalyzed by $Al_2(SO_4)_3$ in GBL/H_2O co-solvent is reported. With the cellulose mostly intact, $Al_2(SO_4)_3$ promoted the hemicellulose depolymerization to xylose, as well as lignin depolymerization to produce monophenols and oligomers in 25% GBL/H_2O. The cellulose-rich solid residues could be further used to produce value-added chemicals and materials. This enabled to achieve the use of corn stover to its fullest. This is the first example to discuss the unique functions of $Al_2(SO_4)_3$ in GBL/H_2O for corn stover valorization. Additionally, the recyclability of GBL and $Al_2(SO_4)_3$ from the developed process was studied. This gives important insights to design new pretreatment methods for maximizing the value of waste biomass.

2. Materials and methods

2.1 Materials

Corn stover (CS) was collected from Shuangliu district of Chengdu, Sichuan province, China, which contained 17.1 wt% hemicellulose, 35.2 wt% cellulose, 19.2 wt% lignin, 6.4 wt% ash, 9.8 wt% moisture, 11.2 wt% extractives, and 1.1 wt% others. Before use, it was ground into a 40 meshes powder and dried overnight in an oven at 105 °C. Gama-butyrolactone (GBL, AR, 99%, Adamas), ethanol (EA, AR, 95%, Greagent), 2-methyltetrahydrofuran (2-MeTHF, AR, 99%, Adamas), aluminum sulfate octadecahydrate ($Al_2(SO_4)_3 \cdot 18H_2O$, AR, 99%, Greagent), hydrochloric acid (HCl, AR, 36%-38%, Chengdu Kelong Chemicals Co., LTD), sulfuric acid (H_2SO_4, AR, 95%-98%, Chengdu Kelong Chemicals Co., LTD), and various metal salts (sulfate salts and chloride salts) were purchased from commercial sources and utilized without purification.

2.2 The process for corn stover conversion

Corn stover conversion was carried out in a 150 mL sealed autoclave with mechanical agitation (Beijing Century Senlong experimental apparatus Co., Ltd). In a typical run, 3 g corn stover powder and 60 mL co-solvent (*e.g.* GBL/H_2O, EA/H_2O and 2-MeTHF/H_2O) with various organic solvent contents (0, 25%, 50%, 75% and 100%) were added into the autoclave and sealed. With an initial N_2 pressure of 1.0 MPa, the reactor was heated from room temperature to the designed value. When the reactor reached the desired temperature, the reaction time began to be recorded. The reaction was stopped when it reached the desired time, and flow water was used to cool it down to room temperature. The mixture of liquid fraction and solid residues were collected, and filtered by pre-weighed filter paper. The collected liquid fraction and solid residues were used for further analysis. To investigate the roles of $Al_2(SO_4)_3$ in GBL/H_2O for corn stover conversion, a certain amount of metal salts (*e.g.* sulfate salts and chloride salts) and mineral acids (H_2SO_4 and HCl) were added and performed using the same procedure described above.

2.3 Characterization of corn stover and reaction residues

The amounts of hemicellulose, cellulose and lignin in corn stover and reaction residues were determined using the Van Soest chemical titration method.[29] The surface functional

groups of solid samples were determined using a Fourier transform infrared spectroscopy (FTIR, Bruker invenio r). The FT-IR spectra were collected with a resolution of 4 cm^{-1} and 16 scans. The crystalline structures of solid samples were studied using an X-ray diffractometer (XRD, Rigaku Ultima IV, Japan). The crystallinity index (CI) of samples was calculated using the Segal formula.[30] A scanning electron microscope (SEM, Phenom Pharos 20-135X) was used to observe the surface images of solid samples. Prior to analysis, the solid samples were gold coated.

2.4 Characterization of the liquid fraction

The contents of small molecular products mainly from hemicellulose in liquid fraction were analyzed by high performance liquid chromatography (HPLC, SHIMADZU LC-20, Japan). The HPLC was equipped with a Bio-Rad Aminex HPX-87 column, SPD-20 UV/vis detector (UV) and RID-10A refractive index detector (RI). The measurement conditions were set according to previous work.[28] Before analysis, the liquid fraction obtained after treatment with GBL/H$_2$O co-solvent was diluted five times with water. The yield of small molecular products mainly from hemicellulose was calculated using the following equations:

$$\text{Yield (\%)} = \frac{\text{Liquid product amount (g)}}{\text{Weight of biomass (g)}} \times 100\% \quad (1)$$

$$\text{Xylose yield}^a(\%) = \frac{\text{The amount of xylose (g)}}{\text{Weight of hemicellulose in biomass (g)}} \times 100\% \quad (2)$$

Qualitative and quantitative analysis of monophenol contents derived from lignin in liquid fraction were performed on Gas chromatography equipped with a flame ionization detector (GC-FID, PERKINELMER Clarus 580), according to the standard curves of monophenol mixture. The measurement conditions were set according to previous work.[31] Before analysis, the liquid fraction obtained after treatment with GBL/H$_2$O co-solvent was subjected to a rotary evaporator to remove water at 50 °C.[21] The contents of monophenols were quantified using benzyl alcohol (0.5 mg mL^{-1}) as an internal standard. The yield of monophenols was based on the weight of lignin in corn stover, as shown in the equation below:

$$\text{Yield(\%)} = \frac{\text{Monophenol amount (g)}}{\text{Weight of lignin in biomass (g)}} \times 100\% \quad (3)$$

The oligomers in liquid fraction were analyzed by gel permeation chromatography (GPC, Waters), two dimensional heteronuclear single quantum coherence (2D HSQC NMR, BRUKER ADVANCE 400 MHz spectrometer) and electrospray ionization-mass spectrometry (ESI-MS, Shimadzu). For 2D HSQC NMR analysis, the liquid fraction was firstly precipitated by adding a large amount of H$_2$O ($V_{\text{H}_2\text{O}} : V_{\text{liquid}} = 8$–$10$) to obtain powder samples that mainly contained lignin-derived oligomers.[19,20] After centrifugation, the obtained powder samples were then fully dissolved in DMSO-d6 for 2D HSQC

NMR analysis. The measurement methods were the same as in the previous work.[31]

2.5 Quantum chemical calculation

All density functional theory (DFT) calculations were carried out with the Gaussian 09 programs.[32] The PBE0 functional method[33,34] was employed with the 6-311++G(d, p) basis set for C, H, O, and S atoms[35] and the aug-cc-pvtz basis set for Al atoms.[36] Solvent effect was considered in optimization employing the self-consistent reaction field (SCRF) method based on the universal solvation model SMD.[37] Geometry optimizations were run to locate all the stationary points. Unless otherwise specified, the relative Gibbs free energies (ΔG, kcal mol^{-1}) were obtained at the level of PBE0/6-311++G(d, p), aug-cc-pvtz at 433.15 K with the pressure of 10 atm. In aqueous solution (25% GBL/H$_2$O), the formed Gibbs free energy (ΔG) of each $[\text{Al}(\text{HSO}_4)_p(\text{OH})_m(\text{H}_2\text{O})_n]^{3-m-p}$ species starting from three independent species (HSO_4^-, OH^- and H_2O) with Al^{3+} for five coordination was computed following the reaction: $\text{Al}^{3+} + p \text{ HSO}_4^- + m \text{ OH}^- + n \text{ H}_2\text{O} \rightarrow [\text{Al}(\text{HSO}_4)_p(\text{OH})_m(\text{H}_2\text{O})_n]^{3-m-p}$, and using the equation: $\Delta G = G[\text{Al}(\text{HSO}_4)_p(\text{OH})_m(\text{H}_2\text{O})_n]^{3-m-p} - G\text{Al}^{3+} - p\text{GHSO}_4^- - m\text{GOH}^- - n\text{GH}_2\text{O}$.

3. Results and discussion

3.1 Performance of GBL/H$_2$O co-solvent on the transformation of corn stover

As a kind of readily available raw material in China, the achievement of corn stover valorization is a two-win strategy that benefits both the economic and environment. Currently, the effective utilization of the three main components in corn stover, that is, hemicellulose, cellulose and lignin is a hot topic. Here, "hemicellulose and lignin-first" strategy is provided to achieve corn stover valorization and its goal is to first simultaneous fractionation of hemicellulose and lignin, while keeping as much cellulose as possible in solid residues that can be further used. According to previous research,[38,39] water tends to dissolve hemicellulose, while organic solvents have a higher affinity for lignin. As a result, three types of green solvents, EA, 2-MeTHF and GBL, were mixed with water to make co-solvents for corn stover transformation at 160 °C for 2 h, respectively (Fig. 1 and Fig. S1†). In the three pure organic solvent systems, the transformation of corn stover were all less than 30%, indicating that pure organic solvent was not beneficial for corn stover transformation. In pure H$_2$O, the transformation of corn stover was 44.4%. For EA/H$_2$O co-solvent system, the transformation of corn stover gradually decreased from 44.4% to 32.1% with increasing EA concentrations to 75% (Fig. S1(A)†). In 2-MeTHF/H$_2$O co-solvent system, the corn stover transformation increased gradually, peaking at 47.1% when 2-MeTHF content reached 50% (Fig. S1(B)†). With further increasing 2-MeTHF content to 75%, the transformation of corn stover reduced. The transformation of corn stover in GBL/H$_2$O co-solvent exhibited a similar trend as that in 2-MeTHF/H$_2$O co-solvent system, reaching a maximum of
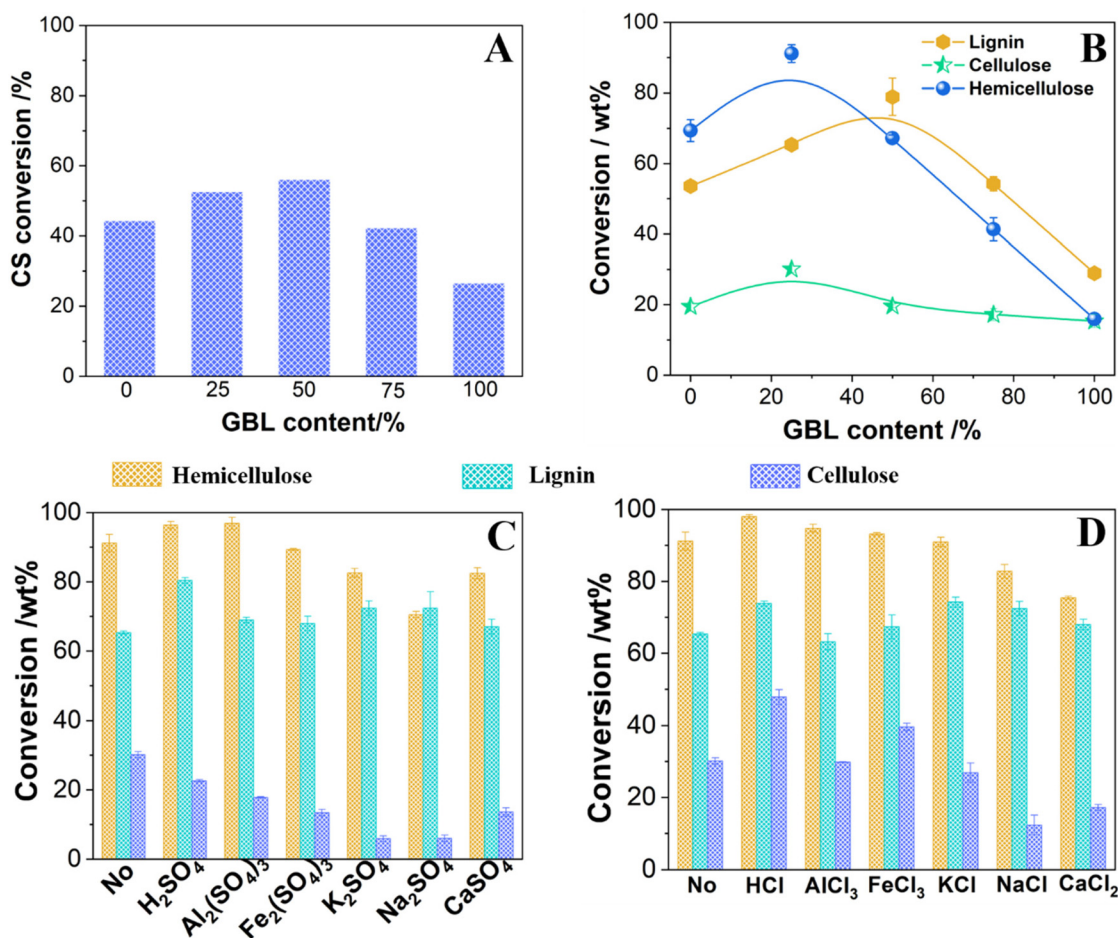
Fig. 1 The transformation of corn stover (A) and the three main components in corn stover (B) at 160 °C for 2 h in GBL/H_2O co-solvent with different proportions (Reaction condition: 3 g corn stover, 60 mL GBL/H_2O co-solvents with different GBL contents (0, 25, 50, 75 and 100%), 160 °C, 2 h); (C and D) Effects of sulfate salts, chloride salts and mineral acids (H_2SO_4 and HCl) added in 25% GBL/H_2O co-solvent on the transformation of the three main components in corn stover at 160 °C for 2 h (Reaction condition: 3 g corn stover, 60 mL 25% GBL/H_2O, sulfate salts with 2.8 mmol SO_4^{2-} or chloride salts with 5.6 mmol Cl^- or mineral acids (2.8 mmol H_2SO_4 and 5.6 mmol HCl), 160 °C for 2 h).

56.2% at 50% GBL/H_2O (Fig. 1(A)). GVL is also a biomass-derived green solvent that has similar properties as GBL. In the previous work,[31] GVL contents in GVL/H_2O system showed a significant effect on the transformation of corn stover, and reached a maximum of 46.4% in 25% GVL/H_2O. In terms of corn stover transformation, GBL/H_2O outperformed the above three co-solvent systems.

The amount of organic solvent in co-solvent was thought to be the most important factor influencing the behavior of the three main components in corn stover.[38] The efficient conversion of biomass in EA/H_2O and 2-MeTHF/H_2O generally required higher temperatures (>200 °C) or acid catalysts.[21,40] After being treated with pure H_2O, the co-conversion and dissolution of hemicellulose and lignin were 69.4 and 53.6 wt%, respectively (Fig. 1(B)). With the change of organic solvent concentrations at a lower temperature of 160 °C for 2 h, EA/H_2O and 2-MeTHF/H_2O exhibited a lower co-conversion and dissolution of hemicellulose and lignin than pure H_2O system (Fig. S1(C) and (D)†). The change of GBL or GVL contents in

solvent systems, on the other hand, increased the co-conversion and dissolution of hemicellulose and lignin. It was previously reported that 25% GVL/H_2O gave notably higher hemicellulose (74.4%) and lignin (51.4%) removal, while 89.5% cellulose was kept intact at 160 °C for 2 h.[31] Compared to GVL, GBL exhibited better performance on the simultaneous removal of hemicellulose and lignin (Fig. 1(B)). With the treatment of 25% GBL/H_2O, the maximum hemicellulose removal of 91.2 wt% was obtained, and the dissolution of lignin was 65.3 wt%. The maximum lignin removal of 78.9 wt% was obtained after being treated with 50% GBL/H_2O, but the removal of hemicellulose was only 67.2 wt%. At any GBL/H_2O proportion, the dissolution of cellulose in corn stover was less than 30 wt% at 160 °C for 2 h. XRD analysis of solid residues obtained after GBL/H_2O co-solvent treatment revealed higher CI values than raw corn stover (Fig. 2(A)). The CI values of solid residues obtained at 25% GBL/H_2O (CI = 79.7%) and 50% GBL/H_2O (CI = 81.5%) were significantly higher than those obtained at other proportions of GBL/H_2O co-solvents,
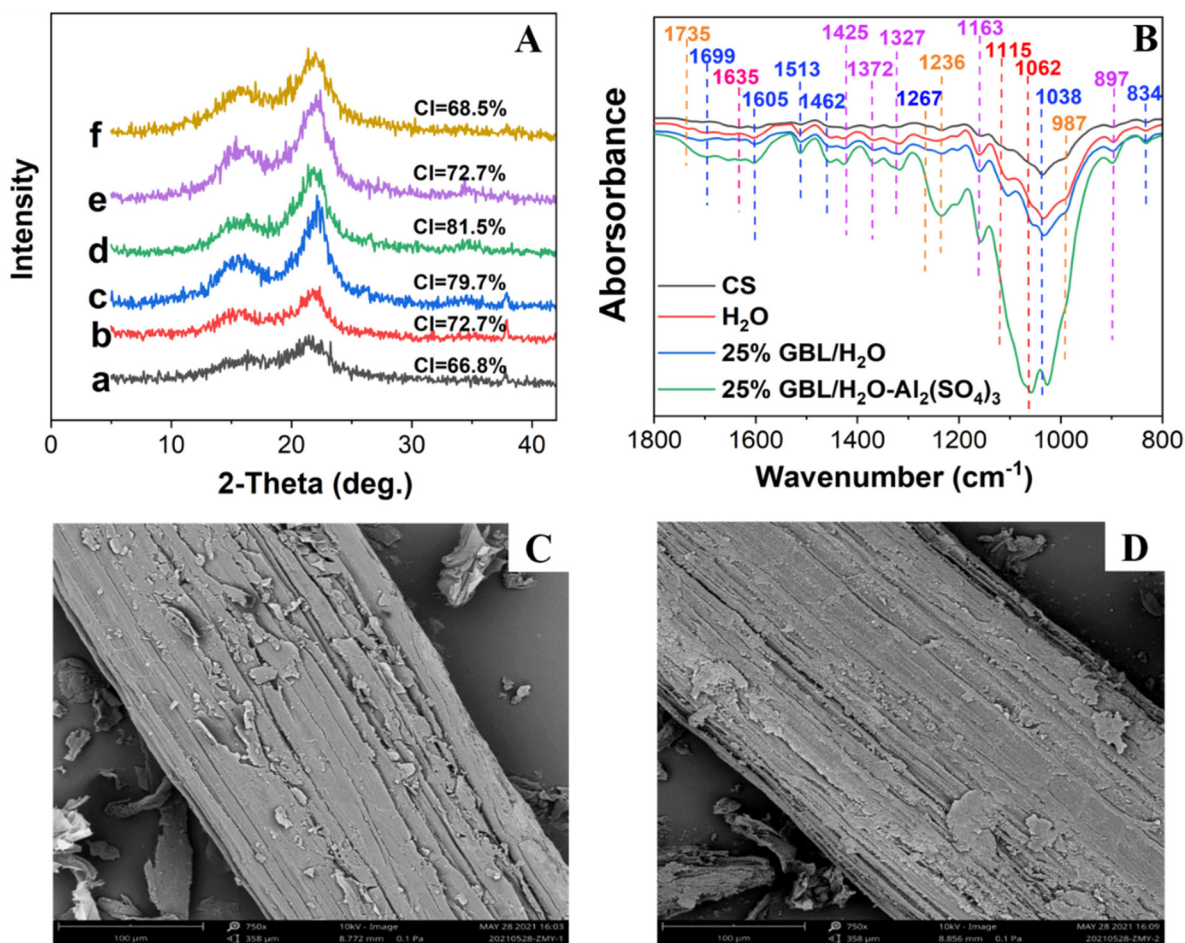
Fig. 2 (A) XRD (a, corn stover; b, H$_2$O; c, 25% GBL/H$_2$O; d, 50% GBL/H$_2$O; e, 75% GBL/H$_2$O; f, 100% GBL) and (B) FT-IR spectra of corn stover and solid samples obtained after being treated by different systems; SEM results of corn stover (C) and solid residues obtained after treatment with 25% GBL/H$_2$O–Al$_2$(SO$_4$)$_3$ system at 160 °C for 0.5 h (D).

indicating that the relative content of cellulose in the solid residues was higher. While compared to 50% GBL/H$_2$O, 25% GBL/H$_2$O required less organic content and yielded significantly higher co-conversion and dissolution of hemicellulose and lignin, hence 25% GBL/H$_2$O was chosen for further research.

3.2 Al$_2$(SO$_4$)$_3$ improved the fractionation of hemicellulose and lignin from corn stover in GBL/H$_2$O co-solvent

3.2.1 Al$_2$(SO$_4$)$_3$ promoted the co-conversion and dissolution of hemicellulose and lignin. Some metal salts (*e.g.* sulfate salts and chloride salts), as one type of environmentally acceptable and low-toxicity catalysts, have been found to be effective for the transformation of biomass-derived oligomers in organic/water co-solvents.[6,26,27] Previously,[28] it was discovered that Al$_2$(SO$_4$)$_3$ with around 2.8 mmol SO$_4^{2-}$ could inhibit the conversion of cellulose from corn stover at 130 °C under hydrothermal conditions. Therefore, different kinds of sulfate salts (Al$_2$(SO$_4$)$_3$, Fe$_2$(SO$_4$)$_3$, K$_2$SO$_4$, Na$_2$SO$_4$ and CaSO$_4$) were added in 25% GBL/H$_2$O, and the formed solvent systems were used to convert corn stover at 160 °C for 2 h firstly (Fig. 1(C)). Expecting for CaSO$_4$, all the sulfate salts were completely dis-

solved at room temperature. However, only part of CaSO$_4$ was dissolved at room temperature, and it was fully dissolved after reaction at 160 °C for 2 h. These sulfate salts are all strong electrolytes that can dissociate completely. According to previous work,[28] the concentrations of SO$_4^{2-}$ in these sulfate salts were set as 2.8 mmol. When compared to 25% GBL/H$_2$O, the addition of Al$_2$(SO$_4$)$_3$ among these sulfate salts resulted in a greater removal of hemicellulose and lignin from corn stover with most cellulose kept intact (Fig. 1(C)). In 25% GBL/H$_2$O–Al$_2$(SO$_4$)$_3$ system, the conversion of the three main components in corn stover along with varying reaction temperature, time and Al$_2$(SO$_4$)$_3$ amounts were carried out (Fig. S2†). 96.9 wt% hemicellulose and 68.0 wt% lignin could be removed by adding 0.9 mmol Al$_2$(SO$_4$)$_3$ to 25% GBL/H$_2$O at 160 °C for 0.5 h, while 88.7 wt% cellulose was kept intact. SEM results proved that the cellulose structure was nearly intact after being treated in 25% GBL/H$_2$O–Al$_2$(SO$_4$)$_3$ system at 160 °C for 0.5 h (Fig. 2(C) and (D)). Therefore, Al$_2$(SO$_4$)$_3$ promoted the hemicellulose and lignin-first removal from corn stover in 25% GBL/H$_2$O, while leaving cellulose intact in solid residues by adjusting and controlling the reaction conditions.

FT-IR analysis of the samples obtained after various treatments were carried out (Fig. 2(B)). After being treated with pure H_2O, the FT-IR peak at 1635 cm^{-1} (assigned to a hydrogen bond between hemicellulose and lignin) disappeared.[41] The two peaks at 1115 and 1062 cm^{-1} shifted to 1107 and 1057 cm^{-1}, respectively, which was related to the disruption of interactions among the three main components.[39,42] When 25% GBL was added in pure H_2O, the two peaks were almost not significantly changed. With the addition of $Al_2(SO_4)_3$ into 25% GBL/H_2O, the peak at 1115 cm^{-1} was completely disappeared and the peak at 1062 cm^{-1} greatly increased. Therefore, $Al_2(SO_4)_3$ aided H_2O in the cleavage of the intermolecular linkages among the three main components in corn stover, while GBL did not show any effect. When 25% GBL was added in pure H_2O, the absorption peaks at 1735 cm^{-1} (assigned to carboxylic acid in hemicellulose) greatly reduced.[41] With the addition of $Al_2(SO_4)_3$ in 25% GBL/H_2O, the peak nearly disappeared. This indicated that GBL and $Al_2(SO_4)_3$ aided the co-conversion and dissolution of hemicellulose. After being treated with 25% GBL/H_2O, the characteristic absorption peaks of lignin at 1038 cm^{-1} mainly assigned to aromatic C–H in-plane deformation of G unit in lignin showed a blue shift.[42] The absorption peak at 1267 cm^{-1}, which corresponds to the C–O stretching vibration of G unit in lignin,[39] showed a slight decrease. With the addition of $Al_2(SO_4)_3$ in 25% GBL/H_2O, the peak at 1038 cm^{-1} significantly shifted, and the peak at 1267 cm^{-1} was completely disappeared. This suggested that $Al_2(SO_4)_3$ could further enhance the conversion-dissolution of G unit in lignin with the help of GBL. After being treated by $Al_2(SO_4)_3$ in 25% GBL/H_2O system, the relative content of cellulose in the solid residues increased due to the removal of hemicellulose and lignin, thus the absorbance peaks of cellulose at 1425, 1372, 1327, 1163 and 897 cm^{-1}[39] slightly increased compared to raw corn stover (Fig. 2(B)). According to FT-IR and chemical titration results, $Al_2(SO_4)_3$ assisted H_2O in breaking down the intermolecular linkages among the three main components in corn stover. With the help of GBL solvation, $Al_2(SO_4)_3$ promoted the co-conversion and dissolution of hemicellulose and lignin, keeping most cellulose intact. The hydrolysis of $Al_2(SO_4)_3$ could produce aluminum species $[Al(OH)_2(H_2O)_x]^+$, H^+ and SO_4^{2-}.[26,28] The following research was to study the roles of these species in the organosolv fractionation of corn stover.

3.2.2 The roles of aluminum species $[Al(OH)_2(H_2O)_x]^+$. As shown in Fig. 1(C), different sulfate salts with the same amount of SO_4^{2-} (2.8 mmol) performed differently when it came to dissolving the three main components in corn stover. $Al_2(SO_4)_3$ among these sulfate salts was the best catalyst to promote the co-conversion and dissolution of hemicellulose and lignin. Fig. 1(D) shows the effects of chloride salts ($AlCl_3$, $FeCl_3$, KCl, NaCl and $CaCl_2$) on transformation of the three main components in corn stover. These chloride salts are all strong electrolytes, which can dissolve completely with the present concentration used, allowing them to fully dissociate. Therefore, the concentrations of Cl^- in these chloride salts were set as 5.6 mmol. Among these chloride salts, $AlCl_3$ was

also found to be more effective for simultaneously removing hemicellulose and lignin. Aluminum salt ($Al_2(SO_4)_3$ and $AlCl_3$) or ferric salt ($Fe_2(SO_4)_3$ and $FeCl_3$) will be hydrolyzed as the reaction processes, resulting in the changes of ionic strength in solutions. Without considering the salt hydrolysis, the ion strength of different solutions were calculated (Table S1†). It was found that ion strength had no significant effects on the conversion of the three main components in corn stover. For example, the ion strength of K_2SO_4, Na_2SO_4 and $CaCl_2$ were the same (0.12 mol kg^{-1}), but they performed differently on the conversion of the three main components in corn stover. Therefore, this indicated that aluminum species $[Al(OH)_2(H_2O)_x]^+$ from $Al_2(SO_4)_3$ hydrolysis promoted the co-conversion and dissolution of hemicellulose and lignin. The complete hydrolysis of $Al_2(SO_4)_3$ could produce 2.8 mmol H_2SO_4. When the same amount of H_2SO_4 was added in 25% GBL/H_2O, a higher conversion of cellulose (22.6 wt%) was obtained when compared to $Al_2(SO_4)_3$ (17.8 wt%). When HCl with the same amount (5.6 mmol) as that from the complete hydrolysis of $AlCl_3$ was added into 25% GBL/H_2O, it also resulted in a higher conversion of cellulose (47.8 wt%) than $AlCl_3$ (29.8 wt%). This meant that aluminum species $[Al(OH)_2(H_2O)_x]^+$ were also responsible for the inhibition of cellulose conversion.

3.2.3 The roles of H^+ and SO_4^{2-} from H_2SO_4 by $Al_2(SO_4)_3$ hydrolysis. The pH values of different solvent systems before and after reaction have been measured (Table S2†). Before reaction, the pH values of solution mainly related to salt hydrolysis. After reaction, the change in pH values of solution mainly related to the hydrolysis of metal salts and acidic products produced from hemicellulose. With the addition of aluminum salts or ferric salts, it provides an acidic environment with lower initial pH values. Compared to the other salts, aluminum salts or ferric salts also gave a higher removal of hemicellulose and lignin, which might be related to the lower pH values. When H_2SO_4 with the same amount as that from the complete hydrolysis of $Al_2(SO_4)_3$ was added to 25% GBL/H_2O, 96.4% hemicellulose and 80.4% lignin were simultaneously removed, which were higher than that using $Al_2(SO_4)_3$ as the catalyst. When HCl with the same amount as that from the complete hydrolysis of $AlCl_3$ was added to 25% GBL/H_2O, higher removal of hemicellulose and lignin were also obtained than that using Al_2Cl_3 as the catalyst. This suggested that the H^+ produced by $Al_2(SO_4)_3$ hydrolysis could promote the co-conversion and dissolution of hemicellulose and lignin. The addition of metal salts all resulted in a decrease in pH values, however, the simultaneous removal of hemicellulose and lignin was not always higher than that being treated with only 25% GBL/H_2O. This proved that H^+ was not the only factor to promote the co-conversion and dissolution of hemicellulose and lignin.

When different sulfate salts and chloride salts with equal molar concentrations of cations were added in 25% GBL/H_2O, respectively, it showed that the added sulfate salts greatly inhibited the conversion of cellulose in corn stover (Fig. 1(C) and (D)). For example, the conversion of cellulose were 17.8

and 13.4 wt% with the addition of $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$, respectively, while those were 29.8 and 39.6 wt% with adding $AlCl_3$ and $FeCl_3$. When H_2SO_4 was added in GBL/H_2O co-solvent, the cellulose removal reduced from 30.1 to 22.6 wt%. In previous work,[28] it was discovered that the H_2SO_4 produced by $Al_2(SO_4)_3$ hydrolysis promoted cellulose removal from corn stover in pure H_2O. However, this work found that H_2SO_4 produced by $Al_2(SO_4)_3$ hydrolysis could inhibit cellulose conversion in 25% GBL/H_2O. Li *et al.* reported that GBL/H_2O could mediate the distribution of catalyst around reactants and products.[43] This could be due to the solvation of GBL/H_2O that resulted in the catalytic performance of H_2SO_4 from $Al_2(SO_4)_3$ hydrolysis being different, preventing cellulose removal. It is also worth noting that, despite the fact that the H^+ concentrations of H_2SO_4 and HCl are close, H_2SO_4 achieves significantly lower cellulose conversion (Fig. 1(C) and (D)). Furthermore, the ion strength of H_2SO_4 (0.06 mol kg^{-1}) was close to that of HCl (0.09 mol kg^{-1}), indicating that ion strength was not related to the inhibition of cellulose conversion (Table S1†). This suggested that the role of H_2SO_4 from $Al_2(SO_4)_3$ hydrolysis in inhibiting cellulose conversion might be also related to SO_4^{2-} rather than H^+.

3.2.4 The roles of the formed $AlHSO_4(OH)_2H_2O$ active species. In 25% GBL/H_2O, SO_4^{2-} and aluminum species $[Al(OH)_2(H_2O)_x]^+$ from $Al_2(SO_4)_3$ hydrolysis both exhibited better advantages on inhibiting cellulose conversion. It might form a new active species by combining with SO_4^{2-} and $[Al(OH)_2(H_2O)_x]^+$, so that $Al_2(SO_4)_3$ showed abilities on inhibiting cellulose conversion. The possibly formed active species $[Al(HSO_4)_p(OH)_m(H_2O)_n]^{3-m-p}$ starting from three independent species (HSO_4^-, OH^- and H_2O) with Al^{3+} for five coordination was computed by density functional theory (DFT) calculation (Fig. S4†). For the seven possible species, the relative Gibbs free energies increase as $AlHSO_4(OH)_2H_2O < [Al(HSO_4)_2(OH)_2H_2O]^- < AlHSO_4(OH)_2(H_2O)_2 < AlHSO_4(OH)_2(H_2O)_2 < [AlHSO_4OH(H_2O)_3]^+ < [Al(HSO_4)_2(OH)_3]^+ < [AlHSO_4(H_2O)_4]^{2+}$. It is indicated that the $AlHSO_4(OH)_2H_2O$ ($\Delta G = -1028.4$ kcal mol^{-1}) is the most stable active species, which might be acted as an inhibitor for cellulose conversion in 25% GBL/H_2O.

Therefore, with help of GBL/H_2O, it was speculated that the H^+ and $[Al(OH)_2(H_2O)_x]^+$ species from $Al_2(SO_4)_3$ hydrolysis increased the co-conversion and dissolution of hemicellulose and lignin. The formed $AlHSO_4(OH)_2H_2O$ by combining with SO_4^{2-} and $[Al(OH)_2(H_2O)_x]^+$ was found to be the active species to inhibit cellulose conversion.

3.3 Catalytic performance of $Al_2(SO_4)_3$ on the depolymerization of hemicellulose and lignin in GBL/H_2O co-solvent

3.3.1 Hemicellulose depolymerization to produce xylose. In the liquid fraction, the yield of small molecular products mainly from hemicellulose after treatment with various ratios of GBL/H_2O co-solvent was investigated (Fig. 3(A)). In pure H_2O and GBL/H_2O co-solvent, the predominant product was acetic acid, which originated from the cleavage of acetyl groups in hemicellulose.[19] The maximum total yield of small molecular products (14.3%) was obtained in 25% GBL/H_2O.

With the addition of $Al_2(SO_4)_3$ in the 25% GBL/H_2O at 160 °C for 2 h, 8.1% xylose was produced, thus increasing the total yield of small molecular products to 18.7%. With prolonging time, the produced small molecular products could be further repolymerized, resulting in a decrease in the total yield.[30,44] When the reaction time was reduced to 0.5 h, 14.1% xylose was produced, and the total yield of small molecular products reached 27.6%. If based on the weight of hemicellulose in corn stover, the yield of xylose would be 87.6%. ESI-MS results showed that the signal assigned to xylo-oligosaccharides (m/z = 437.13 (3xylose-$2H_2O$ + Na^+) and m/z = 453.10 (3xylose-$2H_2O$ + K^+)) significantly decreased with the addition of $Al_2(SO_4)_3$ in 25% GBL/H_2O (Fig. 4), proving that $Al_2(SO_4)_3$ enhanced the depolymerization of xylo-oligosaccharides from hemicellulose to xylose.

In 25% GBL/H_2O system, the effects of sulfate salts and chloride salts on the distribution of small molecular products at 160 °C for 2 h were investigated (Fig. S5†). It was also found that ion strength had no significant effects on the hemicellulose depolymerization. With the addition of chloride salts in 25% GBL/H_2O, the main products were acetic acid and furfural, and the yield of xylose was around 0.1–3.7%. While in addition to acetic acid and furfural, 1.4–8.3% xylose was produced with the addition of sulfate salts in 25% GBL/H_2O. $Al_2(SO_4)_3$ produced more xylose than the other sulfate salts, suggesting that xylose production was also related to aluminum species ($[Al(OH)_2(H_2O)_x]^+$). Interestingly, adding $AlCl_3$ only resulted in 0.1% xylose, but it did promote the production of furfural. When compared to HCl with the close concentration of H^+, H_2SO_4 promoted the production of xylose (8.1%). It is possible that the catalytic performance of H_2SO_4 derived from $Al_2(SO_4)_3$ hydrolysis in the depolymerization of hemicellulose to xylose is not solely dependent on H^+ in 25% GBL/H_2O. Therefore, the synergistic actions of aluminum species $[Al(OH)_2(H_2O)_x]^+$ and H_2SO_4 (H^+ and SO_4^{2-}) produced by $Al_2(SO_4)_3$ hydrolysis promoted the depolymerization of hemicellulose to xylose, while inhibiting furfural production by dehydration reaction. According to DFT calculation, $AlHSO_4(OH)_2H_2O$ species was found to be the most stable form by combined with $[Al(OH)_2(H_2O)_x]^+$, H^+ and SO_4^{2-} from $Al_2(SO_4)_3$ hydrolysis, which was the active catalytic species to promote the production of xylose (Fig. 3(C) and Fig. S4†).

To further investigate the catalytic mechanism of $AlHSO_4(OH)_2H_2O$ in the depolymerization of hemicellulose to xylose with 25% GBL/H_2O as solvent, DFT calculation was performed with xylobiose (XB) as the model compound. The reaction energy diagram for the depolymerization pathway of XB on $AlHSO_4(OH)_2H_2O$ species was shown in Fig. 5. It was found that the XB can first adsorb on $AlHSO_4(OH)_2H_2O$ species by hydrogen bond, forming an intermediate of XB-$AlHSO_4(OH)_2H_2O$-1. The H^+ from $AlHSO_4(OH)_2H_2O$ species can migrate to the bridge oxygen on XB, promoting the cleavage of glycosidic bonds and the formation of the stable intermediate XB-$AlHSO_4(OH)_2H_2O$-2 (-36.9 kcal mol^{-1}) with xylose moiety. Next, the –OH group on the $AlHSO_4(OH)_2H_2O$ species will then migrate to the xylose moiety, forming the intermedi-
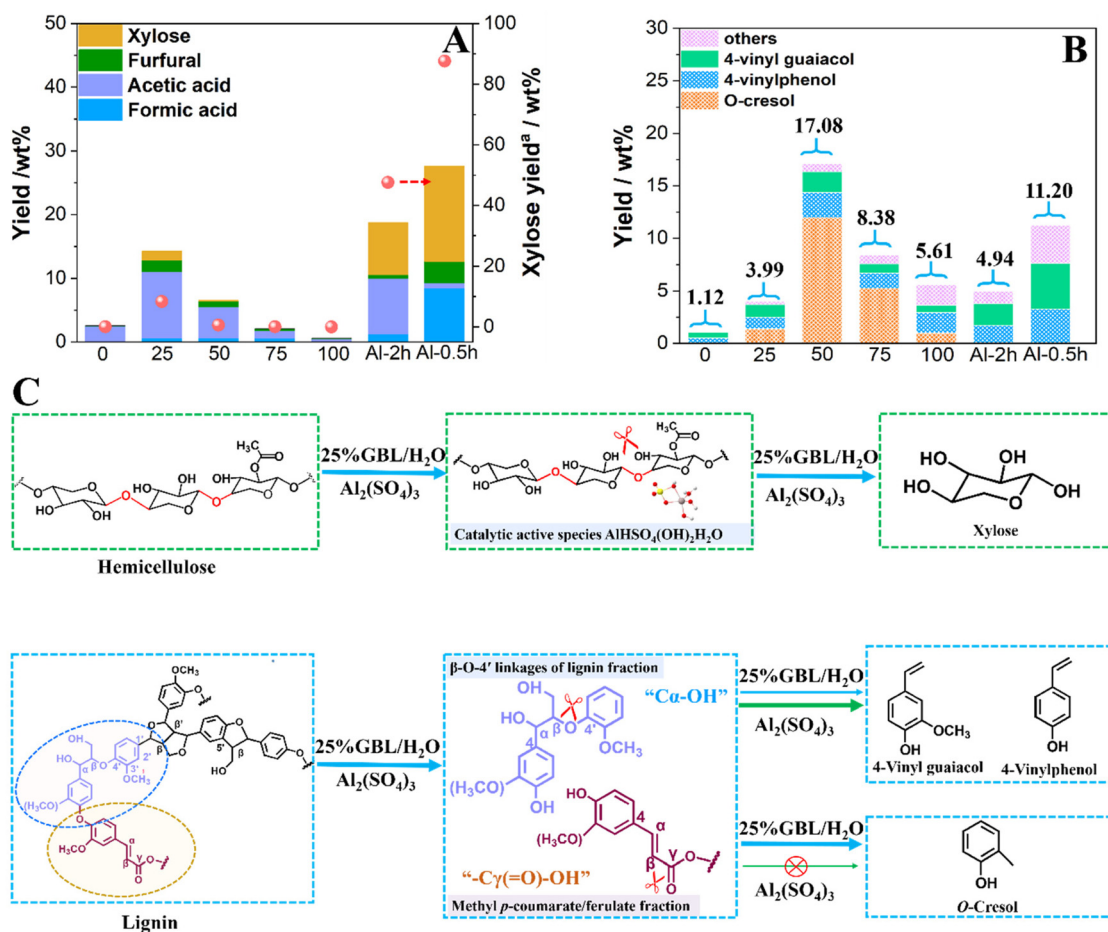
Fig. 3 The yield of small molecular products mainly from hemicellulose (A) and monophenols from lignin (B) in GBL/H_2O co-solvent (Reaction condition: 3 g corn stover, 60 mL GBL/H_2O co-solvent, 0–100% GBL, 160 °C for 2 h) and 25% GBL/H_2O–$Al_2(SO_4)_3$ systems (Reaction condition: 3 g corn stover, 60 mL 25% GBL/H_2O, 0.9 mmol $Al_2(SO_4)_3$, 160 °C for 0.5 and 2 h); (C) Proposed reaction pathway for the depolymerization of dissolved hemicellulose and lignin to xylose and monophenols; The yield of small molecular products was based on the weight of corn stover; Xylose yield[a] was based on the weight of hemicellulose in corn stover; The yield of monophenols was based on the weight of lignin in corn stover.

ate XB-AlHSO$_4$(OH)$_2$H$_2$O-3 with −25.1 kcal mol^{-1}. Finally, the formation of two molecular xylose requires an energy of −38.4 kcal mol^{-1}, indicating that this process being thermodynamically favorable. These findings indicated that the H$^+$ from AlHSO$_4$(OH)$_2$H$_2$O species interacted with glycosidic bonds in hemicellulose *via* hydrogen bonds, followed by glycosidic bonds cleavage and –OH group migration of catalytic species to form xylose. In the traditional acid hydrolysis reaction, H$^+$ can promote the cleavage of glycosidic bonds in hemicellulose to produce xylose. However, less xylose was obtained using HCl as the catalyst in 25% GBL/H_2O. Therefore, the formed AlHSO$_4$(OH)$_2$H$_2$O species also acted as a "stabilizer" to prevent the further degradation of xylose to improve its yield from hemicellulose depolymerization.

3.3.2 Lignin depolymerization to produce monophenols and oligomers. The yield of monophenols from lignin in liquid fraction after treatment with various ratios of GBL/H_2O systems was studied (Fig. 3(B), Fig. S6† and Table S3†). In pure H_2O, the main products were found to be 4-vinyl guaiacol (VG, 0.57%) and 4-vinylphenol (VP, 0.46%), with a total monophe-

nol yield of only 1.12% based on the weight of lignin in corn stover. In the GBL/H_2O co-solvent, the total monophenol yield was around 3.99–17.08%, and O-cresol was identified (Fig. S6(B)†). In 50% GBL/H_2O co-solvent system, 11.97% O-cresol as the main product with a small amount of VG and VP was detected. With the addition of $Al_2(SO_4)_3$ in 25% GBL/H_2O at 160 °C for 2 h, the total yield of monophenols increased to 4.94% compared to 25% GBL/H_2O (3.99%). The main products were VG and VP while O-cresol was almost undetectable (Fig. S6(C)†). Prolonging time could result in further repolymerization of monophenols.[44] When the time was reduced to 0.5 h, the total yield of monophenols increased to 11.20%. VG and VP with the yield of 3.37 and 4.42% were obtained, respectively. The total selectivity to VG and VP in obtained monophenols reached 70.0%. This suggested that $Al_2(SO_4)_3$ promoted the depolymerization of lignin to produce VG and VP, while inhibiting the production of O-cresol. Compared to the dissolution of lignin (68.0 wt%) in 25% GBL/H_2O-$Al_2(SO_4)_3$ at 160 °C for 0.5 h, it suggested that the liquid products were abundant with lignin-derived oligomers. GPC results showed
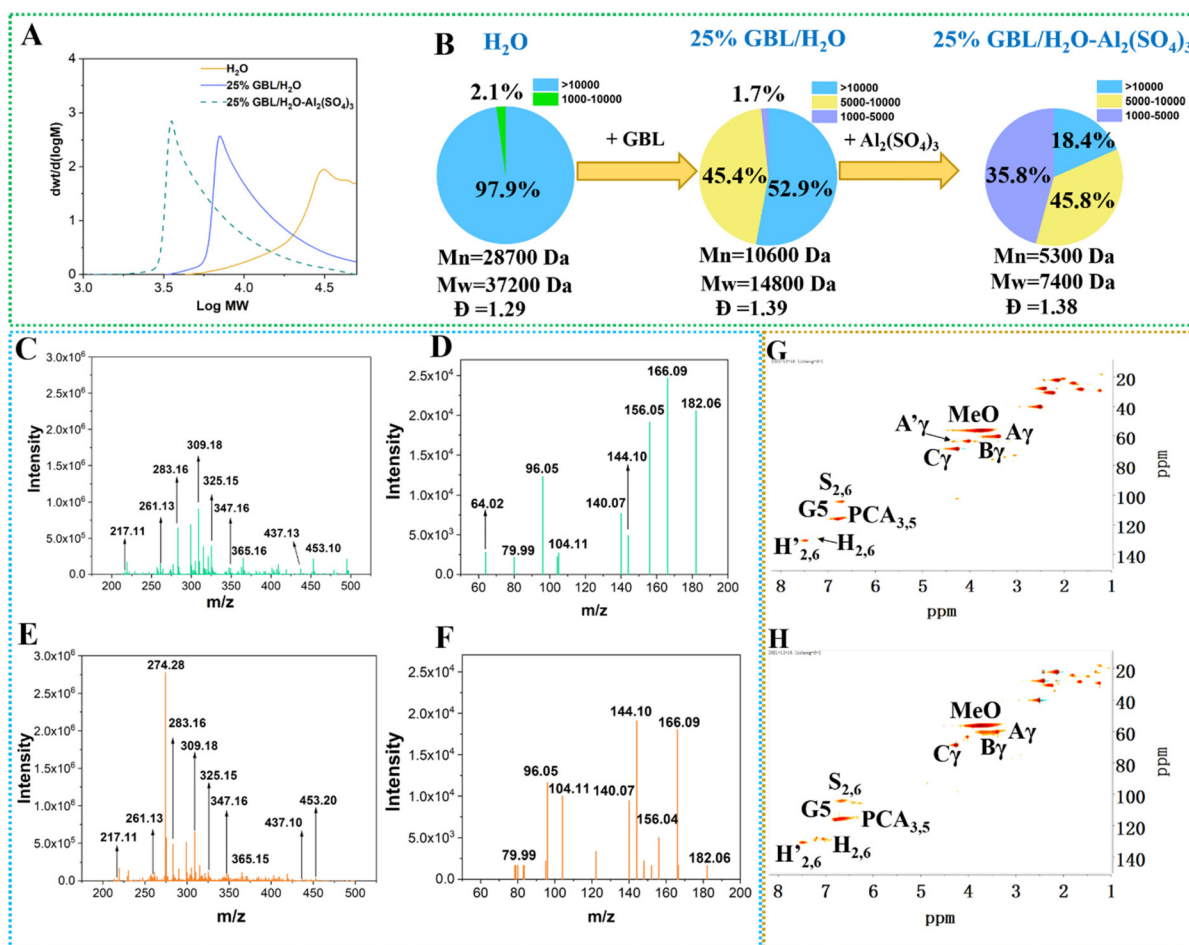
Fig. 4 Molar mass distribution curves of liquid fraction obtained from different solvent treatment (A); GPC analysis of liquid product distribution obtained from different solvent systems (B); ESI-MS results of liquid fraction obtained after the treatment of 25% GBL/H_2O (C and D) and 25% GBL/H_2O–$Al_2(SO_4)_3$ (E and F) at 160 °C for 2 h; and 2D HSQC NMR results of liquid fraction obtained after the treatment of 25% GBL/H_2O (G) and 25% GBL/H_2O–$Al_2(SO_4)_3$ (H) at 160 °C for 2 h.

that the weight-average molecular weight (M_w) of liquid products was 8200 Da with dispersity ($Đ$) of 1.51. According to 2D HSQC NMR results, the lignin-derived oligomers mainly included β-O-4′ linkages (A_γ), phenylcoumaran (B), and β-β′ resinol (C) with syringyl ($S_{2,6}$), guaiacyl (G_5), p-hydroxyphenyl ($H'_{2,6}$) units, and p-coumarate (PCA)/ferulate (FA) structure (Fig. S7 and Table S4†).

GPC analysis of liquid fractions obtained from three kinds of systems including pure H_2O, 25% GBL/H_2O and 25% GBL/H_2O–$Al_2(SO_4)_3$ at 160 °C for 0.5 h were studied (Fig. 4). Compared to pure H_2O, the molar mass distribution curve of liquid fraction obtained from 25% GBL/H_2O shifted to a lower molecular weight (Fig. 4(A)). The addition of $Al_2(SO_4)_3$ could enhance this shift. After being treated with pure H_2O, the M_w and number-average molecular weight (M_n) of liquid fraction were 37 200 and 28 700 Da, respectively. The value of $Đ$ was 1.29. Compared to pure H_2O, the liquid fraction had a lower M_w (14 800 Da) and M_n (10 600 Da) after being treated with 25% GBL/H_2O. The value of $Đ$ slightly increased to 1.39. With the treatment by adding $Al_2(SO_4)_3$ into 25% GBL/H_2O, the M_w

and M_n of liquid fraction significantly decreased to 7400 and 5300 Da, respectively. As shown in Fig. 4(B), more than 95% liquid products with M_w greater than 10 000 Da were observed after being treated with pure H_2O. In 25% GBL/H_2O co-solvent, the liquid products with M_w greater than 10 000 Da decreased to 52.9%, and 45.4% liquid products with M_w of 5000–10 000 were obtained. When $Al_2(SO_4)_3$ was added into 25% GBL/H_2O, only 18.4% liquid products with M_w were greater than 10 000 Da compared to that obtained from 25% GBL/H_2O (52.9%) and pure H_2O (97.9%). The liquid products with M_w of 1000–5000 Da significantly increased from 1.7% to 35.8% with the addition of $Al_2(SO_4)_3$ in 25% GBL/H_2O. In the above mentioned three kinds of systems, hemicellulose and lignin were both dissolved. So the results suggested that the co-existence of GBL and H_2O was beneficial for the depolymerization of oligomers derived from hemicellulose and lignin, and $Al_2(SO_4)_3$ significantly aided in the depolymerization.

To further study the roles of $Al_2(SO_4)_3$ in the depolymerization of lignin-derived oligomers, 2D HSQC NMR and ESI-MS analysis of liquid fractions obtained before and after adding
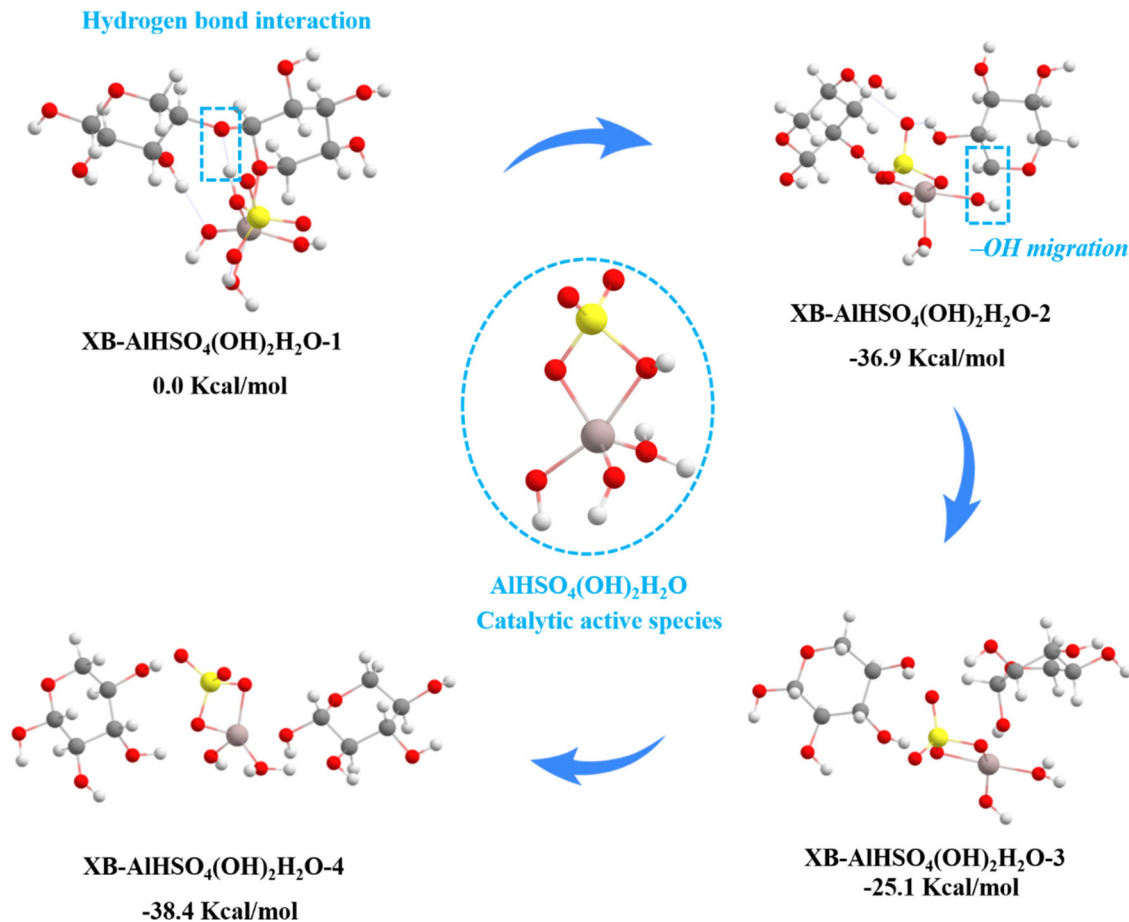
Hydrogen bond interaction

XB-AlHSO$_4$(OH)$_2$H$_2$O-1

0.0 Kcal/mol

–OH migration

XB-AlHSO$_4$(OH)$_2$H$_2$O-2

-36.9 Kcal/mol

AlHSO$_4$(OH)$_2$H$_2$O
Catalytic active species

XB-AlHSO$_4$(OH)$_2$H$_2$O-4

-38.4 Kcal/mol

XB-AlHSO$_4$(OH)$_2$H$_2$O-3

-25.1 Kcal/mol

Fig. 5 The reaction energy diagram for the depolymerization pathway of xylobiose (XB) on AlHSO$_4$(OH)$_2$H$_2$O catalytic active species.

Al$_2$(SO$_4$)$_3$ in 25% GBL/H$_2$O were performed (Fig. 4). 2D HSQC NMR analysis showed that the main signal of side chain region (δC/δH 50–90/2.5–5.0 ppm) assigned to C$_\gamma$–H$_\gamma$ in β-O-4′ structure (A$_\gamma$) was weakened with the addition of Al$_2$(SO$_4$)$_3$ in 25% GBL/H$_2$O. The main signals of aromatic region (δC/δH 100–150/6.0–8.0 ppm) assigned to C$_{2,6}$–H$_{2,6}$ in oxidized(C=O) (H′$_{2,6}$) or non-oxidized p-hydroxyphenyl units (H$_{2,6}$), and C$_{2,6}$-H$_{2,6}$ in syringyl units(S$_{2,6}$) increased (Fig. 4(G) and (H)). This suggested that Al$_2$(SO$_4$)$_3$ promoted the cleavage of β-O-4′ structure in lignin-derived oligomers. From ESI-MS analysis results (Fig. 4(C–F) and Table S5†), it was observed that the peaks assigned to lignin-derived oligomers containing β-O-4′ linkages fraction (m/z = 261.13, 283.16, 309.18, 325.15, 347.16 and 365.16) and methyl p-coumarate/ferulate structure (m/z = 217.11, 182.06, 166.09) decreased with the addition of Al$_2$(SO$_4$)$_3$ in 25% GBL/H$_2$O. Ma et al. reported that the lignin underwent a dehydration-hydrogenolysis reaction to break the β-O-4 ether bonds to form lignin monomers such as methyl p-coumarate and methyl ferulate.[14] And the production of VG and VP was from methyl p-coumarate and methyl ferulate via decarboxylation reaction. In accordance with the work of Liu et al.,[45] previous work also found that the cleavage of β-O-4′ linkages from lignin followed by the dehydration of C$_\alpha$-OH

could produce VG and VP.[31] According to GC-FID, 2D HSQC NMR and ESI-MS results, Al$_2$(SO$_4$)$_3$ promoted the cleavage of β-O-4′ linkages followed by C$_\alpha$-OH dehydration and –C$_\gamma$(=O)–OH decarboxylation reaction from lignin-derived oligomers to produce VG and VP (Fig. 3(C)). Wang et al. reported the production of o-cresol from the pyrolysis of organosolv lignin after pretreated by H$_2$O.[46] Verma et al. reported that the formation of o-cresol was produced from a guaiacyl lignin-derived model compound via hydrodeoxygenation.[47] Therefore, as shown in Fig. 3(C), it was speculated that the depolymerization of guaiacyl lignin-derived oligomers to produce o-cresol was inhibited with addition of Al$_2$(SO$_4$)$_3$ in 25% GBL/H$_2$O. While the mechanism of o-cresol production needs further investigation. Simultaneously, the dehydration reaction of C$_\alpha$–OH and the decarboxylation reaction of –C$_\gamma$(=O)–OH in lignin were promoted, thus the yield of VG and VP increased.

3.4 Recyclability of GBL and Al$_2$(SO$_4$)$_3$ towards corn stover fractionation

Finally, the recyclability of GBL and Al$_2$(SO$_4$)$_3$ towards corn stover fractionation were carried out, as shown in Fig. 6. GBL has excellent thermal stability with a high boiling point of 206 °C, and Al$_2$(SO$_4$)$_3$ is more soluble in water than pure GBL.

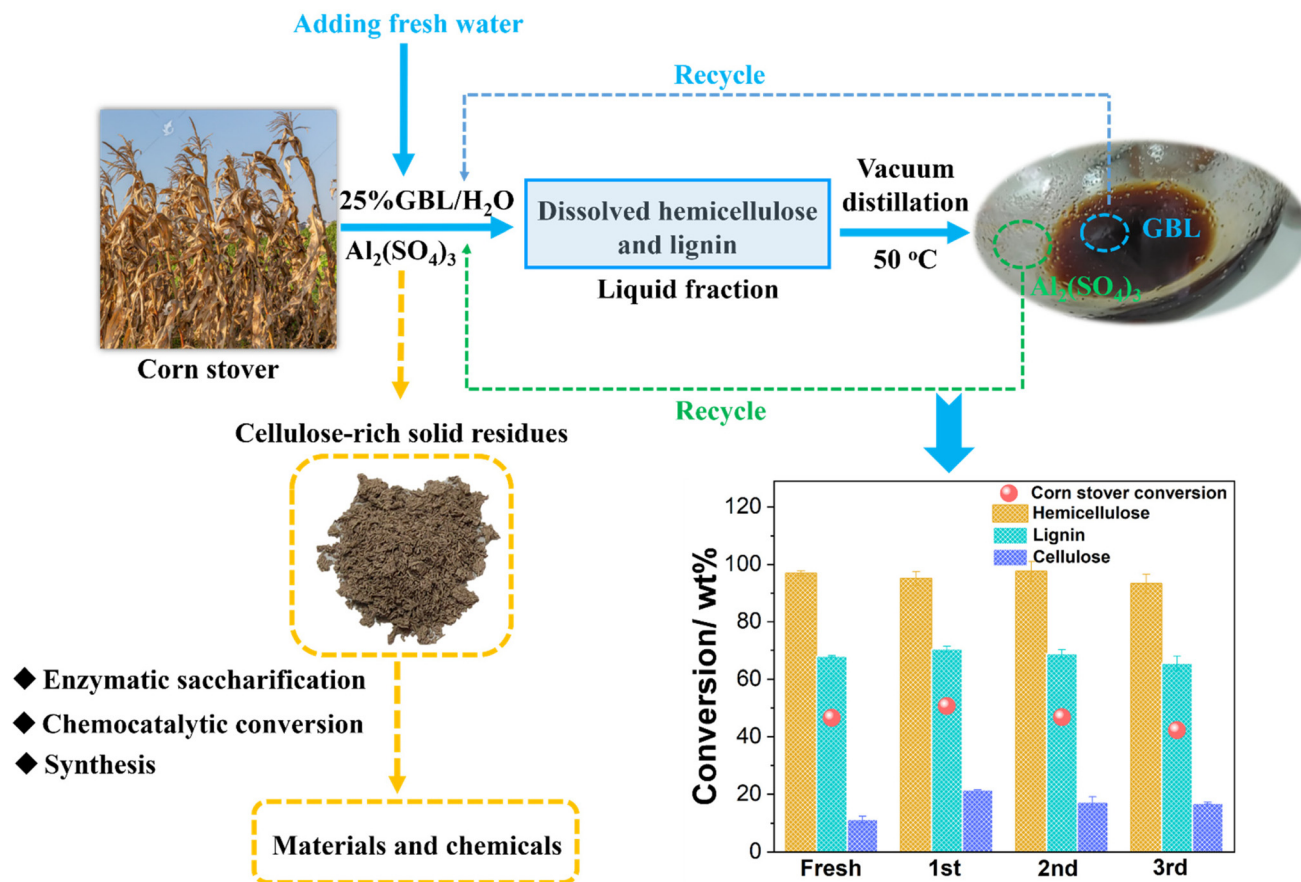**Fig. 6** The removal of the three main components from corn stover with recycled GBL and $Al_2(SO_4)_3$.

According to their properties, vacuum distillation is regarded as a promising method to recover GBL and $Al_2(SO_4)_3$ by removing water at a lower temperature of 50 °C. After removing water from the liquid fraction obtained with the treatment of 25% GBL/H_2O–$Al_2(SO_4)_3$ at 160 °C for 0.5 h, white particles (aluminum sulfate) and GBL were left. The recovered $Al_2(SO_4)_3$ and GBL were then mixed with fresh water to create a 25% GBL/H_2O–$Al_2(SO_4)_3$ system, which was used for a new cycle of corn stover fractionation. After three cycles, corn stover conversion remained around 45%. The removal of hemicellulose and lignin was kept around 95% and 70%, respectively, while cellulose conversion was significantly inhibited (~16.9%). This implied that GBL and $Al_2(SO_4)_3$ showed good recyclability towards corn stover fractionation. Additionally, the obtained cellulose-rich solid residues could be further used as starting materials to prepare materials and value-added chemicals within many industrial processes. Xylose from hemicellulose depolymerization mainly existed in water, which can be recovered with the removal of water *via* vacuum distillation. However, it cannot completely separate liquid products from solvent *via* vacuum distillation, especially those have a high affinity for GBL. As reported in literature,[27,48] the products especially monophenols accumulated at the beginning in the recycling process, and then decreased due to repolymerization

after multiple reactions. The effective separation of monophenols and lignin-derived oligomers from liquid fractions to recover high purity GBL needed further investigation. In addition to separation, the products in the GBL can be also used directly to prepare chemicals and fuels by the development of efficient catalysts. However, such impurity did not have a significant effect on the fractionation of corn stover. This study clearly demonstrated that the novel 25% GBL/H_2O–$Al_2(SO_4)_3$ system is promising to be recycled in corn stover-based biorefineries.

4. Conclusions

This study developed a novel hemicellulose and lignin-first process catalyzed by $Al_2(SO_4)_3$ in GBL/H_2O for corn stover valorization. In 25% GBL/H_2O, the H^+ and $[Al(OH)_2(H_2O)_x]^+$ from $Al_2(SO_4)_3$ hydrolysis increased the co-conversion and dissolution of hemicellulose and lignin, while the formed $AlHSO_4(OH)_2H_2O$ species inhibited cellulose conversion. $AlHSO_4(OH)_2H_2O$ was also found to be the catalytic species for hemicellulose depolymerization to xylose, which acted as a "stabilizer" to prevent the further degradation of xylose to improve its yield. $Al_2(SO_4)_3$ selectively promoted lignin depolymerization to produce lower

M_w oligomers, VG and VP under mild reaction conditions. The cellulose-rich solid residues can be further used to produce value-added chemicals and materials. This enabled to achieve the use of corn stover to its fullest. The developed process is green and recyclable, indicating a promising future to develop a sustainable corn stover-based biorefinery.

Author contributions

Yiping Luo: Methodology, investigation, formal analysis, data curation, wring–original draft and funding acquisition; Min Wei, Bin Jiang, Mingyi Zhang and Qian Miao: investigation, formal analysis and data curation; Hongquan Fu, James H. Clark and Jiajun Fan: writing–review & editing and supervision; All authors approved the final version of the manuscript and contributed to the scientific discussion.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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