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PAPER

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Ionic Liquid-Organics-Water Ternary Biphasic System Enhances 5-Hydroxymethylfurfural Yield in Catalytic Conversion of Glucose at High Concentration

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5 **Conrad Zhang***[a]

Increasing glucose loading in the 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) ionic liquid containing dissolved $CrCl_3$ catalyst system led to excessive formation of humins and serious decrease in 10 5-hydroxymethylfurfural (5-HMF) yield. A biphasic system containing glycol dimethyl ether (GDE) as the extraction phase, and [BMIM]Cl/$CrCl_3$/glucose in combination with a partitioned amount of GDE and an appropriate amount of water as the reaction phase was found highly efficient for the reaction; $CrCl_3$ catalyzed the formation of 5-HMF in 64.5 mol% yield from a very high glucose concentration (80 wt% with respect to the ionic liquid) at 108 ℃. This 5-HMF yield in the [BMIM]Cl-GDE-H_2O ternary biphasic 15 system nearly doubled that obtained in the single [BMIM]Cl/$CrCl_3$/glucose reaction phase. Importantly, the GDE phase contained about 56% of the generated 5-HMF without detectable contamination by the ionic liquid or carbohydrates. GDE served multiple functions: as a hydrogen-bond acceptor, it exhibited excellent extraction performance for 5-HMF; due to its low boiling point and suitable solubility saturation point in the ionic liquid, a sustained GDE bubbling phenomenon in the ionic liquid phase was observed 20 that promoted the rate of inter-phase mass-transfer of 5-HMF under reaction; and GDE mediated the [BMIM]Cl phase to a reduced viscosity. In addition, an appropriate amount of water in the ternary system promoted the extraction efficiency of 5-HMF and also lowered the viscosity of [BMIM]Cl/glucose. The ionic liquid-organics-water ternary biphasic system has been demonstrated for high 5-HMF productivity and separation efficiency.

25 1 Introduction

The diminishing fossil fuel reserves and the growing concern about global warming have driven up the potential utilization of biomass resources as renewable feedstock for the production of fuels and chemicals.[1] Among numerous possible routes currently 30 under investigation, one with potentially high viability for commercial development is the synthesis of 5-HMF, which has been widely recognized as a biomass-derived intermediate for the

production of various non-petroleum based chemicals and fuels.[2,3] Up to now, the C_6 sugars, such as glucose and fructose, 35 as well as polysaccharides, such as cellulose and starch, have been used to produce 5-HMF.[4,5] Many studies adopted fructose as a starting material as it can be readily converted to 5-HMF in high yield by acid catalyzed dehydration.[3,6,7] However, fructose is not a highly prevailing carbohydrate in the nature. In contrast, 40 glucose exists as the building unit of the most abundant carbohydrate polymers, cellulose and starch, in nature.[8] Hence, the perspective to economically convert glucose as the reactant to 5-HMF has motivated tremendous amount of recent researches.[3-5]

Although fructose has been shown to be readily dehydrated to 45 5-HMF, the synthesis of 5-HMF from glucose has been met with considerable technical challenge for needing an efficient catalytic system.[9] A technically viable route for the conversion of glucose to 5-HMF is via isomerization of glucose to fructose, followed by subsequent dehydration of fructose to 5-HMF. Considerable 50 efforts have been focused on one-pot tandem conversion strategies from glucose.[2] Besides the development of efficient catalysts with high selectivity to produce 5-HMF, the selection of

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suitable solvent media is particularly important in enhancing 5-HMF yield and in facilitating 5-HMF separation. Generally, water, aprotic organic solvents, and ionic liquids have been used as the reaction media for the conversion of glucose to 5-HMF in the presence of a catalyst.[2-5] This reaction could hardly be realized in pure water at a mild reaction condition.[10] The reaction in biphasic organic/water system at high temperature (170-175°C) could generate 5-HMF, but the yield was unacceptable due to the low selectivity to 5-HMF (26-33%).[11,12] Some polar aprotic solvents like dimethylsulfoxide (DMSO)[13] or dimethylacetamide (DMA)[14] have been studied as the reaction media or as aqueous solvent modifiers for the conversion of glucose into 5-HMF with AlCl$_3$[13] or LiCl[14] catalysts. However, it has been found that the high boiling point of these organics makes the distillation process energy-intensive and causes serious loss of the 5-HMF product due to the reactive nature of 5-HMF at high temperature. Extractive separation faces great challenge because DMSO is miscible with a wide range of organic solvents.[15] Recently, some ionic liquids have been reported to be highly effective reaction media for one pot conversion of glucose to 5-HMF under mild conditions.[16,17] The first major breakthrough was reported based on the discovery in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) ionic liquid solvent.[18] 5-HMF yields of up to 70% were obtained in this solvent with CrCl$_2$ and CrCl$_3$ as catalysts. Other forms of chloride salt or chromium ion based catalysts in 1-alkly-3-methylimidazolium chloride, [AMIM]Cl, were also effective.[19]

Despite of the significant progress over the recent years, a challenge that must be addressed before commercial production of 5-HMF is the ability to adopt glucose in higher concentrations in the process. Because a dilute system requires high capital investment and operating expenses for a process, a low-concentration process is economically unfavorable on commercial scale. However, most reported works over the past were limited to researches on low glucose concentrations (in loadings in ≤ 10 wt% with respect to the reaction solvent)[2-6] with the purpose of gaining insights on catalytic performance of different catalytic systems. Reaction based on low feed concentration could achieve good results, such as high feed conversion and high product selectivity, but it cannot effectively predict the performance from high-concentration systems.[20,21] Up till now, the effect of higher glucose concentration has received little attention in ionic liquid systems according to the published literature. Therefore, research is critically needed to study catalyst performance, solvent effects and process conditions for 5-HMF production from glucose in high concentrations.

In addition, efficient isolation of 5-HMF from the ionic liquid solvents is also a critical part of the overall 5-HMFproduction process. Separation of 5-HMF by distillation is not practical due to the very low vapor pressure of 5-HMF. An alternative choice is to extract 5-HMF formed in the reaction system into the organic extraction phase. Although a few biphasic systems involving an ionic liquid reaction phase and an organic extraction phase have been reported,[22-24] there are still several issues to be addressed. First, these studies were limited to comparing the glucose conversions and 5-HMF yields between the biphasic systems and the monophase systems. Little attention was given to systematically study the extraction performance, such as the partition coefficient and the 5-HMF concentration in the top organic phase. Second, although a large number of organic solvents such as ethers, ketones, esters and alcohols are potential extractants in biphasic reaction systems for 5-HMF production, the most suitable type of the organics has to be determined, and preferably with essentially predictable properties. Third, some measures for enhancing the inter-phase mass transfer of 5-HMF must be taken to overcome the poor mixing under agitation due to the large density difference between the organic phase and the ionic liquid phase. Most importantly, 5-HMF production from glucose in biphasic solvents should be evaluated in a reaction system with a high glucose concentration, so the results could be relevant for the design of a commercial 5-HMF production process.

This work was specifically carried out for the synthesis of 5-HMF from glucose in high concentration in [BMIM]Cl/CrCl$_3$ under mild reaction conditions. A series of organics and water were evaluated as components of the ternary biphasic system that also effectively mediates the properties of [BMIM]Cl ionic liquid to enhance the 5-HMF yield. The mechanism of the solvency mediation on enhancing the 5-HMF yield and extraction efficiency in the high-concentration systems was investigated.

2 Material and Methods

2.1 Materials

5-Hydroxymethylfurfural (5-HMF, 98%) was obtained from Aladdin (China). Tetrahydrofuran (THF, 99%), butyl ether (99%), methyl tertiary butyl ether (MTBE, 99%), cyclohexanone (Anon, 99%), glycerol (99%) and D-glucose (glucose, 99%) were purchased from Sinopharm (China). Glycol dimethyl ether (GDE, 99%) and acetylacetone (Hacac, 99%) were supplied by Tianjin Guangfu Chemical Reagent Co., Ltd (China). Ethyl acetate (EtOAc, 99%) was purchased from Tianjin Kermel Chemical Reagent Co.,Ltd (China). n-butanol (99%) was bought from Tianjin Damao Chemical Reagent Factory (China). Methyl isobutyl ketone (MIBK, 99%) was supplied by Beijing Chemical Reagent Factory (China). Deionized water (DI H$_2$O) was supplied by Hangzhou Wahaha Group Co., Ltd. (China). All the chemicals above were used as received. [BMIM]Cl was purchased from Lanzhou Greenchem ILS, LICP (China). It was degassed through online-vacuum at 100 °C for 10h. 1H-NMR spectral data of the [BMIM]Cl were determined by using an AV-400 Bruker spectrometer and was found in good agreement with those reported in the literature.[25]

2.2 Viscosity measurement

Capillary viscosities of [BMIM]Cl and its mixtures at atmospheric pressure were measured using an GB/T265 Kinematic viscosity measuring unit (Dalian Zhineng Instrument Group Co., Ltd., China) fitted with flat open Abramovich Standard viscometers. The temperature of the thermostatic glycerol bath was measured with a 100 Ω platinum resistance thermometer with an overall estimated uncertainty of ±0.1 K. The viscosity measurement for each sample was repeated three times and the overall maximum uncertainty of these viscosity measurements was estimated as ≤1%.

2.3 Extraction methods

To establish the extraction parameters, model compounds and solvents were used in the absence of a catalyst. For each extraction sample, a specified amount of [BMIM]Cl (preheated at 100 ^{o}C and kept in liquid state before dispensing), water, 5-HMF, glucose and organic solvent were added into a glass vial with scale lines. The glass vial was sealed with a cap and its volume was calibrated. Chemical dispense was conducted on a Core Module 3 (CM3) high throughput instrument (Freeslate Co., USA), a bench-top platform system that performs complex automated liquid and powder weighing, mixture stirring and temperature monitoring. The dispense accuracies of the powder and the liquid are 0.5 mg and 0.5 μl, respectively. The extraction experiments were operated at room temperature, 24~26 ^{o}C. The compounds in the vial were mixed by sufficient shaking for 30 min, and at last the vial was settled in the static stage for phase separation for 3 h. After several experiments and taking samples at different time intervals, it was found that increasing the agitation time (minimum time 30 min) and the rest time (minimum time 3 h) had no effect on equilibrium phase compositions. After complete phase segregation, the volumes of the top and bottom phases were measured and the samples from the two phases were collected. Then glycerol as an internal analytical standard was added to the samples, and the mixtures were analyzed by HPLC. A mass balance was made between the initial mass of 5-HMF and the amounts in the extraction phase and the raffinate phase in equilibrium. The relative error in the mass balance was within 2 %.

The saturated solubilities of the organic solvents in [BMIM]Cl at a given temperature were conducted as follows: 2 g [BMIM]Cl and 1 ml organic solvent (ensuring excessive amount for dissolution) were loaded in a 4 ml vial by CM3. And then the mixture was sealed, put on the CM3 heating bath, stirred and heated to a specified temperature for 1 h, during which the mixture was shaken manually at 5 min intervals. Finally, the vial was settled in the static stage on the CM3 heating bath for phase separation for 3 h. After that the sample was collected from the raffinate phase for analysis by HPLC.

All samples collected from the extraction phase and the raffinate phase were analyzed on an Agilent 1260 HPLC equipped with a refractive index detector (RID) and a diode array detector (DAD). Components were separated with a Hi − Piex H (300×7.7 mm) column and with H_2SO_4 (5 mM) eluent at a flow rate of 0.6 ml min^{-1} , and the column temperature was maintained at 65 ^{o}C. Glycerol was added as an internal standard for quantitative calculations.

The characteristics of the dispersions of solutes in both phases were determined by the following parameters:[26,27]

The partition coefficient was determined as the ratio of the equilibrium concentrations of the partitioned solute in the extraction phase and the raffinate phase. It was calculated according to the equation (1):

$$\text{Partition} \quad \text{coefficien} \quad t = C_e / C_f \qquad (1)$$

Where C_e and C_f are equilibrium concentrations of the partitioned solute in the extraction phase and the raffinate phase, respectively.

The phase volume ratio was defined as the volume ratio of the extraction phase to the raffinate phase. It was calculated according to the equation (2):

$$\text{Phase} \quad \text{volume} \quad \text{ratio} \quad = V_e / V_f \qquad (2)$$

Where V_e and V_f stand for the volumes of the extraction phase and the raffinate phase, respectively.

The extraction efficiency was the ratio of the 5-HMF partitioned in the extraction phase and the total 5-HMF in the biphasic system. It was calculated according to the equation (3):

$$\text{Extraction} \quad \text{efficiency} \quad = C_e \cdot V_e / (C_e \cdot V_e + C_f \cdot V_f) \times 100 \ \% \qquad (3)$$

The saturated solubility (mg/g) of a organic solvent in [BMIM]Cl at a given temperature was conducted as follow equation (4):

$$\text{Saturated} \quad \text{solubility} \quad = m_{solute} / (m_{sample} - m_{solute}) \times 1000 \qquad (4)$$

Where m_{sample} is the mass (mg) of the sample collected from the raffinate phase and m_{solute} is the mass (mg) of the organic solvent contained in the sample.

2.4 Measurement of ternary phase diagram

The coexistence curve values were determined by means of the cloud point method. The measurement was made in a glass conical flask equipped with a glass stopper at room temperature, 24–26 ^{o}C. A known composition, homogeneous and transparent, of ([BMIM]Cl + water) was prepared in a glass conical flask. The mixture was recorded by mass using a Mettler electronic balance (ML204, accurate to 0.0001 g). Then GDE was progressively added to the mixture using a micro-burette. The cloud point was determined by observing the transition from a homogeneous to a heterogeneous mixture as indicated by the mixture turbidity. The added GDE was also recorded by mass using a balance. The mass distributions of the three components were calculated for the binodal curve measurement. The procedure was repeated by alteration of [BMIM]Cl and water mass ratio. Repeated experiments showed that the maximum deviations from the average value were less than 0.5%.

The tie line for experimental results was determined by using a halogen moisture analyzer (Mettler Toledo V20 Compact Volumetric KF Titrator). The mixtures were prepared inside a glass vial and were vigorously agitated for 30 min at least and left to rest for 3 h or longer. After the necessary rest time, the mixture splits into two clear and transparent liquid phases with a well defined interface. Next, the extraction phase and the reffinate phase were separated and weighted. The extraction phase mixture was sampled and its water content was examined on the halogen moisture analyzer. The water amount of the raffinate phase was calculated by subtracting the water in the extraction phase from the total water initially added in the mixture. The tie line values were obtained by locating the two dots on the coexistence curve with the given water contents.

2.5 Catalytic reactions

All reactions were carried out on the CM3 high throughput instrument. A test protocol consisting of the following steps was used. First, each 4 ml vial was dispensed with given amounts of [BMIM]Cl (in liquid, preheated at 100 ^{o}C), $CrCl_3.6H_2O$ (in powder), glucose, water and organic solvents automatically by a robotic arm of the CM3. Then the vials were sealed with caps. Finally, the bottom parts (one third of the vial height) of the vials were heated up on the CM3 heating board (temperature resolution,

0.5 °C) with a stirring at 300 RPM. When the bottom reaction temperature reached to 108 °C (in about 15 min), reaction time was started (Time = 0 min). The CM3 monitored the reaction time, removed the vial away from the heating board and quenched the reaction in a cool board immediately after reaching the designed time. For the mixtures that generated two phases after reaction, the volumes of the extraction phase and the reaction phase (in bottom) were measured according to the scale lines on the wall of the vail. Then, the two phases were separated into two vails and analyzed individually. Glycerol was added as an internal standard for quantitative calculations. The mixtures with the addition of the internal standard were diluted by water, filtered with a 0.2 mm syringe filter and analyzed by HPLC (adopting the same procedure as described in the extraction method).

The conversion of glucose, the selectivity and yield of the products were the factors used to evaluate the performance of the total reaction system. For those generated two phases after reaction, besides the partition coefficient as defined in equation (1), the 5-HMF yield in the extraction phase was also analyzed. They are defined by the following equations. The data variation in this work was no more than ±2% (relative value).

$$\text{Conversion (mol\%)} = \frac{\text{mole of glucose reacted}}{\text{mole of glucose initially charged}} \times 100\% \quad (5)$$

$$\text{Yield (mol\%)} = \frac{\text{mole of product produced}}{\text{mole of glucose initially charged}} \times 100\% \quad (6)$$

$$\text{Selectivity (mol\%)} = \frac{\text{Yield}}{\text{Conversion}} \times 100\% \quad (7)$$

$$\text{5-HMF yield in extraction phase (mol\%)} \quad (8)$$
$$= \frac{\text{mole of 5-HMF in the extract phase}}{\text{mole of glucose initially charged}} \times 100\%$$

3　Results and Discussion

3.1　Issues in the conversion of glucose in high concentration

Results in Figure 1 show that increasing the initial glucose concentration has a significantly negative impact on the 5-HMF yield in pure [BMIM]Cl solvent. The almost complete conversion of glucose even at a loading as high as 100 wt% with respect to [BMIM]Cl indicates that the CrCl$_3$ catalyst was highly active. However, the selectivity to 5-HMF showed a gradual decrease with the increase of glucose loading. The yield of 5-HMF at 20 wt% glucose loading is 66.4 mol%, and it quickly decreases to 43.6 mol% when the glucose loading is doubled to 40 wt%. Further increase in the glucose loading continues to lower the 5-HMF yield. For instance, when the initial glucose loading is 80 wt%, the yield of 5-HMF is only 30.3 mol%.

The lower yield of 5-HMF at high glucose concentration may be attributed to the higher rates of side-reactions to undesired by-products. When the mixtures after reaction were diluted by water, most of the humins were observed as insoluble solid that adhered to the wall of the vial. 5-HMF is formed from glucose via two steps, CrCl$_3$ catalyzed isomerization of glucose to fructose and acid catalyzed dehydration of fructose to 5-HMF. The preferred reaction pathway to 5-HMF is a unimolecular transformation in each of the steps. It has been postulated that 5-HMF is formed via a first order reaction, while humins are formed via reactions with

an order higher than one.[28] Therefore, when the glucose concentration is raised, the rate of humins formation is expected to accelerate over that of 5-HMF formation. In addition, the low 5-HMF yield at high glucose concentration may be partly attributed to poor mass transfer due to increased viscosity. The kinematic viscosity of [BMIM]Cl at 80 °C is 109.4 mm^2/s. Addition of 80 wt% glucose to [BMIM]Cl sharply increases the kinematic viscosity of the [BMIM]Cl/glucose mixture at 80 °C to 454.6 mm^2/s, which is more than 4 times that of the pure [BMIM]Cl. The increased viscosity slows the desired catalytic molecular reaction while favors the localized side reactions as the rates of heat and mass transfers are largely dependent on the fluid flow dynamics of the system.
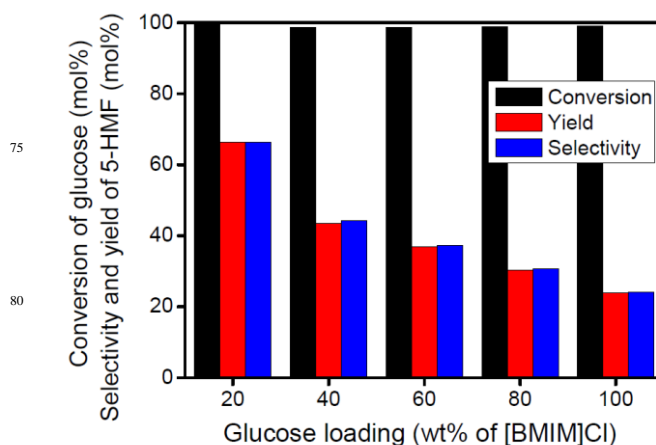

Figure 1. Effect of glucose loading on CrCl$_3$ catalyzed synthesis of 5-HMF in [BMIM]Cl monophasic system. (Reaction conditions: 250 mg [BMIM]Cl; molar ratio of CrCl$_3$:glucose = 1:10; 108 °C; 60 min; 300 RPM).
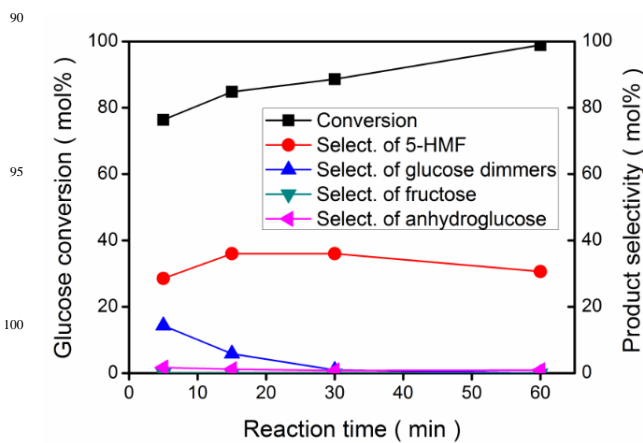

Figure 2. Effect of the reaction time on the glucose conversion and product selectivity under a high glucose concentration in [BMIM]Cl/CrCl$_3$ monophasic system. (Reaction conditions: 250 mg [BMIM]Cl; 200 mg glucose; molar ratio of CrCl$_3$:glucose = 1:10; 108 °C; 300 RPM).

The influence of reaction time on glucose conversion and product selectivity at 80wt% glucose loading was investigated and the results are shown in Figure 2. The conversion of glucose quickly reaches 76.4 mol% in 15 min, but the selectivity to 5-

HMF is only 36.0 mol%. The results suggest that oligomerization dominates from the very beginning of the reaction with the high glucose concentration. Further increase in the reaction time results in further-increased conversion of glucose, but also resulted in concomitant decrease in 5-HMF selectivity. In this reaction the primary by-products is humins, along with glucose dimmers, anhydroglucose and trance amount of fructose. The mechanism of humins formation is still not fully understood, but it has been proposed that humins are formed due to oligomerization of glucose, fructose (an intermediate in the conversion of glucose to 5-HMF), 5-HMF, and/or other reaction intermediates.[2,6,29,30] At high glucose concentration, bimolecular and sequential oligomerization are favored, so side-reactions to form oligomers and humins become serious. The detected glucose dimmers manifested that some of the glucose has condensed into glycopolymers, thus further reaction can result in excessive humins formation.

Even though the [BMIM]Cl/CrCl$_3$ system is known to be efficient in converting glucose to 5-HMF at 10 wt% glucose loading, the 5-HMF yield is quite low at a high glucose concentration. One strategy to enhance the 5-HMF yield at a high glucose concentration is by constructing a [BMIM]Cl-organics-water ternary biphasic system to facilitate the continuous recovery of 5-HMF to an extraction phase during the reaction.

3.2 Effect of organics

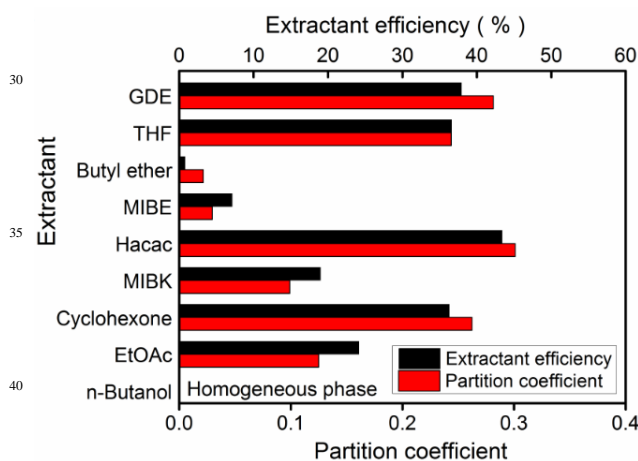### 3.2.1 Organics as potential extractants

Figure 3. The partition coefficients and extraction efficiencies of 5-HMF in different organics / [BMIM]Cl systems(GDE—glycol dimethyl ether; THF—Tetrahydrofuran; MIBE—methyl tertiary butyl ether; Hacac—acetylacetone; MIBK—Methyl isobutyl ketone; EtOAc—Ethyl acetate) (Extraction conditions: 500 mg [BMIM]Cl; 2 ml extractant; 210 mg 5-HMF, 100 mg glucose; 90 mg H$_2$O; 25 $^{\circ}$C.)

In a biphasic reaction system, the organic phase over [BMIM]Cl reaction phase is expected to act as an extraction phase for continuous transfer of 5-HMF into the organic phase after its formation in the reaction phase. The extraction behaviors of the organics are of great importance. In this section, a series of organic solvents, including ethers, ketones, ester and alcohol, are evaluated as extractants for extracting 5-HMF from the model

reaction phase, simulating a scenario of 75 mol% glucose conversion into 5-HMF and H$_2$O based on 80 wt% loading with respect to [BMIM]Cl. The partition coefficient and the extraction efficiency are plotted to manifest the amount of extractable 5-HMF from [BMIM]Cl. The results in Figure 3 show that the extraction performances of the solvents vary widely even if among the same type. Among the ethers, GDE shows the best extraction performance, as indicated by the high extraction efficiency and the high partition coefficient, 37.9% and 0.28, respectively. THF, another ether molecule, also performs well, even though a little less effective than GDE in extracting 5-HMF. The rest of the evaluated ether molecules, butyl ether and MIBE, show much poorer extraction performances. The extraction efficiency of the ketones follows the order of hacac > cyclohexone > MIBK. EtOAc as an ester shows moderate extraction performance. n-butanol is fully miscible with the [BMIM]Cl solvent. The hydrogen bonding between the oxygen in the extraction solvents and the proton in the hydroxyl group of 5-HMF appears important; the extraction efficiency of a solvent largely dependent on its capability of accepting protons. GDE with a higher O/C ratio can theoretically provide more hydrogen-bond-acceptor sites for 5-HMF, so it exhibits stronger extraction than MIBE or butyl ether, both of which have smaller O/C ratios in their molecules. Hacac and MIBK follow similar patterns, that is, hacac has a higher O/C ratio and hence shows higher extraction efficiency as compared to MIBK. However, although THF and cyclohexone have relatively low O/C ratios, as cyclic compounds they both exhibit strong extraction efficiency. The cyclic structures of the two organics may be favorable in exposing the O sites for hydrogen bonding with the hydroxyl proton of the 5-HMF molecule. n-butanol and isobutanol have been used as phase modifier to promote production of 5-HMF from fructose in a two-phase system involving an aqueous phase and an organic phase.[6,7,31] However, these butanols are not suitable extractant, since they form homogenous phase with the [BMIM]Cl solvent. According to the results above, some organics such as GDE, THF, hacac and cyclohexone show good 5-HMFextraction efficiencies from the model reaction phase.

3.2.2 Effect of organics on 5-HMF yield

The organics discussed above have been combined with [BMIM]Cl to form functional solvent systems for the CrCl$_3$ catalyzed conversion of glucose in high concentration to 5-HMF, as shown in Figure 4. The results in Fig 4 (a) indicate that all the CrCl$_3$ catalyzed systems have catalytic activities in converting glucose, but the 5-HMF yield varies in a wide range depending on the organics used. A high 5-HMF yield of 64.5 mol% was achieved in the GDE/[BMIM]Cl solvent system. This yield nearly doubled that obtained in the monophasic [BMIM]Cl/CrCl$_3$ system. Besides the GDE/[BMIM]Cl solvent system, the use of THF, MIBK and MIBE over the glucose/[BMIM]Cl/CrCl$_3$ reaction phase also resulted in higher 5-HMF yield than the single glucose/[BMIM]Cl/CrCl$_3$ reaction phase. The other organic/[BMIM]Cl solvent systems are close to or even less effective than the single glucose/[BMIM]Cl/CrCl$_3$ system. Although hacac and cyclohexone exhibit good extraction behaviors in the model systems as shown in Figure 3, little or a very low 5-HMF yield was obtained from the reaction systems

contained them. These two types of ketones were found to carry out Aldol reactions[32] with glucose and 5-HMF in the [BMIM]Cl/CrCl₃ catalytic system. Addition of n-butanol not only cannot form two phase with [BMIM]Cl solvent but also suppresses 5-HMF yield. These results manifests that the real reaction systems are more multi-factorial and complicated.
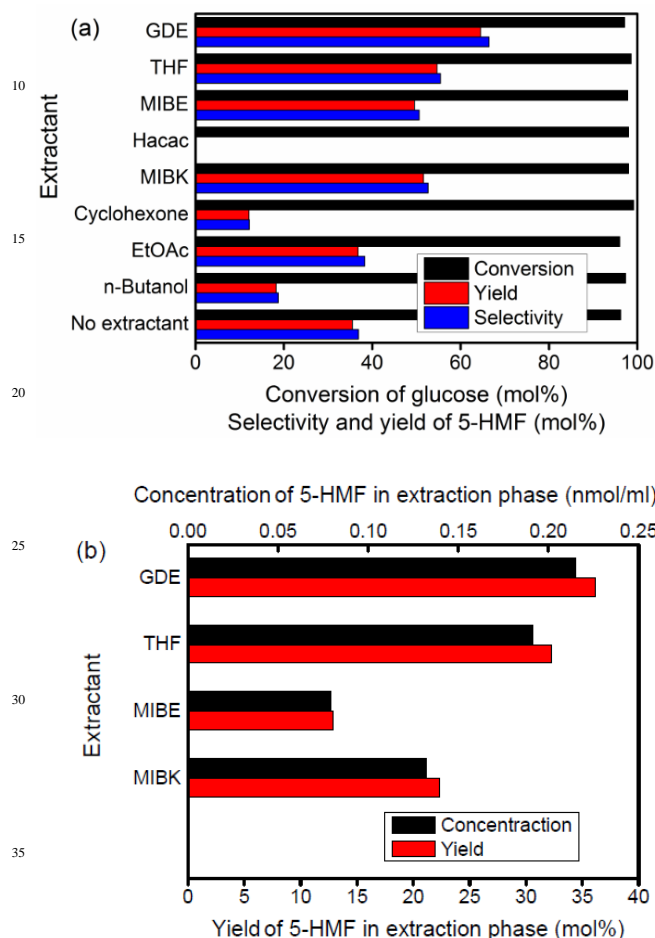

Figure 4. Synthesis of 5-HMF from high-concentration glucose in [BMIM]Cl catalyzed by CrCl₃ in the presence of different organics, of which GDE, THF, MIBE and MIBK form separate extraction phases with [BMIM]Cl and hacac, cyclohexone, EtOAc and n-butanol form homogeneous solutions with [BMIM]Cl. (a) Glucose conversion, 5-HMF selectivity and yield in the total system; (b) 5-HMF concentration and yield in the extraction phase (Reaction conditions: 250 mg [BMIM]Cl; 2 ml solvent; 200 mg glucose; 80 mg water; molar ratio of CrCl₃:glucose = 1:10; 108 ℃; 60 min; 300 RPM).

Among the organics studied, it was found that only four organic solvents can form two phase with the [BMIM]Cl solvent, as shown in Figure 4 (b). It is remarkable that the amount of 5-HMF in the top GDE phase of the GDE/[BMIM]Cl biphasic system corresponds to a 5-HMF yield of 36.1 mol%. The amount of 5-HMF in other organics/[BMIM]Cl biphasic systems follows the order of THF > MIBK > MIBE in the top phase. This order of 5-HMF yield among the organics in the top phase (shown in Figure 4 (b)) agrees with that in the whole system (shown in Figure 4 (a)), indicating that the extraction performance and the

enhanced 5-HMF yield are well correlated. As expected, we found that almost 56% of the produced 5-HMF was transferred into the GDE phase due to the excellent GDE extraction efficiency. Moreover, the 5-HMF concentration in the top GDE phase of the GDE/[BMIM]Cl solvent system reaches 0.215 mmol/ml, which is higher than those reported for glucose dehydration in MIBK/water biphasic systems[11,33] and in THF/water biphasic system,[34] which only reached a low 5-HMF concentration of about 0.05 mmol/ml at the optimized conditions. Because 5-HMF in the extraction phase can be recovered by distillation of the extraction solvent, the much increased 5-HMF concentration in the extraction phase can be expected to result in significant energy saving in the production of 5-HMF.

It was reported that the stability of 5-HMF was reduced in [BMIM]Cl/CrCl₃ system when glucose was introduced.[29] The loss of 5-HMF due to humins formation from its oligomerization with glucose in the current glulocse/[BMIM]Cl/CrCl₃ system is expected to occur in a significant extent at the high glucose concentration. The organics that efficiently extract 5-HMF away from the [BMIM]Cl solvent to the top extraction phase effectively protect 5-HMF from humins formation with high concentration glucose and also promote the positive reaction, thus provide a pathway for 5-HMF yield in the current systems.

3.2.3 Properties of the organics saturated [BMIM]Cl and effects of the organics on glucose conversion

Table 1 Relevant physical properties of the organics and [BMIM]Cl containing dissolved organics.

Items	GDE	THF	MIBK	MIBE
Saturated solubility of solute in [BMIM]Cl at 80 ℃ (mg/g)	202	204	103	10
Boiling point of the solute (℃)	83	65	116	55
Bubbling state of [BMIM]Cl with dissolved solute at 108 ℃	Strongly	Strongly	None	Weakly
Kinematic viscosity of [BMIM]Cl with dissolved solute at 80 ℃ (mm²/s)	26	29	52	105

Based on the results in Figure 4, GDE, THF, MIBK and MIBE are potential extractants. These organics have different boiling points and different saturated solubilities in [BMIM]Cl, as listed in Table 1. Careful observation of the biphasic systems revealed that abundant bubbles rose up from the ionic liquid phase to the organic phase in the GDE/[BMIM]Cl and THF/[BMIM]Cl systems during reaction in the CM3 heating bath at 108 ℃. The bubbling phenomenon in the MIBE/[BMIM]Cl system was very weak, but no bubbling was observed in the MIBK/[BMIM]Cl system. The heated reaction portion of the vial is about 1/3 of the vial height. The temperature in this portion (the reaction phase) is 108 ℃. The extraction phase occupies the remaining 2/3 height of the vial and the temperature in the top part of the vial is about 88 ℃. Therefore, a temperature gradient exists between the reaction phase and the extraction phase in the vial. The wall of the vial and the rotor provide the nucleation sites. The boiling points of GDE, THF and MIBE are lower than the temperature (108 ℃) in the reaction phase, while that of MIBK is above 108 ℃. Because their boiling points are lower than the reaction temperature, during the reaction, the GDE, THF and MIBE partitioned in the [BMIM]Cl phase are dynamically gasified from

the overheated reaction portion of the vial and are condensed in the extraction phase below the dew point of the vapor. MIBE with low solubility in [BMIM]Cl generated little bubbling. MIBK partitioned in [BMIM]Cl shows no bubbling at 108 °C due to its higher boiling point. According to the reflux phenomena, it can be established that the organics dissolved in [BMIM]Cl, especially GDE and THF with higher solubilities and lower boling points, exhibit dynamic equilibrium between the two phase by constant gasification from and dissolution in the [BMIM]Cl phase. The bubbling is beneficial to facilitate mixing. The organic layer of the biphasic system acts as an extraction phase for continuous removal of 5-HMF from the reaction phase. The bubbles increase the interface area and also the bubbling dynamically enhances the turbulence of the mixture; both are beneficial for the transfer of 5-HMF from the reaction phase to the extraction phase. In addition, the low boiling points of GDE and THF can allow significant energy saving in the recovery of 5-HMF by distillation.
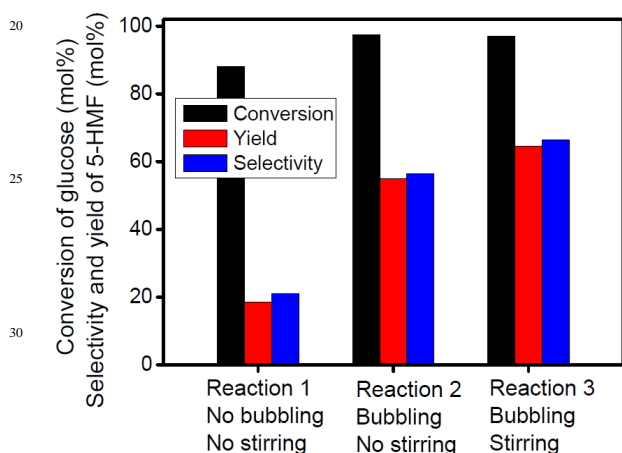

Figure 5. Influence of bubbling and stirring on the glucose conversion and product selectivity under a high glucose concentration in GDE/[BMIM]Cl biphasic system. (Reaction conditions: 250 mg [BMIM]Cl; 2 ml GDE; 200 mg glucose; 80 mg water; molar ratio of CrCl$_3$:glucose = 1:10; 108 °C; 300 RPM).

In order to quantify the contribution of bubbling to 5-HMF production, special reaction conditions with or without bubbling and stirring were studied at a high glucose concentration (Figure 5). "Reaction 1" was carried out in an incubator at 108 °C. There was no temperature gradient between the extraction phase and the reaction phase in the vial of Reaction 1. No bubbling phenomenon of bubbling was observed during the reaction period. "Reaction 2" and "Reaction 3" were carried out on the CM3 heating board with temperature gradient in the vials as described above. The experimental conditions of "Reaction 2" were similar to those of "Reaction 3" except that the former was not stirred. As shown in Figure 5, the 5-HMF yield of Reaction 2 is about triple that of Reaction 1, which means that bubbling plays a critical role in improving reaction performance. Stirring also has positive effect since the 5-HMF yield of Reaction 3 is about 10 mol% higher than that of Reaction 2. It is most remarkable that internal GDE buddling in the reaction phase is much more effective than mechanic stirring for improving the 5-HMF yield.

In addition, when [BMIM]Cl is used as the reaction medium for the conversion of glucose in high-concentrationss, the high viscosity of the [BMIM]Cl/ CrCl$_3$/glucose system is expected to negatively impact on heat and mass transfers, especially at high glucose concentration. The dissolved organics help to reduce [BMIM]Cl viscosity to a varying degree. As shown in Table 1, the saturated solubility of GDE in [BMIM]Cl at 80 °C is 202 mg/g, and the corresponding kinematic viscosity of [BMIM]Cl with dissolved GDE at 80 °C is 26 mm^2/s, which is nearly one-quarter the value of pure [BMIM]Cl (109.4 mm^2/s). THF showed a similarly pronounced decrease in viscosity as GDE. In comparison, MIBK and MIBE are much less effective in lowering the viscosity due to their lower saturated solubility in [BMIM]Cl. According to the results in Table 1, the decrease in viscosity due to saturated dissolution of the organic extractants in [BMIM]Cl is well correlated with the solubility of the organics in [BMIM]Cl. The reduced viscosity of the mediated [BMIM]Cl solvent due to the dissolved organics is expected to effectively facilitate the mass and heat transfers of the reaction system. It is important to note that, although [BMIM]Cl is able to dissolve the organics to a varying degree, the organic phase in excess of the soluble amount in [BMIM]Cl does not show [BMIM]Cl contamination. In the real biphasic reaction systems as listed in Figure 4, [BMIM]Cl and glucose weren't detected by HPLC in the samples from the extraction phase of the four biphasic systems. Freeing of [BMIM]Cl contamination in the extraction phase is a highly desirable feature of the current biphasic systems that show largely enhanced 5-HMF yield and make it feasible to recover 5-HMF in high-purity.

It has been reported that addition of some organics in aqueous solvent greatly reduces the solubility of sugars.[35,36] Since [BMIM]Cl can dissolve GDE up to their solubility as shown in Table 1, it is necessary to determine the impact of the dissolved GDE on glucose solubility in [BMIM]Cl, especially to maintain a high glucose concentration. The concentration of glucose in the GDE saturated [BMIM]Cl at 80 °C was determined to be above 1.0g/g [BMIM]Cl. A transparent and homogeneous liquid was prepared even when 1.1g glucose was mixed with 1g [BMIM]Cl saturated with GDE. Therefore, glucose solubility in GDE saturated [BMIM]Cl solvent is not a limiting factor. Importantly, it was found that the organics like GDE dissolved in [BMIM]Cl can reduce insoluble humins formation. After reaction at the conditions as described in Figure 4, no apparent insoluble substances were observed in the mixture from the GDE/[BMIM]Cl/CrCl$_3$ catalytic system when it was diluted by water. Similar phenomena have been reported with the addition of DMSO[37] and acetone[35] in the aqueous reactions. The organics reduced humins formation by protecting the hexose from oligomerization and thereby increasing the selectivity to 5-HMF.

3.3 Effect of water addition to the biphasic system

3.3.1 Effect of water loading on reactions

The influence of water on the catalytic performance of the GDE/[BMIM]Cl biphasic reaction systems with high glucose concentration was investigated and the results are shown in Figure 6. The conversion of glucose shows a small decrease with the increase of water from no added water to 6:1 mole ratio of water:glucose. The selectivity to 5-HMF in the biphasic system

without the addition of water is 55.5 mol%, and it gradually approaches 68.0 mol% when the reaction is conducted at 5:1 mole ratio of water:glucose, above which the selectivity 5-HMF shows a slight decrease. The trend of 5-HMF yield with the added water follows a similar pattern as that of 5-HMF selectivity. The maximum 5-HMF yield was obtained with H_2O:glucose molar ratio of 4:1 for the reaction. As to the extraction performance (Figure 6 b), the 5-HMF concentration in the GDE phase does not reach its maximum plateau until at H_2O:glucose ratio of 4:1. However, with the increase in the water loading in the range of 0:1 to 6:1 H_2O:glucose molar ratio, the amount of 5-HMF in the extraction phase exhibits a volcano trend with a maximal value achieved at 4:1 molar ratio, corresponding to a 5-HMF yield of 36.1 mol% in the GDE phase. The amount of extracted 5-HMF corresponds to about 56% of the total 5-HMF produced in the biphasic system. The above results manifested that appropriate amount of added water in the reaction system is significantly beneficial for promoting the 5-HMF yield of both the total system and its partitioning in the extraction phase.
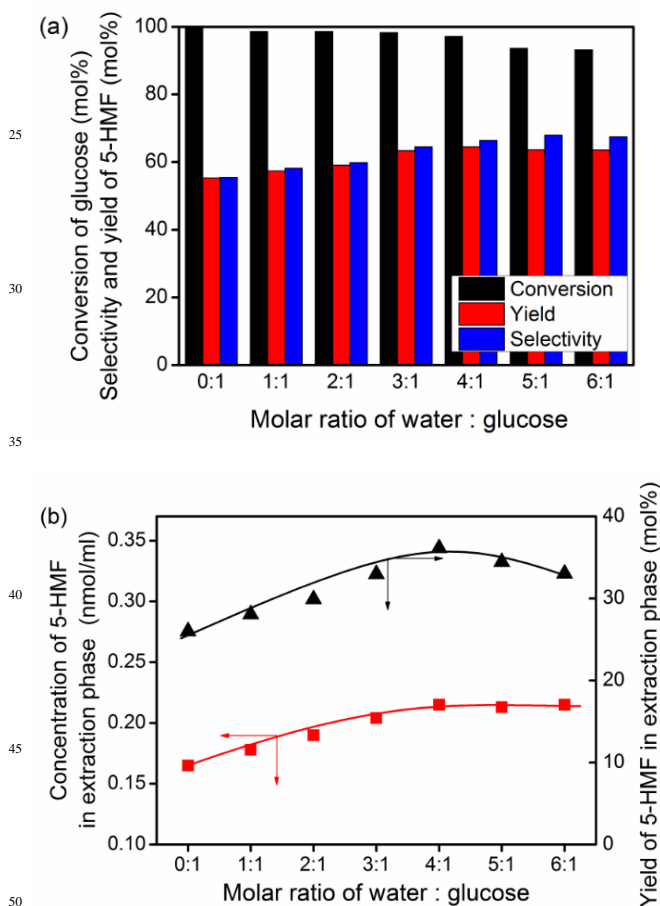

Figure 6. Effect of water on $CrCl_3$ catalyzed synthesis of 5-HMF from glucose in high-concentration in GDE/[BMIM]Cl biphasic systems. (a) Glucose conversion, 5-HMF selectivity and yield in the total system with varying molar ratio of water to glucose; (b) 5-HMF concentration and yield in the GDE phase with varying molar ratio of water to glucose (Reaction conditions: 250 mg [BMIM]Cl; 2 ml GDE; 200 mg glucose; molar ratio of $CrCl_3$:glucose = 1:10; 108 ^{o}C; 60 min; 300 RPM).

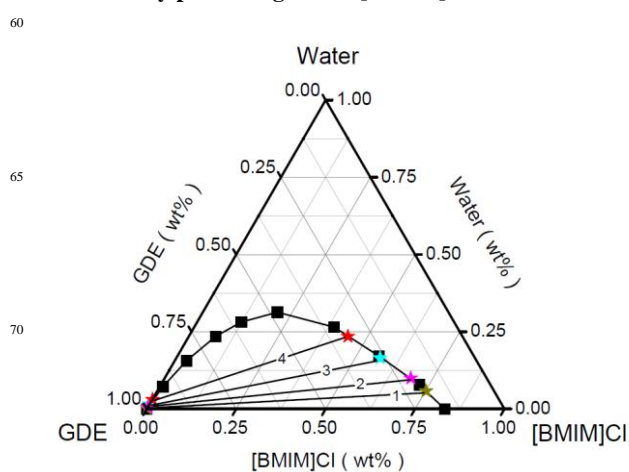### 3.3.2 Ternary phase diagram of [BMIM]Cl/water/GDE

Figure 7. A ternary phase diagram of the [BMIM]Cl/water/GDE system with tie lines at room temperature.(The original compositions of GDE (ml) : [BMIM]Cl (mg) : water (mg) for establishing tie line 1 , 2 , 3 and 4 are 2:500:40, 2:500:80, 2:500:160 and 2:500:250, respectively).

Figure 7 shows the ternary phase diagram of the [BMIM]Cl/water/GDE system. Water and GDE are miscible with each other at any proportion, and so are water and [BMIM]Cl. While GDE and [BMIM]Cl form two phases, a pure GDE phase and a [BMIM]Cl dominant phase containing17 wt% GDE. Addition of water increases the miscibility of [BMIM]Cl and GDE. The tie lines 1, 2, 3 and 4 were obtained via gradual increase of water in the biphasic systems. The equilibrium compositions of the two phases in each tie line are provided in the endpoint positions of the tie line. It was found that the GDE dominant extraction phases of tie line 1 to 3 are located on the water-GDE side line and are close to the GDE point in the ternary phase diagram. The GDE dominant extraction phase of tie line 4 contains a small amount of [BMIM]Cl. The [BMIM]Cl dominant raffinate phases of tie line 1 to 4 are shifted from containing a small amount to a large amount of water and GDE with the increasing water content.

The [BMIM]Cl/water/GDE phase behavior is very beneficial for the GDE/[BMIM]Cl biphasic reaction system. In particular, addition of water up to 32 wt% of [BMIM]Cl, do not result in the contamination of the GDE extraction phase by [BMIM]Cl. This behavior was also confirmed by the absence of [BMIM]Cl peak in the chromatographic analysis of the extraction phase of the GDE/[BMIM]Cl biphasic reaction system originally loaded with glucose:water in 1:4 molar ratio. In addition, the added water is mainly retained in the [BMIM]Cl dominant raffinate phase. This behavior is particularly beneficial because water can further lower the viscosity of the [BMIM]Cl/$CrCl_3$/glucose mixture, in addition to GDE. For instance, the kinematic viscosity of the water/[BMIM]Cl mixture (water content is 32 wt% of [BMIM]Cl) at 80 ^{o}C is only 4.0 mm^2/s. , It is also important to emphasize that water also promotes the phase transfer of 5-HMF from the [BMIM]Cl phase to the extraction phase. Under the experimental conditions (with added water) described in Figure 3, the partition coefficient and the extraction efficiency of GDE for 5-HMF from [BMIM]Cl are 0.281 and 37.9%, respectively. However, the two

values fall to 0.125 and 21.4%, respectively, with no added water. The significant difference between the values with or without water demonstrates the positive role of water in promoting 5-HMF extraction. The possible promoting mechanism by water is rationalized as follows: In the [BMIMCl]/5-HMF mixture, 5-HMF is strongly associated with [BMIM]Cl mainly through hydrogen bonding between the Cl^- anion and the hydroxyl proton of 5-HMF. Added water can also form hydrogen bonding with [BMIM]Cl. Water to form strong and abundant hydrogen bonding with [BMIM]Cl effectively weakens the 5-HMF-[BMIM]Cl interaction force. As a result, 5-HMF is liberated from the [BMIM]Cl phase, resulting in the enhanced extraction efficiency by the organic extractant phase.

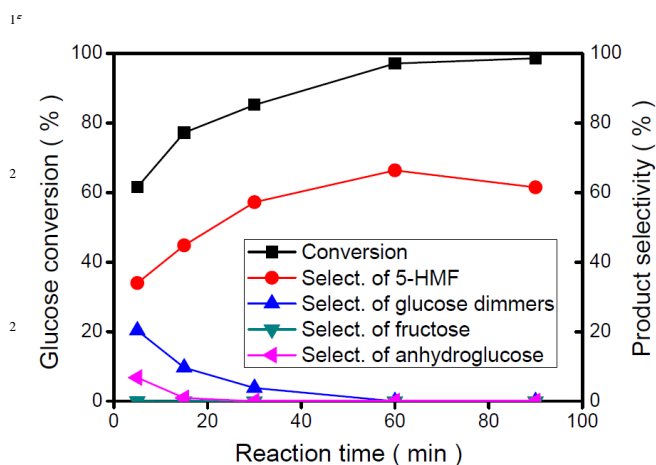### 3.4 Effects of reaction time and catalyst loading

Figure 8. Effect of reaction time on $CrCl_3$ catalyzed synthesis of 5-HMF from 80 wt% glucose in the GDE/[BMIM]Cl biphasic system. (Reaction conditions: 250 mg [BMIM]Cl; 2 ml GDE; 200 mg glucose; 80 mg water; $CrCl_3$:glucose = 1:10; 108 ^{o}C; 300 RPM).
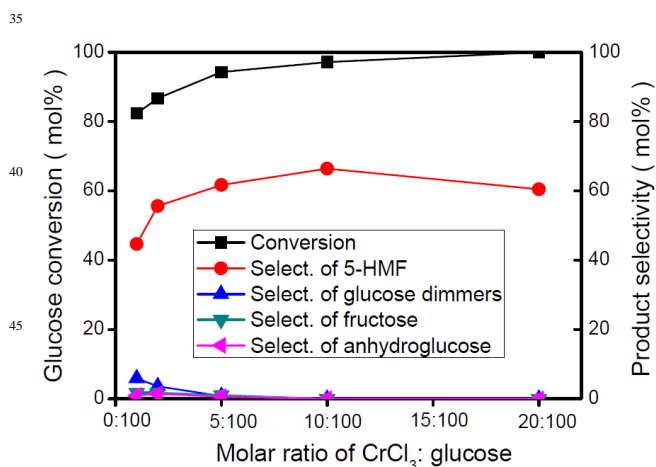

Figure 9. Effect of $CrCl_3$ catalyst loading on 5-HMF synthesis from 80 wt% glucose in the GDE/[BMIM]Cl biphasic systems. (Reaction conditions: 250 mg [BMIM]Cl; 2 ml GDE; 200 mg glucose; 80 mg water; 108 ^{o}C; 60 min; 300 RPM).

Figure 8 shows the results obtained at different reaction time for $CrCl_3$ catalyzed conversion of 80 wt% glucose in the GDE/[BMIM]Cl biphasic system. The glucose is almost completely consumed after 90 min. Similar to the monophasic reactions in Figure 2, appreciable amount of glucose dimmers and anhydroglucose form from the beginning of the reaction. A small amount of fructose can be detected. Further increase in the reaction time results in gradual decrease of the byproducts. However, unlike the monophasic reaction in which the 5-HMF stops growing in 15min even as the remaining glucose continues to be converted, in the biphasic reaction system the selectivity to 5-HMF does not reach its maximum until 60 min. Further reaction beyond 60 min is not beneficial as the conversion of glucose barely increases and the selectivity of 5-HMF starts to decrease.

Figure 9 shows the effect of the catalyst loading on 5-HMF synthesis from 80 wt% glucose in the GDE/[BMIM]Cl biphasic systems. The total yield of 5-HMF at 1:100 catalyst loading was only 36.8 mol% due to the low glucose conversion (82.3 mol%) and the poor selectivity to 5-HMF (44.7 mol%). With the increase in catalyst loading in the range of 1:100 to 20:100, the selectivity toward 5-HMF shows a volcano trend with a maximal value of 66.4 mol% achieved when the catalyst loading is at 10:100 $CrCl_3$: glucose, above which the selectivity slightly decreases. Because both of the two tandem reactions in glucose conversion to 5-HMF, which include an isomerization step and a dehydration step, depend on $CrCl_3$ catalyst, a larger amount of catalyst loading favors simultaneous conversion of each step. But too much catalyst may also catalyze undesired side reactions. With all these considered, 10:100 is considered the optimal amount for the catalyst loading.

In our experiments, we did not observe obvious reduction in the efficiency of the reaction solvent and the catalyst in the first re-use of the [BMIM]Cl/$CrCl_3$ system (data not shown here) without removing the humins from the first run. But successive cycles can be expected to reduce the glucose solubility, and therefore the efficiency of the reaction system due to accumulation of humins. It will be a subject of continued study to evaluate the methods of humins separation from this system.

Conclusions

In summary, the enhanced 5-HMF yield from glucose in high concentration and the efficient separation of the product have been realized by constructing a [BMIM]Cl-organics-water ternary biphasic system. Increased glucose loading in the single [BMIM]Cl/$CrCl_3$/glucose reaction phase led to increasingly excessive formation of humins and serious decrease in 5-HMF yield. Mediation of the ionic liquid property by suitable organics and water efficiently facilitated the glucose conversion to 5-HMF and the continuous recovery of 5-HMF to an extraction phase during the reaction. GDE as a hydrogen-bond acceptor not only exhibited excellent extraction performance for 5-HMF, but also played an important role in mediating the [BMIM]Cl phase. Due to its low boiling point and suitable solubility saturation point in the ionic liquid, a sustained GDE bobbling phenomenon in the ionic liquid phase was observed, which promoted the rate of inter-phase mass-transfer of 5-HMF during the reaction. In addition, GDE helped to reduce the viscosity of the [BMIM]Cl phase. Water present in the [BMIM]Cl-organics-water ternary biphasic systems is mainly retained in the [BMIM]Cl phase. Appropriate amount of water in the solvent systems promoted the

extraction efficiency of 5-HMF and further lowered the viscosity of [BMIM]Cl/glucose. Particularly, [BMIM]Cl mediated with GDE and water still possess high capacity in dissolving glucose to high concentrations. In a biphasic system containing GDE as the extractant, [BMIM]Cl with partitioned GDE and an appropriate amount of water and $CrCl_3$ as the reaction medium, an unprecedented 5-HMF yield of 64.5 mol% was achieved from glucose in high concentration (80 wt% with respect to the ionic liquid). This yield nearly doubled that obtained in the single [BMIM]Cl/$CrCl_3$/glucose reaction phase. Remarkably, the GDE phase contained about 56% of the generated 5-HMF without detectable contamination by the ionic liquid or carbohydrates.

Acknowledgements

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Graphical abstract

Ionic liquid-organics-water ternary biphasic system has high 5-HMF productivity and separation efficiency in CrCl₃ catalyzed conversion of glucose in high concentration.