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COMMUNICATION

Extraction of 5-HMF from the conversion of glucose in ionic liquid [Bmim]Cl by compressed carbon dioxide

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The efficient extraction of 5-hydroxymethylfurfural (HMF) from the conversion products of glucose in ionic liquid has been achieved *via* charging compressed CO₂ into the mixtures. The targeted and tunable extraction of HMF could be realized because of the insolubility of glucose and the tunable solubility of HMF in compressed CO₂.

With increasing concern about environmental issues and the shortage of fossil fuels, it is urgent to search for sustainable alternatives for chemicals and energy supply. Because of its abundance and possibility of conversion into various valuable chemicals, biomass has caught much attention in recent years.^{1, 2} Dehydration of carbohydrates into 5-hydroxymethylfurfural (HMF), which is an important platform compound for further producing fine chemicals, plastic resins, liquid fuel and materials,³⁻⁵ is one of promising and important routes to replace the current derivatives of petroleum. Among the isomeric hexose monosaccharide, glucose is the cheapest and could be easily obtained through the hydrolysis of natural cellulose.⁶ Although conversion of glucose into HMF is more difficult than that of fructose, much endeavor has been devoted to and many catalysts have been developed for the production of HMF from glucose, of which included Lewis acid catalysts, zeolites and ionic liquids (ILs), etc.⁷⁻⁹

ILs are ionic salts with a melting point below 100 °C, which have become omnipresent in the recent literatures.¹⁰ Due to the possibility to tune the composition of cations and anions, they can be designed to display many desirable properties such as negligible vapor pressure, and high thermal and chemical stability, to satisfy a surprising number of applications.¹¹ Based on the latter two properties, ILs have been recognized as green solvents not only for dissolving numerous carbohydrates, but also for catalytic conversion of carbohydrates into value-adding products.¹²⁻¹⁴ It is relevant to use ILs as new potential media for two advantages: (1) ILs can offer relatively high solubility and have no limit in many applications; (2) most of the enzymes traditionally used in carbohydrate chemistry can also maintain better activity in ILs. Due to the negligible vapour pressure of ILs, development of new systems to both enhance the yield of HMF and efficiently separate the products from ILs remains a major challenge. It is necessary to achieve these goals via

exploring the discrepancies in the interactive forces between glucose, HMF, IL and anti-solvents. Traditionally, some toxic, irritant and harmful solvents, including ethyl acetate, tetrahydrofuran, toluene and ether, have been employed to extract HMF from reaction systems.^{8, 12, 15} Therefore, it is necessary to develop a new method to efficiently and sustainably extract HMF from IL.

Compressed CO₂ has been the focus of attention because it is cheap, nontoxic, tunable, non-flammable and can be easily recycled after use.¹⁶ In particular, compressed CO₂ is soluble in many organic solvents including ILs to expand the solvent volume, and can tune the properties of the solvent continuously by controlling the temperature and pressure. This kind of CO₂-switchable liquids has been used in a variety of fields, including hierarchical extraction, particle formation, processing polymer and acting as reaction media.¹⁷⁻²⁰ It has been reported that CO₂ dissolved in liquid facilitated organic compounds extraction since IL is immiscible with CO₂, and therefore pure product can be recovered.¹⁶

Herein, we propose the CO₂-mediated extraction of HMF. By using compressed CO₂, HMF can be dissolved and separated, while glucose and IL, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), cannot (Fig. 1). In comparison with traditional methods for the extraction of HMF from the mixtures of glucose conversion, the product can be obtained and purified efficiently. Afterwards, CO₂ can be easily removed by reducing pressure. In addition, the system of IL/glucose may be highly effective and reusable for HMF production.

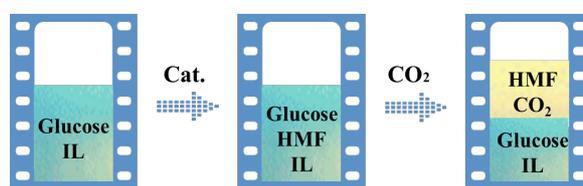


Fig. 1 The use of CO₂ for the efficient extraction of HMF after the transformation of glucose.

Fig. 2 shows the solubility of HMF in compressed CO₂ at different temperatures. X (HMF) is the mole fraction in compressed

CO₂, which can be calculated on the basis of the amount of CO₂ charged into a transparent cell. As expected, the solubility of HMF increases with the increasing CO₂ pressure at a given temperature. Under a fixed pressure, it can be inferred that the HMF solubility approximately decreases with the increasing temperature. Although the increase in the volatility of HMF is favored over its solubility, the decrease in fluid density may ultimately reduce the ability of HMF dissolution. Our results indicated that the latter is the key factor to the HMF solubility in compressed CO₂.

To better understand the effect of compressed CO₂ on the extraction of HMF, the volume expansion of [Bmim]Cl after charging of CO₂ were determined (Fig. S1). It was found that [Bmim]Cl expanded after CO₂ injection, in which case the high quadrupole of CO₂ molecule²¹ may render strong interactions between CO₂ and cation-anion. It is interesting that the volume expansion ratio (V_m/V_0) increases with the increasing of CO₂ pressure and decreases with the increasing of temperature, which has the same effects as the HMF solubility in CO₂. As the volume of solvent expanding, HMF became insoluble in IL, thereby it may be extracted by CO₂ and separated through the varying CO₂ pressure. This phenomenon complies with the result of HMF extraction from [Bmim]Cl.

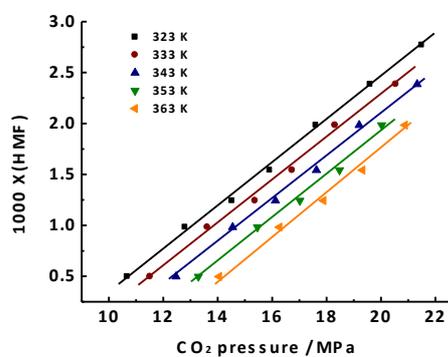


Fig. 2 The solubility of HMF in compressed CO₂ at different temperatures.

Based on the results presented above, the extraction effect of HMF after the conversion of glucose in [Bmim]Cl was also studied. We chose CrCl₂ as the dehydration catalyst to convert glucose into HMF.³ 5 mg catalyst was added in the system (50 mg glucose was added to 0.5 g IL) at 373 K with a reaction time of 3 h, which can achieve a 62 % HMF yield. We examined the influence of HMF extraction by using compressed CO₂ under different conditions and the results are given in Fig. 3. It can be known that the extraction efficiency of HMF obtained in the reaction has the same trend as the HMF solubility in CO₂ under different temperatures and pressures, and increases with the CO₂ extraction time in the meantime. Here the extraction efficiency of HMF refers to the mass ratio of extracted HMF by CO₂ and produced HMF from glucose. Through High Performance Liquid Chromatography (HPLC), about 70 % of HMF product can be separated from reaction system with a high purity in 20 MPa compressed CO₂ at 343 K in no longer than 60 min. We can improve the extraction efficiency of HMF by either repeated extraction or controlling the conditions of compressed CO₂. By combining the results shown in Table S1, it is worth noticing that the extraction efficiency of HMF in CO₂ is much higher than those in the other traditional extraction solvents. Hence, no additional solvent was used after the conversion of glucose and pure HMF can be obtained just by depressurization.

Furthermore, our study also focused on the solubility of glucose in compressed CO₂ and [Bmim]Cl. First, we found that glucose cannot

be dissolved in CO₂. Then, as the solubility of glucose in [Bmim]Cl (100 g) in our experiment is 26 g, we analyzed different glucose solutions by the application of Attenuated Total Reflection Fourier Transform Infra-Red (ATR-IR) spectroscopy. The IR spectra of pure IL and its glucose solutions are shown in Fig. S2. For the applicability of IR spectroscopy in quantitative analysis,²² we used extinction E to response the concentration of the absorbing species according to the Lambert-Beer law,

$$E = -\log_{10}(1 - A)$$

where A is the absorption in the IR spectra.

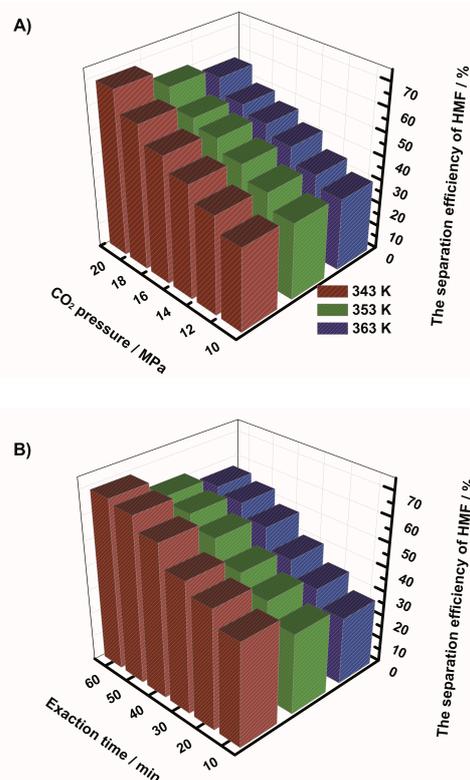


Fig. 3 The extraction efficiency of HMF using compressed CO₂ under different pressures in 60 min (A), and in different extraction time under 20 MPa (B).

Some characteristic features can be assigned to the corresponding vibrational modes. The rocking vibration of C-O bond in glucose is observed around 1080 cm⁻¹, which cannot be shown in the spectra of pure IL. The ring in-plane asymmetric stretching and the bending mode of C-H on the cation is found at 1420 cm⁻¹ and 1480 cm⁻¹, respectively. Besides, a broad band corresponding to the intermolecular -OH vibrations caused by hydrogen bond can be found between 3000 cm⁻¹ and 3500 cm⁻¹. These appropriate detection wavenumbers are further necessary to be selected for accurate quantitative concentration measurements, which are contributed from either glucose or IL as the extinction intensity increases or decreases with the concentration of glucose. As is shown in Fig. 4A, the six data points can be fitted to a simple linear function for 1082, 1427, and 3132 cm⁻¹. We can use these lines for the quantitative analysis of glucose in the appropriate concentration range.

When the experiments were carried out under CO₂ atmosphere, an additional dissolution phenomenon can be found. As can be shown in Fig. 4B, the solubility of glucose in [Bmim]Cl increased with the

increasing CO₂ pressure at certain temperatures. It was a seemingly amazing detail, whose reason can be seen clearly. Towards this goal, we carried out NMR study of IL, IL/CO₂ and IL/glucose. Considering that NMR chemical shift *per se* is affected by the change of temperature, we should analyze and compare them at the same temperature.

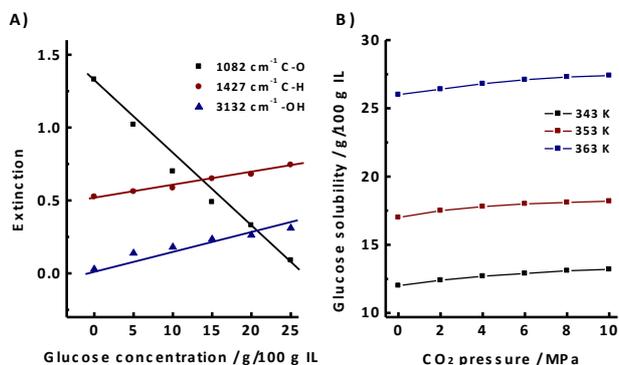


Fig. 4 A) The linear correlation between the extinction at the special wavenumbers and the concentration of glucose in [Bmim]Cl. B) The change of glucose solubility in [Bmim]Cl under different CO₂ conditions.

From the detailed NMR spectra in Fig. S3 and Table S2, we can find that the dissolution of glucose in [Bmim]Cl produces an upfield shift for every carbon atom. The interaction between [Bmim]⁺ and glucose leads to the increasing of the electron cloud density around the carbon atoms. It is interesting to note that the relative chemical shifts increase with the increasing temperature. Due to the decreasing of the shielding effect, the molecular motion rate can be accelerated and the intermolecular interaction becomes weakened at high temperature. In the same way, since no change can be shown in the ¹³C NMR spectra after charging compressed CO₂, the physical combination between CO₂ and [Bmim]⁺ makes the transformation of the diffusion particles in IL change from ion pairs to individual ions and provides more opportunities for Cl⁻ to interact with glucose, which plays a key role in glucose dissolution.²³ Besides, the contribution of the pH change to the glucose dissolution cannot be neglected.

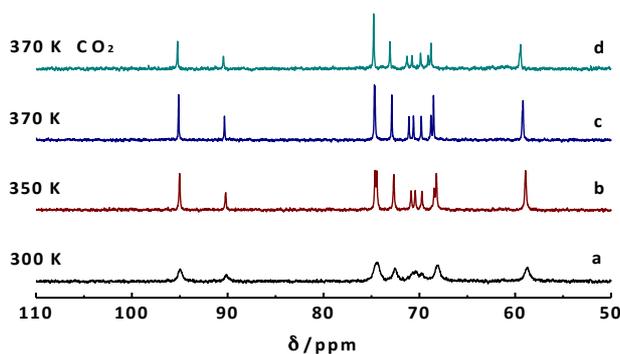


Fig. 5 ¹³C NMR spectra of glucose in [Bmim]Cl at 300 K (a), 350 K (b) and 370 K (c), and after CO₂ processing at 370 K (d) using DMSO-d₆ as external standard.

Since [Bmim]Cl displays no signals in the 50 to 110 ppm region of the ¹³C NMR spectra, we examined the glucose structure in [Bmim]Cl under different conditions. As evidenced by the spectra at 300 K in Fig. 5, lower sensitivity and resolution can be seen due to the molecular tumbling reduced by the high viscosity of solution. As

the temperature increases, the viscosity of IL/glucose decreases, resulting in the improvement of the sensitivity and resolution of ¹³C signals. In the meantime, it is significant to note that the addition of compressed CO₂ in the IL system has no obvious impact on the chemical shifts of glucose, with the largest variation being less than 0.1 ppm (Fig. 5d).

Conclusion

In summary, this work shows the potential use of compressed CO₂ as extractant, which also allow the extraction of HMF with high purity from the conversion of glucose. The extraction efficiency can be tuned by changing the conditions of compressed CO₂. It has been demonstrated clearly that the addition of CO₂ into [Bmim]Cl can enhance the solubility of glucose at high temperature. This should be attributed to the increase of the diffusion particles in the mixture of CO₂ and IL. Herein, the present method can easily remove the product and achieve the subsequent recycling of IL without adding any other organic solvents, which would be a significant step for other analogous reactions toward a more sustainable future.

Acknowledgements

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Notes and references

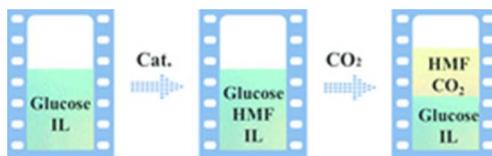
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Electronic Supplementary Information (ESI) available: experimental Techniques and some other data. See DOI: 10.1039/c000000x/

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The efficient separation of 5-hydroxymethylfurfural from the conversion of glucose in [Bmim]Cl has been achieved by using compressed CO₂.
20x6mm (300 x 300 DPI)