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An integrated process for the valorization of corn stover promoted by NaCl in a GVL/H₂O system†

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An integrated green process for the valorization of corn stover promoted by NaCl in GVL/H₂O was developed. With the addition of NaCl in 25% GVL/H₂O at 170 °C for 2 h, the interactions of NaCl (Na⁺ and Cl[−]) with the −OH group in hemicellulose and G units in lignin were enhanced, which facilitated a high extraction of hemicellulose (96.4 wt%) and lignin (86.6 wt%), obtaining cellulose-rich solid residues. NaCl promoted the extracted hemicellulose degradation to produce small molecular products (85.6%). NaCl also promoted the cleavage of β-O-4' linkages and the decarboxylation reaction in lignin to obtain lower *M_w* (438 Da) oligomers and monophenols (14.2%) with high selectivity of 81.9% to 4-vinylphenol, 4-vinyl guaiacol and isoeugenol. Due to the salt effects of NaCl, most of the liquid products derived from hemicellulose and lignin were *in situ* separated by dissolving into the aqueous and GVL phases, respectively, which provided a possibility for further utilization. In addition, the obtained cellulose-rich solid residues were activated by steam to prepare high performance activated carbon (*S_{BET}* = 819 m² g^{−1}, *A_{methylene blue}* = 212 mg g^{−1} and *A_{Iodine}* = 914 mg g^{−1}), which showed great potential for pollution control within many industrial processes. This opened an avenue to integrate the valorization of corn stover.

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1. Introduction

Against the background of the increased energy crisis and environmental pollution, lignocellulosic biomass as a renewable carbon resource to produce fuels and chemicals is a promising alternative to replace petroleum.¹ Currently, about 300 million tons of corn stover, known as one of the major agricultural residues, are produced in China.^{2,3} In previous practices, corn stover was openly burned, resulting in severe atmospheric pollution and the loss of valuable resources.⁴ To solve this problem, the Chinese government has made great efforts to forbid open burning and guided a multiple utilization strategy for corn stover.⁵ The preparation of value-added chemicals (such as furfural, xylose and monophenols) and bioethanol by the conversion of corn stover is a promising valorisation approach that has attracted attention from researchers.² However, most of the proposed processes are currently unable to compete economically with petroleum refineries, which is in part due to the incomplete utilization of biomass components.⁶ It has been demonstrated that effective

complete utilization of biomass is challenging due to the recalcitrant nature and complex interactions of the biomass constituents including hemicellulose, cellulose and lignin.⁷ Therefore, it is necessary to develop an approach for the valorization of all three main components in corn stover.

Thermochemical technologies for the utilization of biomass mainly consist of combustion, pyrolysis, gasification, high-pressure liquefaction and solvothermal conversion.^{8,9} Solvothermal conversion is considered as an attractive method for efficient utilization of biomass.⁹ The use of organic/water co-solvent (*e.g.* 2-methyltetrahydrofuran/water (2-MTHF/H₂O), tetrahydrofuran/water (THF/H₂O), and γ-valerolactone/water (GVL/H₂O)) for the solvothermal fractionation of biomass is promising.^{10–12} GVL is a safe, recyclable, and green biomass-derived solvent, which has a low melting point (−31 °C), a high boiling point (207 °C), and a lower vapor pressure even at high temperatures.^{13–16} The recognizable smell of GVL enables easy detection of leakage or spilling and it is a stable chemical unsusceptible to degradation and oxidation at standard conditions, making it a safe substance for large-scale storage, transportation and application.¹⁷ GVL has high solubility in water but it does not form azeotropes with water.¹³ GVL mixed with water brings a clear advantage at lower reaction pressures over the most renowned organosolv process, which would potentially reduce the risk of high pressure.¹⁷ Therefore, GVL/H₂O is considered to be an ideal solvent medium among these organic/water co-solvents. Luterbacher *et al.* applied GVL/H₂O

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to produce high yields of soluble carbohydrates (70 to 90%) at higher temperatures (430–490 K) by “one-pot” conversion of corn stover, hardwood, and softwood in the presence of 0.05% H_2SO_4 .¹⁸ Since then, many articles have reported the achievement of biomass fractionation to recover pure cellulose, sugar components and lignin fraction by adjusting the reaction temperature, time and acid concentration of the GVL/ H_2O co-solvent.^{13–15} We had discovered previously a process for the co-dissolution of hemicellulose (93.6%) and lignin (80.2%) from *pubescens* in a 25% GVL/ H_2O system at 160 °C for 4 h, leaving high-purity cellulose (83.3 wt%).¹⁹ The above research indicated that the simultaneous removal of hemicellulose and lignin from biomass could be achieved through a GVL/ H_2O system, obtaining cellulose-rich solid residues. It was also reported that the dissolved lignin could be recovered by liquid CO_2 extraction and precipitated with the addition of water.^{14,18} Thus, GVL/ H_2O exhibited better performance toward the fractionation of biomass. However, it was found that the dissolved hemicellulose contained oligo- and polysaccharides, and dissolved lignin with higher molecular weight ($M_w > 1500$ Da) was obtained even with the addition of corrosive sulfuric acid.^{15,19} Higher molecular weight products were obtained, which inhibited the further utilization of the dissolved hemicellulose and lignin to produce value-added chemicals. Therefore, there is a need to develop a solvent system to separate each component in corn stover and then achieve further valorization.

Sodium chloride (NaCl), the most common salt, is often added to organic/ H_2O co-solvents (e.g. GVL/ H_2O , THF/ H_2O) to improve the selectivity of products due to its salt effects.^{16,20} In addition, it was reported that NaCl promoted the decomposition of oligomers derived from biomass (such as cellulose and xylo-oligomers).^{21,22} Yu *et al.* found that NaCl promoted the phase transition and glycosidic bond cleavage of starch under microwave heating conditions.²³ Previous work found that the addition of NaCl to form the NaCl–GVL/THF solvent system achieved a maximum furfural yield of 76.9 mol% by further depolymerization of hemicellulose-derived oligomers.¹⁹ However, the roles of NaCl in the GVL/ H_2O solvent system for the integrated utilization of the three main components in biomass were ignored and needed further investigation.

Herein, an integrated green process for the effective solvent transformation of corn stover promoted by NaCl in the GVL/ H_2O co-solvent is reported, wherein hemicellulose and lignin are simultaneously extracted while keeping most cellulose intact in the solid residues. It shows that the water-rich phase mainly contained hemicellulose-derived small molecular products, which could be *in situ* separated from the GVL-rich phase that contains monophenols and low molecular weight lignin-derived oligomers. The cellulose-rich solid residues show great potential for preparing activated carbon with high performance towards the control of pollutants. The multiple roles of NaCl in the GVL/ H_2O co-solvent for the valorization of the three main components of corn stover have also been addressed. The developed approach provides the basis for achieving an integrated corn stover-based biorefinery.

2. Materials and methods

2.1 Materials

Corn stover was collected from the Shuangliu district of Chengdu city in Sichuan province, China, and was smashed to obtain 40 mesh powder before use. The corn stover powder contained 35.7 wt% cellulose, 17.1 wt% hemicellulose, and 19.9 wt% lignin. Gama-valerolactone (GVL, AR, 98%, Damas-beta) and sodium chloride (NaCl, AR, $\geq 99.5\%$, Greagent) were purchased from commercial sources, and used without any purification.

2.2 Solvothermal transformation of corn stover in the NaCl–GVL/ H_2O system

The solvothermal transformation of corn stover was carried out in a 150 mL sealed autoclave (Beijing Century Senlong experimental apparatus Co., Ltd) with mechanical agitation. Typically, 3 g of corn stover powder with a certain amount of NaCl (0–36%) and 60 mL of the GVL/ H_2O co-solvent with different contents of GVL (0, 25%, 50%, 75% and 100%) were added into the autoclave and then sealed. The concentration of NaCl is referred to as that in the aqueous phase. The inner air was replaced by N_2 for 2 min, and then was added 1.0 MPa N_2 at the beginning. The temperature of the reactor increased to the designed value very quickly and the reaction time was recorded at this moment. The reaction time was set as 0.5–6 h. After reaching the desired time, the reaction was stopped. Then the reactor was cooled down by water flow. When the reactor was cooled to room temperature, it was opened to collect the mixture of liquid phase products and solid residues, and then filtered by pre-weighed filter paper. The solid residues collected were dried at 105 °C for 12 h in an oven.

2.3 Further utilization of cellulose-rich solid residues to prepare activated carbon

After the removal of hemicellulose and lignin from corn stover, the cellulose-rich solid residues obtained were further used to prepare activated carbon. Typically, a certain amount of solid residues was firstly carbonized in a tube furnace at 500 °C for 2 h in N_2 (30 mL min^{-1}), and then activated at 800 °C for 1 h at a heating rate of 5 °C min^{-1} under a steam flow of 500 mL min^{-1} . The specific surface area (S_{BET}), and adsorption capacity on methylene blue ($A_{\text{methylene blue}}$) and iodine (A_{iodine}) of the obtained samples were measured.

2.4 Characterization of solid samples

The Van Soest chemical titration method was used to measure the contents of hemicellulose, cellulose and lignin in the solid samples before and after solvothermal treatment. The details of this method could be found in the literature.²⁴ A Fourier transform infrared spectrometer (FT-IR, Bruker invenio r) was used to collect the spectra from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} and 16 scans. The crystalline structures of the solid samples were characterized by a DANDONG FANGYUAN DX-1000 diffractometer using X-ray diffraction (XRD). The crystallinity index (CI) of the different samples was



calculated by the Segal formula.²⁵ A scanning electron microscope (SEM, HITACHI SU3500) was applied to observe the surface morphology of the solid samples. Thermogravimetric analysis (TG) was performed using a NETZSCH STA 449 F5 (Germany), where about 10 mg of sample was heated from 30 °C to 800 °C at a heating rate of 20 °C min⁻¹ in N₂ (60 mL min⁻¹). The derivative thermogravimetric (DTG) curves of different samples were obtained.

2.5 Liquid product analysis

The products derived from hemicellulose were quantitatively measured by liquid chromatography (HPLC, SHIMADZU LC-20, Japan). The products in pure water were detected directly, while those in the liquid phase that contained GVL were diluted by water before analysis. The HPLC analysis used a Bio-Rad Aminex HPX-87 column with SPD-20 UV/vis detector (UV) and RID-10A refractive index detector (RI). The temperatures of the column oven and detector were set as 50 and 35 °C, respectively. The mobile phase was 0.005 M H₂SO₄ with a flow rate of 0.6 mL min⁻¹. RI was used to measure the contents of monosaccharides such as glucose, arabinose and xylose, while UV was used to analyze the contents of organic acids (e.g. lactic acid, acetic acid, formic acid and levulinic acid) and furans (e.g. 5-hydroxymethylfurfural and furfural) at 210 nm. The yields of monosaccharides, organic acids, and furfural were calculated based on the weight of hemicellulose in corn stover.

The monophenols derived from lignin were analyzed by gas chromatography equipped with a flame ionization detector (GC-FID, PERKINELMER Clarus 580). A DB-5 capillary column (30 mm × 0.25 mm × 0.25 μm) was used and the flow rate of the nitrogen carrier gas was 1 mL min⁻¹. The injector and detector temperatures were set at 280 and 330 °C, respectively. The temperature program was set as increasing from 50 to 250 °C with 5 °C min⁻¹. 0.5 mg L⁻¹ benzyl alcohol was used as an internal standard. Because lignin has a higher affinity to GVL compared with water, the yields of monophenols in the GVL-rich phase were detected, which were calculated based on the weight of lignin in corn stover.^{14,15} For GVL/H₂O co-solvent, saturated NaCl was added to obtain the GVL-rich phase before analysis.

The analysis of oligomers in liquid products was carried out by gel permeation chromatography (GPC), two dimensional heteronuclear single quantum coherence (2D HSQC NMR) and electrospray ionisation-mass spectrometry (ESI-MS). GPC (Waters 1525) was used to determine the molecular weight distribution of liquid products using a refractive index detector (Waters 2414). The instrument was equipped with a guard column (6 × 40 mm, Waters) and an analysis column (7.8 × 300 mm, Waters). The mobile phase of 10% methanol/H₂O with a flow rate of 1 mL min⁻¹ was used, and the injection volume was set as 5 μL. To study the depolymerization ability of NaCl, the products both from the aqueous and GVL phases were mixed before analysis, while the products in the GVL phase were detected to study the molecular weight of the liquid products derived from lignin. The 2D HSQC NMR analysis of lignin-derived oligomers in the liquid fraction was per-

formed using a Bruker Advance 400 MHz spectrometer. The liquid fraction was precipitated by adding a large amount of H₂O ($V_{\text{H}_2\text{O}}:V_{\text{liquid}} = 8\text{--}10$) and then powder samples were obtained. About 50 mg of the powder sample was fully dissolved in 0.55 mL of deuterated dimethyl sulfoxide (DMSO-d₆) to prepare samples for NMR analysis. The liquid products obtained from different systems were also detected by ESI-MS (Shimadzu). The nuclear magnetic analyses (¹H NMR, ²³Na NMR and ³⁵Cl NMR) were performed using a Bruker Advance 400 MHz spectrometer at 298 K to study the interactions of hemicellulose and NaCl.

3. Results and discussion

3.1 Corn stover fractionation promoted by NaCl in GVL/H₂O co-solvent

GVL derived from biomass has attracted a lot of attention from researchers who commonly use it with water as excellent green media for the transformation of lignocellulose.^{15,19,26} The effects of GVL content in a GVL/H₂O system on the fractionation of corn stover that contained 35.7 wt% cellulose, 17.1 wt% hemicellulose and 19.9 wt% lignin at 160 °C for 2 h were first studied and the results are shown in Fig. 1(A). In accordance with a previous work,¹⁹ it was found that the cellulose fraction in corn stover is recovered almost quantitatively (89.4–94.0%) at any GVL/H₂O content at a lower reaction temperature of 160 °C. However, the content of GVL in the GVL/H₂O system has been identified as a key parameter for hemicellulose removal and delignification. In GVL/H₂O co-solvent, water provides hydrolytic power towards hemicellulose while GVL dissolves the lignin fraction. Taking into account the cost of organic solvent and that 25% GVL/H₂O gives a notably higher hemicellulose removal and the only 3.9% lignin removal difference in comparison to 50% GVL/H₂O, it was decided to use 25% GVL/H₂O for further investigations.

The goal of the next step is to maximize the dissolution of hemicellulose and lignin from corn stover, while retaining as much cellulose as possible. A certain amount of sulfuric acid is usually added in GVL/H₂O co-solvent to improve the efficiency of the organosolv fractionation process.^{13,15} However, considering the corrosion of sulfuric acid, an environmentally friendly catalytic system needed to be developed. It has been reported that NaCl is an additive for better performance in promoting the depolymerization and conversion of biomass-derived oligomers.^{21,22,27} Dutta reported that the yield of levulinic acid from bread waste could be significantly enhanced in GVL/H₂O through the synergistic catalysis of 30 wt% NaCl(aq) and 0.5 M H₂SO₄.¹⁶ NaCl was also found to promote phase separation to obtain the GVL/H₂O biphasic system. Rihko-Struckmann *et al.* reported that the addition of NaCl in THF/H₂O obtained a higher yield of 5-hydroxymethylfurfural (34.4%) from algal biomass.²⁰ However, the roles of NaCl in organic co-solvents for the transformation of the various components in raw biomass needed further investigation. Thus, different contents of NaCl were added into the



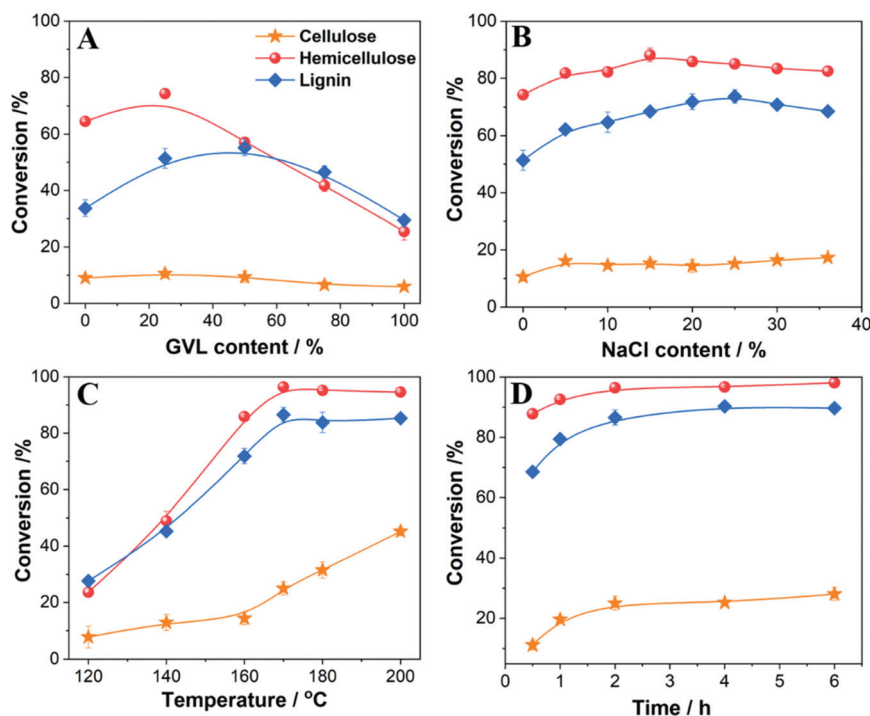


Fig. 1 Effects of different reaction conditions on the removal of the three main components of corn stover: (A) effects of GVL content in GVL/H₂O co-solvent system at 160 °C for 2 h (reaction conditions: 3 g of corn stover and 60 mL of GVL/H₂O with different GVL contents); (B) effects of NaCl content in 25% GVL/H₂O system at 160 °C for 2 h (reaction conditions: 3 g of corn stover and 60 mL of 25% GVL/H₂O with different NaCl contents); (C) effects of temperature in 25% GVL/H₂O–20% NaCl system for 2 h (reaction conditions: 3 g of corn stover and 60 mL of 25% GVL/H₂O and 20% NaCl); (D) effects of time in 25% GVL/H₂O–20% NaCl system at 170 °C (reaction conditions: 3 g of corn stover and 60 mL of 25% GVL/H₂O and 20% NaCl).

25% GVL/H₂O co-solvent in this work to study its effects on the transformation of corn stover (Fig. 1(B) and Fig. S1†). The conversion of corn stover gradually increased from 46.4% to 53.5% with increasing NaCl content up to 36% (Fig. S1†). It was found that increasing the NaCl content led to an obvious improvement in the removal of hemicellulose and lignin, while cellulose was quantitatively preserved (>80%). To further verify the important role of NaCl in the fractionation of corn stover, two different concentrations of NaCl (5% NaCl and 20% NaCl) were added to the co-solvents with different GVL/H₂O ratios (Fig. 2). It was further confirmed that NaCl could promote the conversion of corn stover in the co-solvent with different GVL/H₂O ratios, and the value increased up to 14.0% in the 75% GVL/H₂O system when 20% NaCl was added (Fig. 2 (A)). As shown in Fig. 2(B)–(D), the transformation of hemicellulose and lignin was significantly enhanced with the addition of NaCl in GVL/H₂O co-solvent with different ratios, while cellulose conversion only slightly increased and stayed below 20%. When 20% NaCl was added in 25% GVL/H₂O at 160 °C for 2 h, a higher removal of hemicellulose (85.8 wt%) and lignin (71.9 wt%) was achieved, while 85.6 wt% cellulose remained. Beyond the salt effects of NaCl that are usually reported to separate organic/water co-solvent,^{15,18} this work reveals that NaCl performs a potential catalytical function, which could effectively improve the simultaneous removal of hemicellulose and lignin in GVL/H₂O co-solvent, while most cellulose was kept intact in the solid residues.

Temperature and time were also the key factors of the improvement of hemicellulose and lignin removal from corn stover in the 25% GVL/H₂O–20% NaCl system (Fig. 1(C)). It was found that the removal of cellulose increased slightly from 7.7 to 14.4 wt% upon increasing the temperature from 120 to 160 °C. When the temperature was above 160 °C, it caused an obvious increase in cellulose conversion. The removal of hemicellulose and lignin gradually increased to 96.4% and 86.6%, respectively, upon increasing the temperature from 120 to 170 °C. A further increase in temperature to 200 °C did not significantly increase the removal of hemicellulose and lignin. XRD results showed that the crystallinity index (CI) gradually increased from 72.1% to 82.7% upon increasing the temperature to 170 °C, indicating that the relative content of cellulose increased and the main crystalline cellulose was preserved (Fig. S2†). The effects of time at 170 °C on the conversion of the three main components of corn stover are given in Fig. 1 (D). It shows a gradual increase in the removal of hemicellulose and lignin in the first two hours and remained around 96.4–98.1 wt% and 86.6–90.3 wt% with prolonged time up to 6 h, respectively. The removal of cellulose slightly increased with prolonged time and reached 25 wt% for 2 h which was acceptable for keeping most cellulose in solid residues. SEM confirmed that the cellulose structure was almost intact after being treated in the 25% GVL/H₂O–20% NaCl system at 170 °C for 2 h in comparison with raw corn stover (Fig. S3†). The FT-IR spectra of solid pre-treated samples at



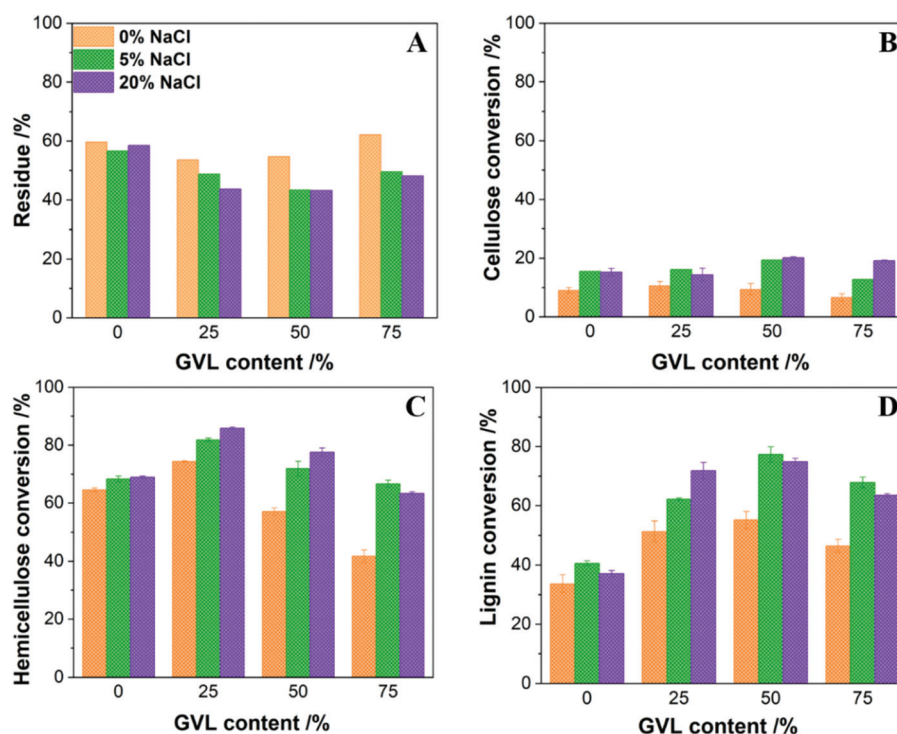


Fig. 2 Comparison of NaCl performance on the fractionation of corn stover at different GVL/H₂O ratios (A, residue percent; B, cellulose conversion; C, hemicellulose conversion; D, lignin conversion. Reaction conditions: 3 g of corn stover and 60 mL of GVL/H₂O with different contents of GVL (0, 25, 50, 75%) and NaCl (0, 5, 20%), the concentration of NaCl is referred to that in the aqueous phase).

various temperatures showed that the absorbance peaks assigned to hemicellulose and lignin almost disappeared upon treatment at 170 °C for 2 h, while the cellulose spectra were not significantly affected (Fig. S4†). Therefore, most of the hemicellulose (96.4 wt%) and lignin (86.6 wt%) could be simultaneously extracted upon treatment at 170 °C for 2 h in the developed 25% GVL/H₂O–20% NaCl system. Jiang *et al.* reported the conversion of microcrystalline cellulose in the 33% GVL/H₂O–30% NaCl system with microwave heating.²² It was found that 76% cellulose was converted to a sugar-rich aqueous solution and a rich HMF organic phase at 220 °C in 18 min. However, there was a big difference between the pure microcrystalline cellulose and the cellulose component in real biomass. In this work, it was found that most hemicellulose and lignin from raw biomass were simultaneously extracted in the GVL/H₂O–NaCl system at a lower temperature of 170 °C for 2 h, keeping most cellulose intact in solid residues. This also provided valuable information that selective removal of hemicellulose and lignin in biomass could be achieved by adjusting the reaction conditions of the GVL/H₂O–NaCl system.

3.2 Effects of NaCl in GVL/H₂O co-solvent on the extraction of hemicellulose and lignin in corn stover

The above results show that NaCl content in GVL/H₂O is responsible for the dissolution efficiency of the three main components of corn stover. To study the roles of NaCl in the extraction of the three main components of corn stover, XRD

analysis was firstly carried out (Fig. S5† and Fig. 3(A)). The major crystalline peak of the samples representing the cellulose crystallographic plane (200) occurred at around $2\theta = 22^\circ$, while the other typical diffraction peak of the amorphous portion appeared at around $2\theta = 18^\circ$.^{15,28} Compared to corn stover feedstock (69.5%), the CI increased after being treated by GVL/H₂O co-solvent with different ratios and reached the maximum of 81.9% at 25% GVL/H₂O (Fig. S5(A)†). This might be attributed to the fact that more amorphous hemicellulose and lignin were selectively extracted after being treated by 25% GVL/H₂O. With the addition of different amounts of NaCl in 25% GVL/H₂O (Fig. 3(A)), the CI of the samples were maintained at around 80%, indicating that the crystalline structures of cellulose were not affected. This was also proved by derivative thermogravimetric results (DTG, Fig. S5(B)† and Fig. 3(B)), where the shoulder peak assigned to hemicellulose was flatter with the addition of NaCl in 25% GVL/H₂O, and the main peak at 330 °C corresponding to cellulose shifted with increasing NaCl content but retained its strength.²⁹ This also confirmed that NaCl promoted the removal of hemicellulose while ensuring the dominant crystalline structure of cellulose was almost unaffected. Moreover, the degradation characteristics of cellulose could be improved as the amount of NaCl increased, so as to facilitate further utilization. The FT-IR spectra of different samples obtained from the GVL/H₂O co-solvent with different ratios confirmed that cellulose was preserved after the removal of hemicellulose and lignin (Fig. S5



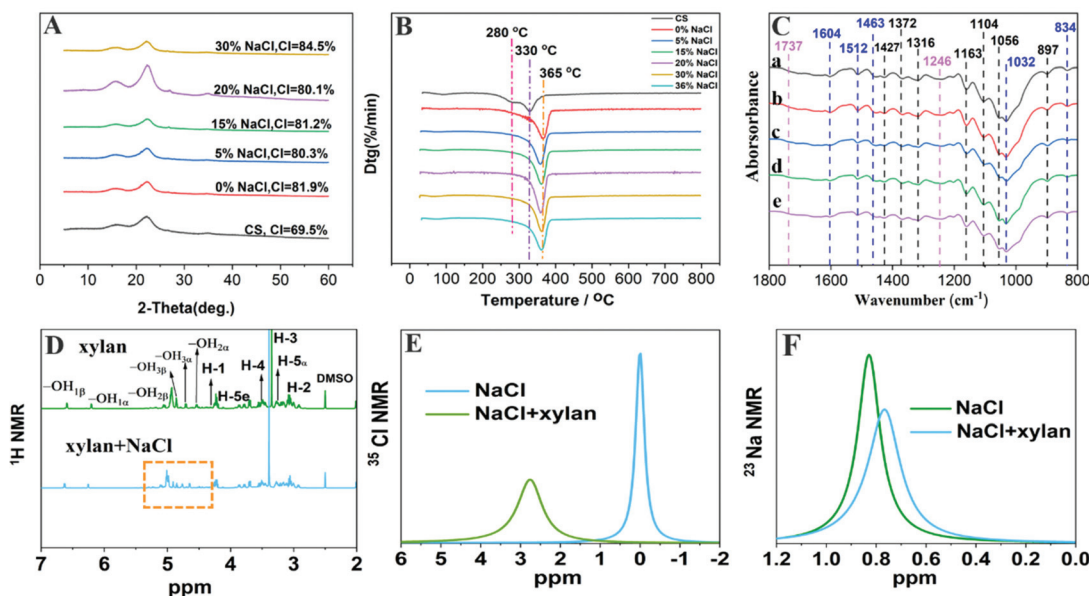


Fig. 3 (A) XRD, (B) DTG and (C) FT-IR results of samples obtained after being treated by 25% GVL/H₂O with different NaCl contents (a, 0% NaCl; b, 5% NaCl; c, 15% NaCl; d, 20% NaCl; e, 30% NaCl). (D–F) ¹H, ³⁵Cl and ²³Na NMR spectra of xylan solutions with and without NaCl. The assignment of signals was according to the literature.^{37,38}

(C)†). The results match well with the above XRD, TG-DTG and chemical titration results. Upon increasing the NaCl content from 5% to 30% in 25% GVL/H₂O co-solvent, the characteristic peaks assigned to hemicellulose at 1737 (corresponding to carbonyl groups from hemicellulose)³⁰ and 1246 cm⁻¹ (assigned to the stretching vibration of C=O in hemicellulose)³¹ decreased as shown in Fig. 3(C). Li *et al.* found that the pH of water rapidly decreased when 5% NaCl was added.³² Song *et al.* reported that the addition of NaCl changed the acidic environment, which then affected the removal of hemicellulose.³³ The pH values of pure water and 25% GVL/H₂O–NaCl system with increasing NaCl amount were detected (Table S1†), which showed that increasing the NaCl amount in pure H₂O and 25% GVL/H₂O decreased the pH values. Yu and Jiang *et al.* both reported that NaCl promoted the formation of acidic products such as formic acids as the reaction proceeded that decreased the pH value.^{21,23} Therefore, the change of the acidic environment by NaCl addition was one of the factors for the removal of hemicellulose.

Jiang and Li *et al.* reported that NaCl enhanced the dissolution of cellulose in biomass at higher temperatures of 180–220 °C for 2 h.^{27,34} In the previous work, the effects of different organic salts such as KCl, K₂SO₄, CaCl₂, NaCl, MgCl₂, AlCl₃ and Al₂(SO₄)₃ on some typical biomass (*e.g.* corn stover and corn cob) were studied. It was found that the cations and anions exhibited important roles in the dissolution of the three main components in biomass.^{35,36} To further study the effects of NaCl on the removal of hemicellulose, xylan was chosen as the model compound. The ¹H NMR spectra of xylan solutions with and without NaCl were analyzed. It was observed that the signals assigned to –OH_{2α} and –OH_{3α} in xylan moved downfield, and –OH_{3β} divided into two peaks

upon NaCl addition (Fig. 3(D)).^{37,38} The ³⁵Cl NMR and ²³Na NMR spectra of NaCl showed an obvious shift when xylan was added into NaCl solution (Fig. 3(E) and (F)). According to the work of Qrtiz *et al.*,³⁸ the observed shifts of NMR signals were due to the interaction between –OH in xylan and NaCl including Na⁺ and Cl⁻. Yu *et al.* found that NaCl had selective interactions with the free hydroxyl groups at the C6 and C2, 3, and 5 positions of starch.²³ Thus, the interactions of –OH in hemicellulose and NaCl in GVL/H₂O co-solvent were another factor for promoting hemicellulose removal. It was previously found that the formation of hydrogen bonds between the –OCH₃ groups in the G and S units of lignin and GVL/H₂O promoted the dissolution of lignin.³¹ From the FT-IR spectra, it was noted that the characteristic peaks associated with the typical features of lignin (1604, 1512, 1463, 1032 and 834 cm⁻¹)^{28,39} decreased, especially the peak at 834 cm⁻¹ (C–H in the G unit of lignin), when more than 15% NaCl was added (Fig. 3(C)). This indicates that NaCl would enhance the interactions and promote delignification. The characteristic peaks assigned to cellulose at 1427, 1372, 1316, 1163, 1104, 1056 and 897 cm⁻¹ were almost unchanged.^{31,35} Therefore, the simultaneous extraction of hemicellulose and lignin could be achieved by adjusting and controlling the amount of NaCl and the ratios of GVL/H₂O. At the same time, most cellulose was kept intact in solid samples under these conditions.

3.3 Roles of NaCl in the depolymerization and transformation of hemicellulose and lignin from corn stover

To study the roles of NaCl in the depolymerization and transformation of hemicellulose and lignin, a variety of analytical techniques (*e.g.*, HPLC, GC-FID, GPC, 2D HSQC NMR and ESI-MS analysis) were used for the analysis of the liquid pro-



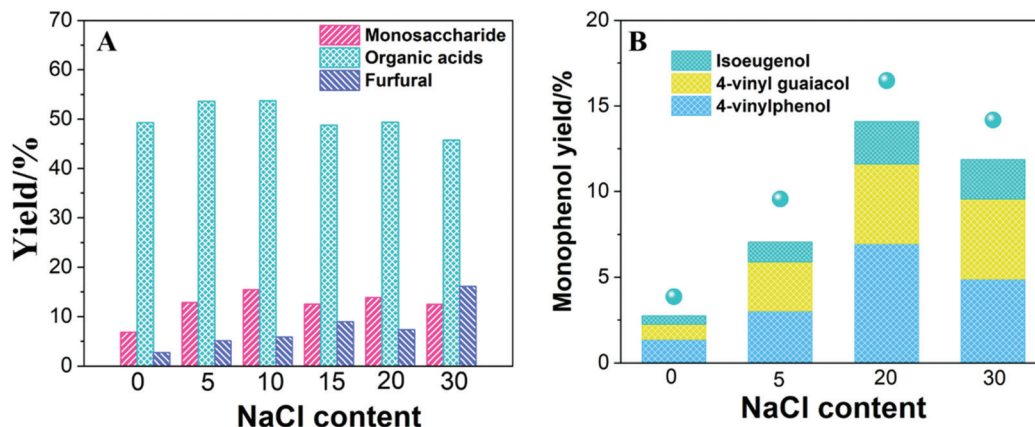


Fig. 4 Effects of NaCl contents in 25% GVL/H₂O on the yields of small molecular products mainly derived from hemicellulose (A) and lignin (B) (reaction conditions: 3 g of corn stover and 60 mL of 25% GVL/H₂O with different contents of NaCl (0–30%), 160 °C for 2 h; the yields of monosaccharides, organic acids, and furfural were calculated based on the weight of hemicellulose in corn stover. The yields of monophenols were calculated based on the weight of lignin in corn stover).

ducts obtained from different systems. After being treated by 25% GVL/H₂O at 160 °C for 2 h, the yield of small molecular products derived from hemicellulose was 58.8% (based on the weight of hemicellulose), containing 49.3% organic acids, 6.8% sugars and 2.7% furfural (Fig. 4(A) and Table S2†). The total yield of monophenols derived from lignin was 8.5% based on the weight of lignin, and 4-vinylphenol (1.36%), 4-vinyl guaiacol (0.88%) and isoeugenol (0.52%) were detected as the main phenol monomers (Fig. 4(B) and Table S5†). Compared to the dissolved hemicellulose (74.4 wt%) and lignin (51.4%), the yield of the obtained small molecular products was low.

With the addition of NaCl to the 25% GVL/H₂O system at 160 °C for 2 h, the yield of monosaccharides and furfural slightly increased. The organic acids were still the main product, and their yield remained around 50%. The total yield of small molecular products derived from hemicellulose was over 70%, while the conversion of hemicellulose was around 82–85 wt% with the NaCl content increasing from 5 to 30% in the GVL/H₂O co-solvent. Furthermore, the total yield of small molecular products derived from hemicellulose increased with increasing temperature and time, respectively (Fig. S6, Tables S3 and S4†). At 170 °C for 2 h in GVL/H₂O–20% NaCl, the yield of hemicellulose-derived small molecular products reached 85.6% including 50.9% organic acids, 23.9% furfural and 10.8% monosaccharides. The organic acids mainly contained 32.2% formic acid and 14.0% acetic acid followed by a small amount of lactic acid (2.75%) and levulinic acid (1.97%). Xu *et al.* reported that the adsorption of H⁺ on the surface of polysaccharides enabled Cl[−] anions to cleave the ether bonds of polysaccharides, which enhanced the hydrolysis of sewage sludge upon the addition of NaCl.⁴⁰ Therefore, NaCl promoted most dissolved hemicellulose depolymerization to small molecular products. In addition, Jiang *et al.* compared the effects of different alkali halide salts at the same molar concentration for the depolymerization of xylo-oligomers.²¹ It was found that

Cl[−] rather than Na⁺ plays the main role in rate enhancement due to the disruption of the hydrogen bonding network of xylo-oligomers and in the depolymerization of xylo-oligomers. In addition to NaCl as an additive, the effects of different sodium salts (Na₂SO₄, Na₂C₂O₄ and NaNO₃) and chlorine salts (KCl, and LiCl) on the yield of products from the conversion of xylan as a model compound in 25% GVL/H₂O at 160 °C for 2 h were also studied (Fig. S7†). It was also found that Cl[−] rather than Na⁺ exhibited better depolymerization ability towards xylo-oligomers to obtain small molecular products. In the 25% GVL/H₂O system, the addition of Na₂SO₄, KCl, LiCl and NaCl exhibited salt effects which promoted the phase separation to obtain a biphasic system. However, the yield of small molecular products with the addition of Na₂SO₄ was lower than that of KCl, LiCl and NaCl. This suggested that Cl[−] played a vital role in the depolymerization of hemicellulose compared to salt effects. Compared to KCl and LiCl, NaCl promoted a higher yield of small molecular products from xylan. This indicated that Na⁺ also helped the depolymerization of xylo-oligomers, which was in accord with the ²³Na NMR and ³⁵Cl NMR results (Fig. 3(E) and (F)).

For the phenol monomers derived from lignin, the total yield of monophenols (based on the weight of lignin in corn stover) significantly increased from 3.86% to the maximum value of 16.5% in 25% GVL/H₂O with the addition of 20% NaCl at 160 °C for 2 h (Fig. 4(B) and Table S5†). 4-Vinylphenol, 4-vinyl guaiacol and isoeugenol were also detected as the main products. This suggested that NaCl promoted the depolymerization of lignin to obtain phenol monomers. Increasing the temperature to 170 °C for 2 h led to more lignin dissolution but the total yield of monophenols slightly decreased to 14.2%. Compared to the dissolution of lignin (86.6 wt%), the liquid products were also abundant with lignin-derived oligomers.

To further confirm the above, the GPC analysis of the distribution of liquid products was carried out. This shows that a higher weight-average molecular product (*M*_w = 6809 Da) with



the polydispersity (PDI) of 17.7 was obtained after being treated by 25% GVL/H₂O (Table 1). Upon increasing the NaCl content from 5 to 30%, the M_w and PDI values significantly reduced to 180 Da and 1.2. As shown in Fig. 5(A), liquid products with a molecular weight of 400–5000 Da accounted for 45.2%, while 11.7% liquid products with molecular weights greater than 10 000 Da were observed in 25% GVL/H₂O co-

Table 1 GPC results of liquid components obtained from the 25% GVL/H₂O system with different NaCl contents at 160 °C for 2 h

Reaction conditions	M_n (Da)	M_w (Da)	PDI ^a
0% NaCl	384	6809	17.7
5% NaCl	209	481	2.3
15% NaCl	190	358	1.9
20% NaCl	187	263	1.4
30% NaCl	180	208	1.2

^a PDI = M_w/M_n .

solvent. When 5% NaCl was added to 25% GVL/H₂O co-solvent, the products with molecular weights of 400–5000 Da only accounted for 7.8% (Fig. 5(B)) compared to 45.2% after being treated by the NaCl-free 25% GVL/H₂O system (Fig. 5(A)). The products with molecular weights of 200–400 Da and 150–200 Da significantly increased from 22.1 and 7.2% to 56.2 and 29.9%, respectively. Further increasing the NaCl content to 30%, the liquid products with molecular weights of M_w = 200–400 Da gradually degraded and the products with molecular weights of 150–200 Da significantly increased from 29.9 to 71.8% (Fig. 5(B)–(E)). This suggests that NaCl exhibits great advantages in the depolymerization of oligomers. This was also proved by the ESI-MS results (Fig. S8†). Because most dissolved hemicellulose has been depolymerized to obtain small molecular products, the lignin-derived oligomers were further analyzed by 2D HSQC NMR analysis.

According to 2D HSQC NMR analysis (Fig. 5(F) and Table S7†), the lignin-derived oligomers mainly contained

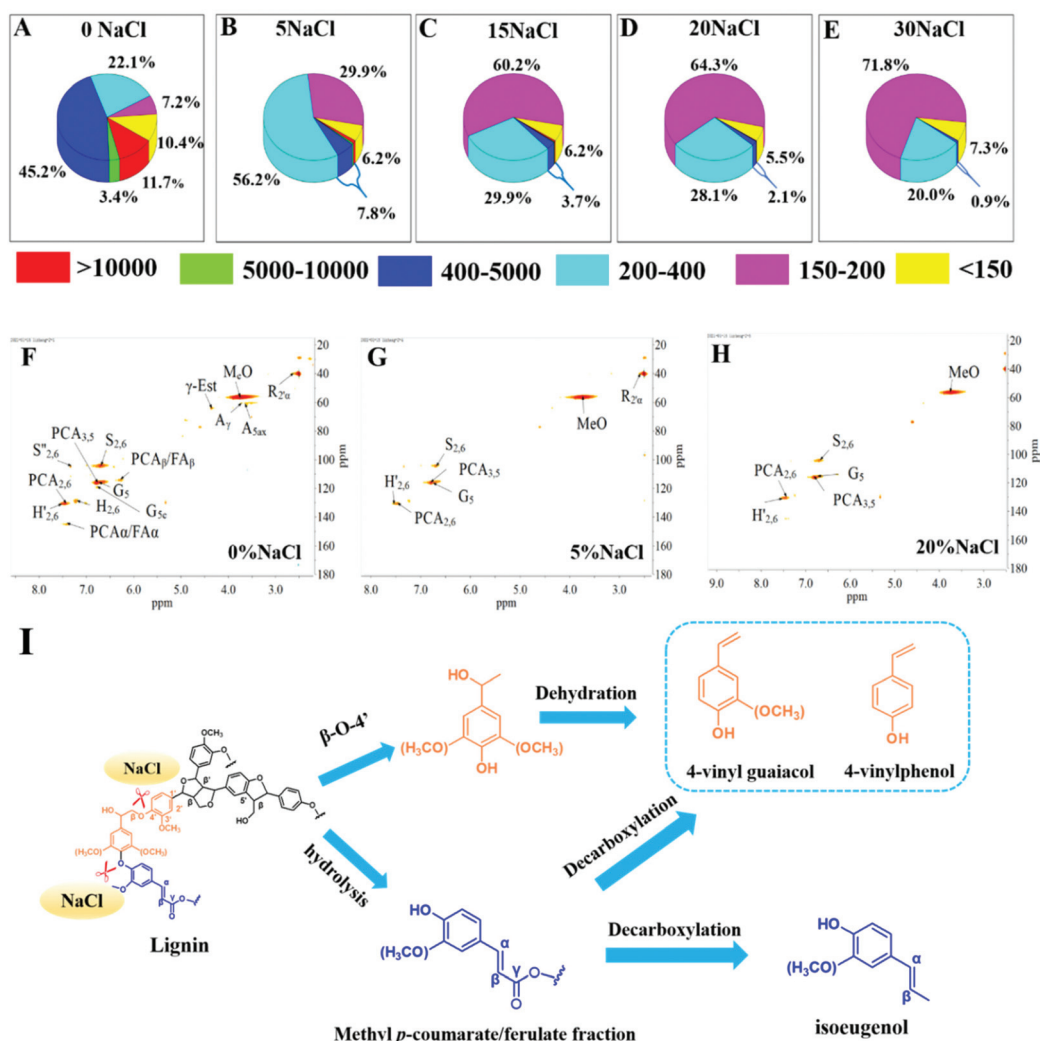


Fig. 5 GPC (A–E) and 2D HSQC NMR (F–H) results of liquid products obtained from different NaCl contents in the 25% GVL/H₂O system at 160 °C for 2 h (reaction conditions: 3 g corn stover and 60 mL of 25% GVL/H₂O with and without 5% or 20% NaCl). (I) The proposed mechanism for the degradation of lignin to produce phenol monomers. The assignments to the 2D HSQC NMR signals derived from lignin are shown in Table S7.†



β -O-4' linkages (A_v) with syringyl (S), guaiacyl (G), *p*-hydroxyphenyl (H) units, and *p*-coumarate (PCA)/ferulate (FA) structures in 25% GVL/ H_2O co-solvent. With the addition of NaCl, the signal assigned to A_v disappeared and the signals assigned to S, G, H and PCA/FA units in aromatic region ($\delta C/\delta H$ 100–150/6.0–8.0 ppm) significantly weakened (Fig. 5(G) and (H)). This suggests that NaCl mainly promotes the cleavage of β -O-4' linkages in lignin to obtain lower molecular weight oligomers. From the GC-FID results, the yields of 4-vinylphenol, 4-vinyl guaiacol and isoeugenol significantly increased with the addition of NaCl. Ma *et al.* reported that the production of 4-vinylphenol and 4-vinyl guaiacol might be from the decarboxylation reaction of methyl *p*-coumarate and methyl ferulate from corn stover.⁴¹ Liu *et al.* found that the production of 4-vinylphenol was ascribed to the cleavage of β -O-4' linkages connecting G units in lignin.⁴² The ESI-MS results also showed that the peaks assigned to lignin derived oligomers containing the β -O-4' linkage fraction and the *p*-coumarate/methyl ferulate fraction (such as m/z = 139.02, 182.06, 186.07, 274.27, 283.16, 318.30) existed in the 25% GVL/ H_2O system. While most of the above peaks disappeared or decreased, the peaks at m/z = 155.07 ($M(4\text{-vinyl guaiacol})\text{-}H_2O + Na^+$), 205.07 ($M(\text{isoeugenol}) + H_2O + Na^+$), and 241.09 ($M(4\text{-vinylphenol}) \times 2 + H^+$) were observed with the addition of 20% NaCl to the 25% GVL/ H_2O system (Fig. S8 and Table S6†). According to the 2D HSQC NMR, ESI-MS and GC-FID results, the addition of NaCl promoted the cleavage of β -O-4' linkages in lignin and produced 4-vinylphenol and 4-vinyl guaiacol by a dehydration reaction. The *p*-coumarate/methyl ferulate obtained by the hydrolysis of lignin might undergo a decarboxylation reaction to produce 4-vinylphenol, 4-vinyl guaiacol and isoeugenol (Fig. 5(I)). Therefore, with the addition of NaCl to 25% GVL/ H_2O co-solvent, part of lignin was depolymerized to obtain 4-vinylphenol, 4-vinyl guaiacol and isoeugenol with high selectivity.

3.4 Further utilization of cellulose-rich solid residues

After being treated with 25% GVL/ H_2O –20% NaCl at 170 °C for 2 h, most hemicellulose and lignin were extracted from corn stover, obtaining cellulose-rich solid residues. The utilization of cellulose-rich residues is important to achieve the integrated utilization of corn stover. Cellulose-rich residues can be used in a variety of ways such as starting materials to produce value-added chemicals (e.g. glucose and bioethanol) and high performance materials such as activated carbon applied in pollution control.^{34,43,44} Although lignocellulosic biomass could be directly carbonized to prepare activated carbon without fractionation, the preparation of activated carbon from cellulose-rich residues with high carbon content was considered as one of the examples to achieve the utilization of cellulose component in this work. Therefore, the cellulose-rich solid residues were firstly carbonized at 500 °C for 2 h in N_2 and then activated by steam at 800 for 2 h to prepare activated carbon. A higher surface area of activated carbon (S_{BET} = 819 $m^2 g^{-1}$) could be obtained, which also showed the higher adsorption of methylene blue ($A_{\text{methylene blue}}$ = 212 $mg g^{-1}$) and iodine (A_{iodine} = 914 $mg g^{-1}$). These values were significantly higher

than those of high-quality activated carbon prepared from coal (S_{BET} = 644 $m^2 g^{-1}$, $A_{\text{methylene blue}}$ = 133 $mg g^{-1}$ and A_{iodine} = 770 $mg g^{-1}$), which was usually used for the adsorption of dioxins and heavy metals in biomass power plants. Therefore, the preparation of activated carbon from the cellulose-rich solid residues of waste biomass is an example to achieve the utilization of the cellulose component, which has shown great potential for pollution control within many industrial processes. It also suggested that the use of cellulose-rich residues as starting materials to prepare activated carbon is a promising alternative to replace coal, which meets the current needs of environmental protection and a low-carbon sustainable economy.

3.5 A strategy for the integrated utilization of corn stover

This work demonstrated an integrated green process for the effective utilization of various components of corn stover (Fig. 6), which is significantly important for developing a sustainable corn stover-based biorefinery. A solvent system of 25% GVL/ H_2O –20% NaCl has been developed for the simultaneous extraction of hemicellulose (96.4%) and lignin (86.6%) from corn stover through a one-step strategy at 170 °C for 2 h, obtaining cellulose-rich solid residues.

In the liquid component, the dissolved hemicellulose was depolymerized and mainly converted to small molecular products (85.6%) including 50.9% organic acid, 23.9% furfural and 10.8% monosaccharides. It was found that a part of dissolved lignin has been depolymerized to produce 14.2% monophenols with high selectivity of 81.9% to 4-vinylphenol, 4-vinyl guaiacol and isoeugenol. While the other dissolved lignin part was in the form of oligomers with a lower molecular weight (M_w = 438 Da), which mainly included β -O-4' linkages connecting the G, S and H units with the *p*-coumarate and ferulate structures. According to the literature, the yield of phenol monomers from the depolymerization of lignin in herbaceous biomass was around 8.4–25.0%.^{41,42,45} Ma *et al.* obtained a yield of 25.1% phenol monomers from corn stover in methanol with H_2WO_4 catalyst at 200 °C for 6 h.⁴¹ Liu *et al.* developed a two-step process using Ni/HZSM-5 catalyst in butanol/ H_2O co-solvent for the conversion of lignin from corn residues and achieved the maximum monophenol yield of 19.5% at 300 °C with 2 MPa H_2 .⁴² Compared to the literature, the yield of monophenols obtained in this work was at a medium level but it only needs mild reaction conditions without the addition of H_2 . Furthermore, the molecular weight of the obtained lignin oligomers was significantly lower than that of the reported technical lignin (such as kraft lignin and alkali lignin, M_w > 844 Da).⁴⁵ This provided a possibility for the further degradation of lignin oligomers directly to produce monophenols in good yield.

With the addition of 20% NaCl in the 25% GVL/ H_2O system, NaCl promoted phase separation to obtain a biphasic system. The distribution of sugars, organic acids and furfural mainly derived from hemicellulose in the water-rich phase and GVL-rich phase for 25% GVL/ H_2O –20% NaCl system were detected, respectively (Table S8†). Furfural was mainly in the



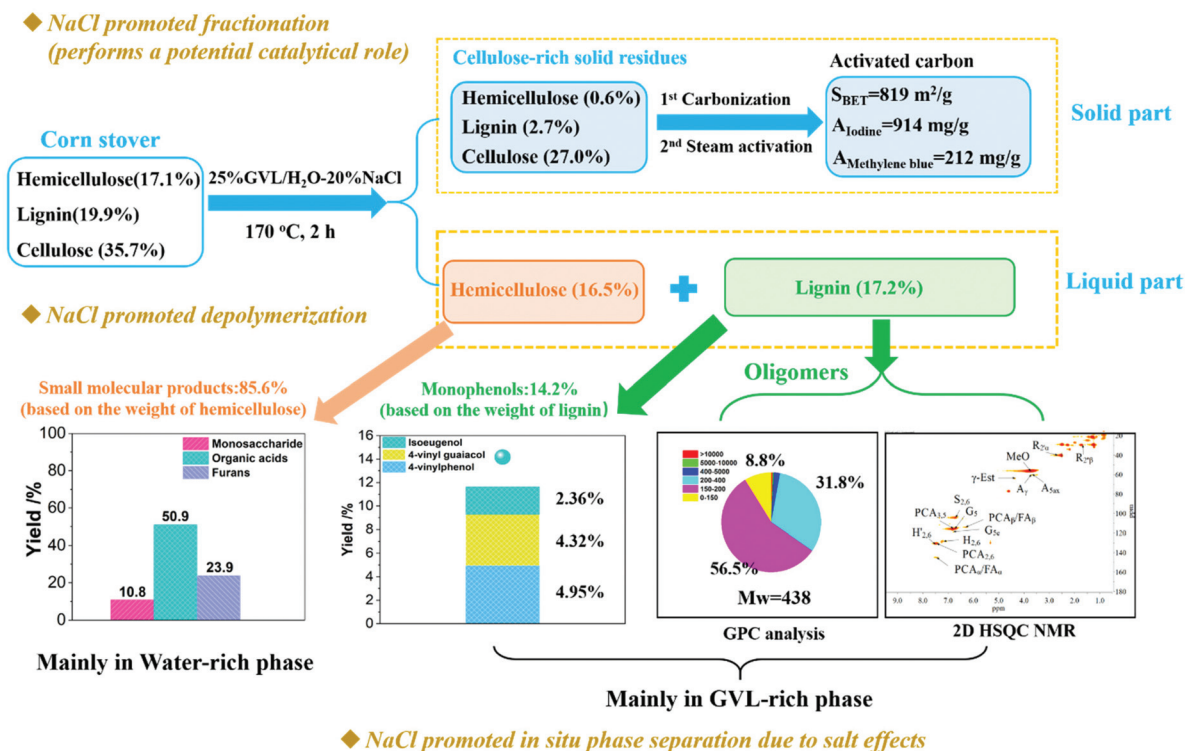


Fig. 6 An integrated process for the valorization of various components in corn stover (reaction conditions: 3 g of corn stover and 60 mL of 25% GVL/H₂O with 20% NaCl, 170 °C for 2 h).

GVL-rich phase, but the yield of furfural in the developed 25% GVL/H₂O-20% NaCl solvent system was relatively low (23.9% based on the weight of hemicellulose). Although a small amount of organic acids derived from hemicellulose were extracted in the GVL-rich phase, the results in Table S8† show that most sugars and organic acids existed in the water-rich phase. This might be because a lower fraction of GVL (25%) was used and that the organic acids as main products have a higher distribution in the GVL-rich phase as compared to the aqueous phase. This was also in accord with the work of Dutta.¹⁶ It was confirmed that GVL is a good solvent to extract lignin-derived products.^{14,15} Based on the Hofmeister series, NaCl added to 25% GVL/H₂O exhibited salt effects including “salting in” and “salting out”. The solubility of hemicellulose-derived products in water increased with increasing salt concentration (“salting in”), while that of lignin-derived products decreased (“salting out”). Therefore, in the liquid component, most of the liquid products derived from hemicellulose and lignin were *in situ* separated into the water-rich phase and the GVL-rich phase, respectively, due to the phase separation promoted by the salt effects of NaCl. In the solid part, the cellulose-rich solid residues were further utilized to produce high-performance activated carbon ($S_{\text{BET}} = 819 \text{ m}^2 \text{ g}^{-1}$, $A_{\text{methylene blue}} = 212 \text{ mg g}^{-1}$, $A_{\text{iodine}} = 914 \text{ mg g}^{-1}$) as one of the examples to achieve the utilization of the cellulose component, which shows great potential for pollution control from many industrial processes.

In addition, in the 25% GVL/H₂O-20% NaCl system, the recovery of GVL as a high boiling point solvent is simple and possible by separation and purification following commonly used techniques such as fractional distillation.^{13,16,46} The NaCl used in the developed solvent system could provide clues to use seawater for large-scale operations. Moreover, the use of organic acids as major products in the aqueous phase can be isolated by reactive distillation, such as esterification with methanol, leaving the aqueous solution containing NaCl, and the latter could be used for fresh corn stover conversion.⁴⁷ The recycling of GVL and NaCl and the application of seawater need further investigation. For products, the mixture in the aqueous phase contained organic acids which can also be used as carbon sources for further use by microbial fermentation, in addition to separation. The lignin-derived oligomers in the GVL-rich phase can be recovered by precipitation, which can then be further used.⁴⁷ The products in the GVL-rich phase can be also used directly to prepare chemicals and fuels.⁴⁶ Therefore, these findings show a route to the integrated valorization of various components in corn stover. In this work, renewable feedstock, green solvents and additives were used. Based on the 12 principles of green chemistry,⁴⁸ the developed solvothermal transformation process is beneficial for the development of economic, energy efficient and zero-waste corn stover based biorefineries compared to traditional thermochemical processes (Table S9†), which is a good choice for a green and sustainable future. Furthermore,



life cycle assessment (LCA) is an important environmental management tool, which could help for the systematic analysis of the potential environmental impacts of products, feedstocks and processes during their entire life cycle. A comprehensive LCA on solvent waste demonstrated that implementing a solvent recovery system can reduce the environmental footprint of the total solvent manufacturing, usage, and disposal process.⁴⁹ We are looking further at the potential environmental impacts of the developed process so as to better promote the efficient utilization of waste biomass.

4. Conclusions

A novel solvent system by the simultaneous application of NaCl and GVL/H₂O for the integrated utilization of corn stover in one step is reported for the first time. The multiple functions of NaCl in the GVL/H₂O system were addressed. NaCl as an additive performs a potential catalytical function in 25% GVL/H₂O at 170 °C, promoting the simultaneous extraction of higher hemicellulose (96.4–98.1%) and lignin (86.6–90.3%) in the liquid fraction, while quantitatively recovering most cellulose as solid residues. NaCl exhibits better depolymerization ability, promoting hemicellulose degradation to small molecular products that mainly contain organic acids and promotes lignin depolymerization to monophenols and lower molecular weight oligomers. NaCl also performs “salting in” and “salting out” functions in GVL/H₂O co-solvent, which *in situ* separates most of the products generated from hemicellulose and lignin by respectively dissolving into the aqueous phase and the GVL phase. Interestingly, the cellulose-rich solid residues have been used to prepare high performance activated carbon with great potential for pollution control in many industrial processes. The developed process is green and sustainable, making it highly favorable for the integrated valorization of all the three main components in corn stover.

Author contributions

Yiping Luo: conceptualization, methodology, investigation, formal analysis, data curation, writing-original draft, writing-review & editing, supervision and funding acquisition; Zhichen Zhao: methodology, investigation, formal analysis and data curation; Bin Jiang and Min Wei: investigation, formal analysis and data curation; Zheng Zhang and Lisha Zeng: formal analysis and data curation; James H. Clark: writing-review & editing, supervision and project administration; Jiajun Fan: writing-review & editing, supervision and project administration. All authors approved the final version of the manuscript and contributed to the scientific discussion.

Conflicts of interest

There are no conflicts to declare.

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