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# Conversion of platform chemical glycerol to cyclic acetals promoted by acidic ionic liquids

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The condensation of glycerol, a platform chemical from renewable materials, with benzaldehyde to generate cyclic acetals was investigated using acidic ionic liquid as catalyst. Evidence was presented that the product mixture of 4-hydroxymethyl-2-phenyl-1,3-dioxolane and 5-hydroxyl-2-phenyl-1,3-dioxane, with *cis* and *trans* two stereo-isomers for each one identified by $^1$H NMR were obtained. Further modification of reaction conditions promoted by *N*-butyl-pyridinium bisulfate ([BPy]$HSO_4$) led to the totally cyclic acetals with 99.8% yield at room temperature. A micro water-removal reactor constituted by ionic liquids was proposed, which favourably shifted the condensation equilibrium to the product side by transferring the produced water out of the organic phase in time, so that the water-carrying agent or reactive distillation was avoided. Moreover, the product separation made this methodology more accessible to sustainable green biomass chemistry.

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## 1. Introduction

Presently, global research is focused on the development of sustainable and renewable resources, driven by declining petroleum reserves and growing concerns about atmospheric greenhouse gas concentrations.[1] Biodiesel, as one of the renewable energy, has attracted worldwide attention and is considered as one of the best candidates for the substitution of petroleum energy in the future.[2] It is generally known that the most traditional route to biodiesel production involves transesterification of vegetable oils, in which the glycerol is produced as a by-product. For each 90 $m^3$ of biodiesel produced, approximately 10 $m^3$ of glycerol is generated.[3]

With the development of biodiesel, the price of glycerol inevitably drop significantly due to the excessive crude glycerol supply,[4] even some glycerol plants were shut down. For example, the glycerol plant of Dow Chemical in Texas was closed in January 2006, and P & G Co. did same thing to the natural glycerol plant in US. Apart from the economic factors, too much crude glycerol would result in a new round of environmental pollution if it was not utilized instrumentally and efficiently. Therefore, it is imperative to explore new applications of glycerol and release environmental and economic pressures.[5]

Generally, glycerol can be used as reagent, additive and basic chemical for a broad range of uses,[6] and the synthesis of value-added chemicals from glycerol is benefit for the industry chain extension, comprehensive economic improvement, environmental protection and biomass & bio-energy development, which have attracted much attention of the scientific community in recent years.[7] Particularly, the condensation of glycerol with aldehyde/ketone to cyclic acetals[8] has become one of the hot topics because the produced cyclic acetals are widely used as flavours, disinfectants, surfactants, fuel additives[9] and important reactants for synthesis of enantiomerically pure compounds, which were widely applied for the preparation of steroids, pharmaceuticals and fragrances.[10] Moreover, the glycerol acetals could offer another method for the preparation of novel green platform chemicals 1,2-propanediol,[11] 1,3-dihydroxyacetone[12] and 1,3-propanediol.[13] Especially, it is a promising and economically viable way when the cyclic acetals are used as the fuel additives, since the yield of bio-fuel could be increased up to 16% with 10 wt% of the cyclic acetals added.[14]

Generally, cyclic glycerol acetals are synthesized in the presence of acidic catalysts,[15] including mineral acids, organic acids,[16] Lewis acid[17] or solid acids,[18] which are usually associated with one of the following disadvantages such as high reaction temperature (*e.g.* 130 °C),[19] long reaction time,[20] tedious isolation procedure, equipment corrosion and environmental problems derived from the toxic organic solvents.[21] In order to abate these deficiencies, several alternative heterogeneous catalysts such as Amberlyst,[14,22] ion exchange resins,[23] heteropolyacids,[24] zeolites,[25] even sulfonated hollow sphere carbon (HSC-$SO_3H$)[26] *etc.* have been investigated. However, the relative instability of catalytic system unquestionably restrained their extensive applications and large-scale production. In addition, the thermodynamic and kinetic study of the acetalization of glycerol with acetaldehyde also were carried out in

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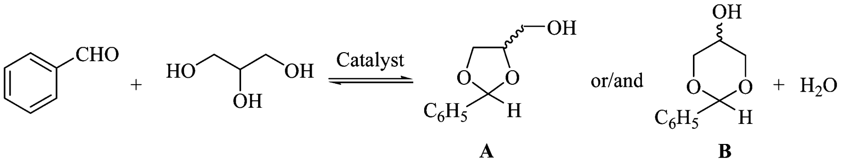

Scheme 1 Acetalization of glycerol with PhCHO catalyzed by acidic ionic liquids.

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order to explain the reaction mechanism and determine the value of the equilibrium constant.[27]

On the other hand, the acetalization is a reversible reaction. The timely removal of by-produced water is favourable for cyclic acetals production. Based on this, the traditional methods usually need reactive distillation,[16,18a] azeotropic distillation with organic solvents (benzene or acetone)[21] or excess of reactant[28] to shift the reversible acetalization to cyclic glycerol acetals side. Undoubtedly, these methods not only raised the technical difficulty and complexity, but also imported extra impurities (water-carrying agent) which obviously increased the energy consumption and production cost.

Ionic liquids are in the focus of interests in various fields of research and development based on their interesting chemical and physical properties.[29] Some acidic ionic liquids have been proved to be the excellent catalytic media and applied to many kinds of organic reactions due to their inherent strong acidity and thermal stability.[30] On the other hand, it has been reported that 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]$PF_6$) could constitute a micro-reactor system with $H_2O$, and improve the oxidation of benzene to phenol benefited from its tri-functions as the solvent, catalyst and transfer reagent.[31] Moreover, metal chlorides ($InCl_3$, $ScCl_3$, *etc.*) immobilized 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-imide ionic liquid were used for acetalization reaction between cyclohexanone and triethyl orthoformate, and 1,1-diethoxycyclohexane were formed with high yield and the selectivity at 0 °C within 5 minutes.[32] In addition, *N*-ethyl imidazole-*N*(*p*-sulfo)benzalhydantoin-chloride imidazole salt ionic liquids was synthesized to catalyze acetalization of benzaldehyde.[33] This prompted us to investigate the synthesis of cyclic glycerol acetals catalyzed by acidic ionic liquids, and the condensation of glycerol with benzaldehyde (PhCHO) was designated as the probe reaction. As shown in Scheme 1, two isomers 4-hydroxymethyl-2-phenyl-1,3-dioxolane (**A**) and 5-hydroxyl-2-phenyl-1,3-dioxane (**B**) were formed, depended on the condensation position of glycerol. Besides, the influence of reaction parameters was also screened. Unlike the previous studies on acetalization of glycerol,[16,18a,21a] this method proceeded in a clean, simple system without water-carrying agent or reactive distillation in the absence of organic solvents.

## 2. Experimental

### 2.1. Materials

All chemicals were analytical grade reagents and used as received without further purification. Pyridine, glycerol, PhCHO were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. *N*-Methylimidazole, butyl chloride, 1,4-butane sultone and trifluoromethanesulfonic acid were supplied by J&K chemical Ltd. and used as received.

### 2.2. Acetalization of glycerol with PhCHO

Ionic liquids were prepared according to the methods in the literatures.[34] The condensation of glycerol with PhCHO was carried out under batch conditions. In a round-bottomed flask equipped with a magnetic stirrer and a reflux condenser, were placed glycerol (2.6 g), PhCHO (2.0 g) and [BPy]$HSO_4$ ionic liquid (0.88 g, 20 mol% based on PhCHO). The reaction mixture was heated to 70 °C with vigorous stir in an oil-bath under atmospheric pressure, and kept at this temperature for 2 h to ensure completeness of the reaction. After cooling to room temperature, the biphasic system was formed automatically. The upper phase containing cyclic glycerol acetal **A**, **B** and PhCHO was isolated by simple decantation. The ionic liquid in the lower phase can be recovered after extraction with ether and treatment under vacuum at 80 °C, and used directly for the next run. After combining organic extract and upper phase followed by the solvent removed, the samples were detected by $^1H$ NMR spectra, which was recorded on a MERCURY-PLUS 400 NMR spectrometer.

### 2.3. Recycling experiments

After cooling to room temperature, the biphasic system was formed automatically. The upper phase containing cyclic glycerol acetal and PhCHO was isolated by simple decantation to be detected by $^1H$ NMR. One-third of volume ether was poured into the lower phase to extract organic components twice. Then, the ionic liquid in the lower phase was extracted with $CH_2Cl_2$, can be recovered after simple evaporation of $CH_2Cl_2$ under vacuum, and finally dried at 80 °C under reduced pressure. After these treatments, the recovery ionic liquid was used directly for the next run.

## 3. Results and discussion

As shown in Fig. 1, the formation of acetal **A** or **B** depend on the different condensation position of hydroxyl groups of glycerol.[14,22] In addition, **B** has *cis–trans* isomerism from the aromatic group on the C-2 position in relation to the secondary hydroxyl group on the C-5 position in the dioxane ring ($^1H$ NMR spectral peaks of **B**-*cis* and **B**-*trans* are $\delta$ 5.54 and $\delta$ 5.39). In regard to acetal **A**, there are two asymmetric carbon atoms in the dioxolane ring, one at the C-2 position, another one at the C-4 position, which should thus give rise to two pairs of DL-isomers ($^1H$ NMR spectral peaks of **A**-*cis* and **A**-*trans* are $\delta$ 5.95 and $\delta$ 5.81).[21b,35]

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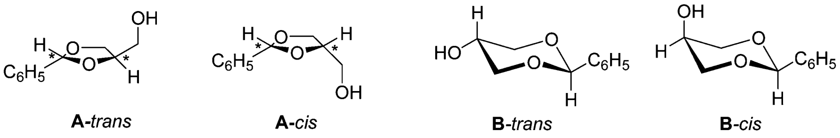

Fig. 1 The *cis*–*trans* isomers of glycerol acetals.

### 3.1. Screening of ionic liquids

In a continuation of our earlier studies on ionic liquid-catalyzed organic reactions,[36] a comparative study on the catalytic activities of several acidic ionic liquids and conventional acidic catalysts was carried out under the same conditions, in order to ascertain if the reaction process and products isomerization were influenced by ionic liquids, and the results were listed in Fig. 2. The weight of the catalysts varied to maintain the mole amount in every reaction.

As shown in Fig. 2, it is worthy noted that the yields of cyclic glycerol acetals were increased obviously when extra acidic catalysts introduced (II–X) compared with that without catalyst (I). Particularly, under the catalyst-free condition, **A** was formed dominantly, and **A**-*trans* was produced a bit more than the **A**-*cis* isomer. Instead, **B** was obtained much more than **A** in the reactions in the presence of acidic catalysts (II–X), and the yields of **B**-*trans* gave a little less than **B**-*cis* isomer.

Generally, the stability of five-membered acetal is usually less than six-membered one in the view of the molecular thermodynamics.[21b] Moreover, taking the better reactivity of the primary hydroxyl than secondary hydroxyl into account, the **B** should have been the major product when PhCHO reacted with glycerol. However, column I indicated that **A** was dominantly produced. Hence, the easier formation of the **A** manifested it was the kinetics product in the reversible acetalization of glycerol. When extra powers were introduced (catalysts or energy), the thermodynamics product **B** become the dominant product. Previous reports described that a slow equilibrium exists between **A** and **B** as shown in Scheme 2, and the transformation of **A** into **B** is extremely sensitive towards acids.[19] Correspondingly, acidic catalysts not only improved the condensation of glycerol with PhCHO, but also increased the transforming rate of **A** into **B**. Therefore, **B** was the predominant product when acidic ionic liquids were used. In fact, the acidity of the glass wall of the reaction vessel is sufficient to promote the isomerisation of the most labile dioxolane isomer to dioxane isomer.[19]

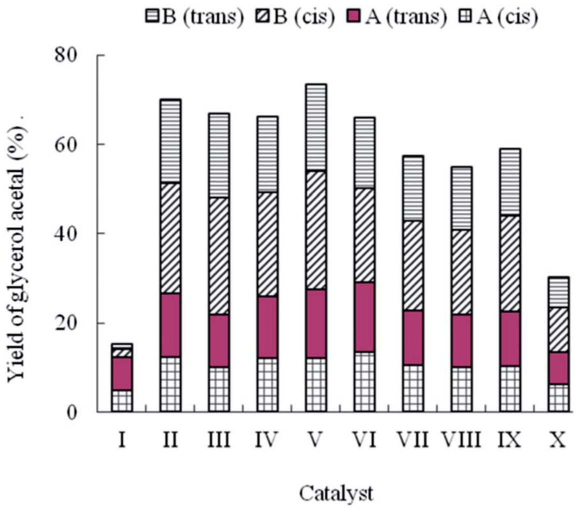

Fig. 2 Condensation of glycerol with PhCHO catalyzed by different acidic catalysts. (A: 4-hydroxymethyl-2-phenyl-1,3-dioxolane, B: 5-hydroxyl-2-phenyl-1,3-dioxane. I: no catalyst; II: [BSPy]$HSO_4$; III: [BSMim]$CF_3SO_3$; IV: [BSMim]$HSO_4$; V: [Bpy]$HSO_4$; VI: [HMim]$HSO_4$; VII: $H_2SO_4$; VIII: HCl; IX: $NH_2SO_3H$; X: 4-toluenesulfonic acid. Reaction conditions: 70 °C, 2 h, molar ratio of glycerol to PhCHO is 1.5 : 1, 20 mol% of catalyst based on PhCHO.)

It is generally known that in the chair conformation of 1,3-dioxane **B**, the large groups in C-2 and C5 positions are usually inclined to the stable equatorial state in view of the axial repulsion between the large group and the axial hydrogen atoms in the C-4 and C-6 positions. On these grounds, **B**-*trans* should have been obtained more than **B**-*cis*. However, Fig. 2 indicated the opposite results. This was probably on account of the stability of intramolecularly hydrogen-bond from the axial hydroxyl groups exclusively with the oxygen atom 1-position and 3-position as shown in Fig. 3(1). In contrast to **B**, **A**-*cis* was shown to be less than **A**-*trans*. The reason is most probably that **A**-*trans* (see Fig. 3(2)) had the relative less steric hindrance and more stability compared with **A**-*cis* when the intramolecularly hydrogen-bond of primary hydroxyl group with oxygen atom 3-position was formed.[19]

From Fig. 2, it also can be seen that, $H_2SO_4$ and HCl gave rise to the parallel yields (57.4% and 54.9%), better than that by organic acidic catalysts such as *p*-toluenesulphonic acid (*p*-TSA, 30.3%), and similar to sulfamic acid ($NH_2SO_3H$, 58.9%) under the same reaction conditions. However, the toxicity, corrosivity and contamination of these catalysts forced people to use more benign alternatives. As shown in Fig. 2, the condensation of glycerol with PhCHO gave the better yields (66.1–73.4%) using several different acidic ionic liquids as catalysts (column II–VII).

As for the difference of catalytic activity of these ionic liquids, their molecular structures should be considered. For example, the conjugated pyridinium cations in both [BPy]$HSO_4$ and [BSPy]$HSO_4$ maybe provide the synergistic effect with aromatic ring of PhCHO. Nevertheless, the hydrogen bond interaction between $-SO_3H$ attached to [BSPy]$HSO_4$ and –OH of glycerol perhaps retarded its catalytic activity, which could account for the better result by [BPy]$HSO_4$. With regard to [BSMim]$CF_3SO_3$ and [BSMim]$HSO_4$, the higher acidity of $CF_3SO_3^-$ than $HSO_4^-$ could explain the higher yield derived from the former. In the case of [HMim]$HSO_4$, although the lower acidity than other ionic liquids, the yield of 66.1% was still better than that of inorganic acids and *p*-TSA. Hence, the cyclic acetal yields

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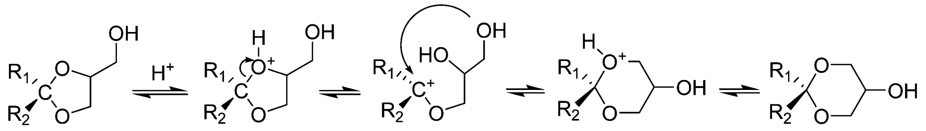

Scheme 2 Equilibrium between 1,3-dioxolane and 1,3-dioxane.

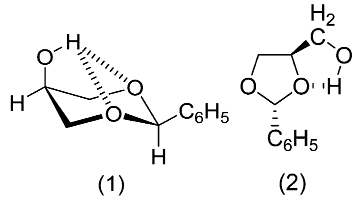

Fig. 3 Hydrogen-bonds in cyclic glycerol acetals.

obtained by ionic liquids decreased in the following order: [BPy]$HSO_4$ > [BSPy]$HSO_4$ > [BSMim]$CF_3SO_3$ > [BSMim]$HSO_4$ > [HMim]$HSO_4$. Certainly, [BPy]$HSO_4$ ionic liquid was selected as the representative catalyst in the following sections.

### 3.2. Optimization of the reaction conditions

We set out to examine the effect of reaction time, temperature, catalyst amount on the condensation of glycerol with PhCHO and on the ratio of **A** to **B** in the presence of [BPy]$HSO_4$. Initially, the kinetics of condensation of glycerol was estimated by withdrawing samples at specific time intervals under the same conditions followed by $^1H$ NMR analysis.

As the data shown in Fig. 4, the reaction proceeded fast in the beginning and 68.4% of yield was obtained after 10 min at 70 °C. Then the increased trends tended to be gentle. For further 140 min prolonged, only 6.6% of yield was added, indicating that the reaction is about to arrive at the equilibrium state. In the case of the composition of product, **A** was more than **B** in the first 40 min. From 40 min to 150 min, the yield of **B** exceeded gradually **A**. Generally, the acetalization of glycerol could be divided into two stages. At the initial stage, the kinetics product of **A** went on forming at a higher rate than that of the **B**. Then, the thermodynamics controlled stage of reaction was initiated gradually, which is the temperature-dependent equilibrium between **A** and **B**, gave rise to the relative high yield of **B**.[18a] If **B** is separated out from product mixture, the left **A** will go on being transformed into **B** till the same stable ratio obtained based on its transformation equilibrium constant.[12] On the basis of the above viewpoints, 120 min was reasonable for the optimal reaction time.

With these data in hand, the influence of catalyst amount on the acetalization of glycerol with PhCHO was investigated. It can be observed from Fig. 5, as the proportion of ionic liquid increased (less than 10 mol% based on PhCHO), a significant rise of reaction rate was observed. Further adding ionic liquid to 40 mol%, the growth trends of product yield started to decrease slightly. When increasing the amount of ionic liquid from 40 mol% to 80 mol%, the yield of total acetal just only increased about 1.9%. This demonstrated that too much ionic liquids were not effective for product yield increase.

As for the proportion of **A** and **B**, in the wake of ionic liquid amount increased to 40 mol%, **A** in the products descended correspondingly, and **B** increased dramatically from 9.6% to

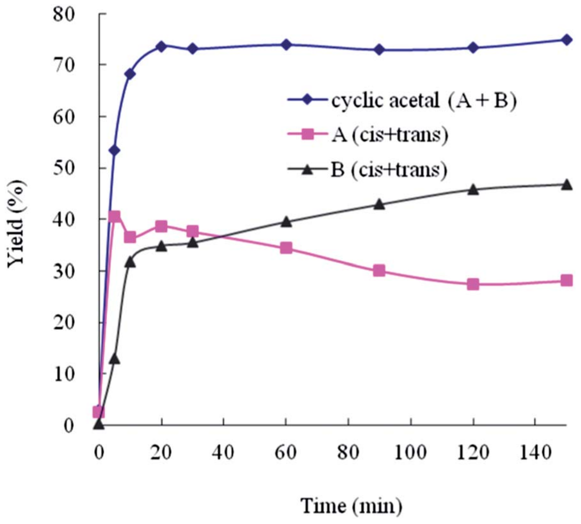

Fig. 4 Effect of reaction time on the acetalization of glycerol with PhCHO using [BPy]$HSO_4$ as catalyst. 70 °C, molar ratio of glycerol to PhCHO is 1.5 : 1, 20 mol% of [BPy]$HSO_4$ based on PhCHO.

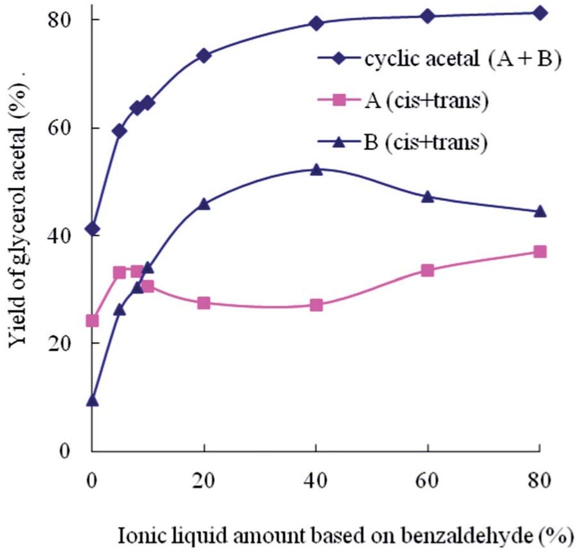

Fig. 5 The influence of [BPy]$HSO_4$ ionic liquid amount (mol% based on PhCHO) on the acetalization and the proportion of isomers. 70 °C, 2 h, molar ratio of glycerol to PhCHO is 1.5 : 1.

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52.3%. That is to say, **B** increased significantly at the expense of **A** in the course of the reaction. However, it looked like that too much ionic liquids had a detrimental effect on the transformation of **A** to **B**, which was probably due to the relatively poor dispersion of ionic liquid in the reaction mixture. As far as the reusability of ionic liquid is concerned, 20 mol% proportion of ionic liquid was chosen as the best option.

In order to evaluate the influence of reaction temperature on the reaction even the isomer ratio, the condensation of glycerol with PhCHO catalyzed by [BPy]$HSO_4$ was monitored over time. According to Fig. 6, it seemed like that the temperature showed little effect on the acetalization of glycerol with PhCHO, because only less than 3% of glycerol acetals were added when the reaction temperature increased from 25 °C to 120 °C. Based on these abovementioned, we believed that at the kinetically controlled stage, **A** was produced firstly and then was consumed gradually along with the formation of **B** due to the acid-catalyzed temperature-dependent equilibrium between **A** and **B**.[16] However, the acetalization proceeded so quick that the two reaction stages have completed and total cyclic acetals yield was nearly stable after 120 min. Anyway, the change of isomer ratio was still detected at the different temperature. Along with the temperature increased, the ratio of **A** to **B** gradually deceased. It is consistent with the research by Aksnes *et al.*,[19] who have established an equilibrium experiment which clearly showed that the yield of every acetal isomer was strongly temperature dependent. The higher temperature is benefit for the acetalization of glycerol with PhCHO and lower temperature is in favour of the transformation of **A** to **B**.

The influence of molar ratio of glycerol to PhCHO on the acetalization and isomer ratio was also studied at ambient because the cost-efficient ratio is favourable for the practical application. Fig. 7 showed that the yield of cyclic acetals increased with the increase in the molar ratio of PhCHO to glycerol when PhCHO was stoichiometric excess. At the same time, the yield of cyclic acetals was improved with increasing molar ratio of glycerol to PhCHO when excessive glycerol was used. Undoubtedly, acetalization is a reversible equilibrium reaction which generates water as by-product. The increase of any one of the substrates could shift the reaction to product side. Therefore, the yield of cyclic acetals could be improved. Moreover, the better result (~100% of yield at the ratio of 1 : 3) could be achieved than that (92.6% of yield at the ratio of 3 : 1 and 96.6% of yield at the ratio of 5 : 1). In the case of the utilization of renewable resource, the excessive glycerol seemed more available for the preparation of glycerol acetals, which has been defined as the platform chemical derived from biodiesel production.[5b] Anyway, these results were comparative with or better than the results reported with water-carrying agent or instant evaporation device.[16,18a]

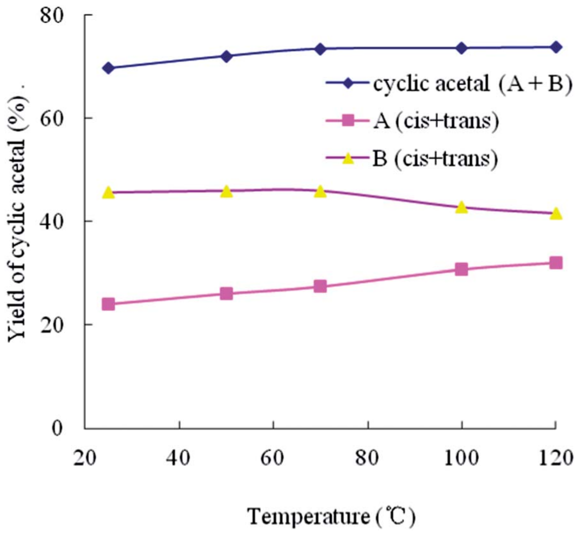

Fig. 6 The influence of temperature on the acetalization of glycerol with PhCHO and proportion of isomers using [BPy]$HSO_4$ as catalyst. 2 h, molar ratio of glycerol to PhCHO is 1.5 : 1, [BPy]$HSO_4$ 20 mol% based on PhCHO.

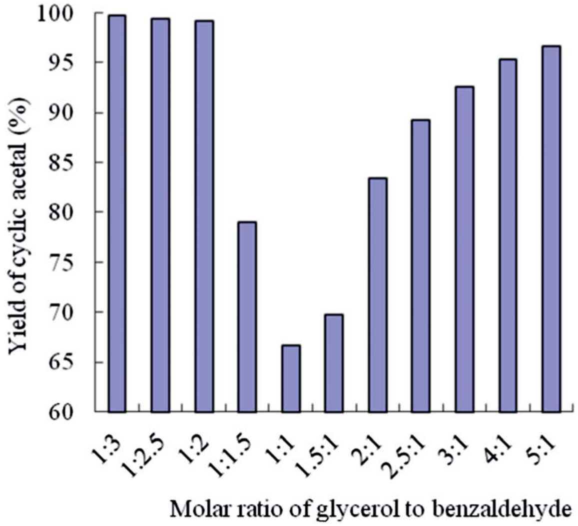

Fig. 7 Effect of molar ratio of substrates on the acetalization of glycerol with PhCHO using [BPy]$HSO_4$ as catalyst. 25 °C, 2 h, [BPy]$HSO_4$ 20 wt% based on PhCHO. (The yield is based on glycerol when benzaldehyde is excess, otherwise, the yield is based on benzaldehyde.)

### 3.3. Mass transfer mechanism of acetalization of glycerol with PhCHO catalyzed by [BPy]$HSO_4$

It is well known that the water formed in the acetalization of glycerol with PhCHO could weaken the catalyst activities and favor the reverse reaction. Most of the acetalizations of glycerol with alcohols need Dean-Strap with organic solvents (benzene or acetone) to shift the reaction to product side. However, these methods are not environmentally recommended since most of these solvents are hazard to humans, and extra water-removing device inevitably raises the energy consumption and cost. In this study, all of the reactions proceeded in a clean and simple system without azeotropic distillation or reactive distillation device in the absence of organic solvents.

As we know glycerol is immiscible with PhCHO, but soluble in [BPy]$HSO_4$ ionic liquid. When the reaction mixture was stirred vigorously, we proposed that a micro water-removing reactor was

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formed as shown in Fig. 8. In this micro water-removing reactor, the condensation was carried out at the interface between polar phase and organic phase catalyzed by [BPy]$HSO_4$. Then the cyclic acetals were produced and transported to organic phase followed by inverted transport of $H_2O$ to polar phase. It looked like a micro reactor equipped with a micro water-removing device, which could separate out the produced water from the organic phase in time to shift the reaction to products side. Thus, it maybe can explain why the ionic liquids could finally achieve the satisfactory product yields compared with other methods. Moreover, ionic liquid could be reused four times and nearly kept its initial activity (98.5% of yield, 2 h, at ambient, PhCHO to glycerol is 2 : 1), which demonstrated the good stability and operability of ionic liquid.

### 3.4. Catalytic activity of [BPy]$HSO_4$ for acetalization of other aldehydes/ketone

It is well known that glycerol acetals can be used to reduce particulate emissions, to increase octane number in gasoline, to improve the properties of biodiesel (viscosity, oxidation stability, flash point, *etc.*), or as antifreezing agents of biodiesel. Especially the glycerol acetals from short chain aldehydes, such as acetaldehyde and butyraldehyde, present flash points close to the diesel specifications, combine positive environmental effects through lower emissions and suitable octane numbers. Thus, the acetalizations of several carbonyl compounds suitable to prepare the fuel additives were carried out in [BPy]$HSO_4$ catalytic system. Table 1 shows the results for some aldehydes or ketone investigated.

Obviously, the first three aldehydes gave relative better yields of acetals compared with acetone, which based on the higher reactivity of aldehyde than ketone in the acetalization. As for the isomer, acetalization of furfural with glycerol provided the higher 1,3-dioxane proportion in the products. The steric hindrance of furan ring may account for this result similar as benzene ring in benzaldehyde. Acetaldehyde and furfural may be prepared from the renewable resources. The former can be obtained from bioethanol following a dehydrogenation or partial oxidation process,[37] and the latter is achieved through the dehydration of sugar and is being regarded as one of the platform chemicals for the petroleum based products alternative.[38] From abovementioned, it can be said [BPy]$HSO_4$ ionic liquid as catalyst has the acceptable application for the preparation of 1,3-dioxolane and 1,3-dioxane by the acetalization of various carbonyl compounds with glycerol, especially of some bio-based aldehydes.

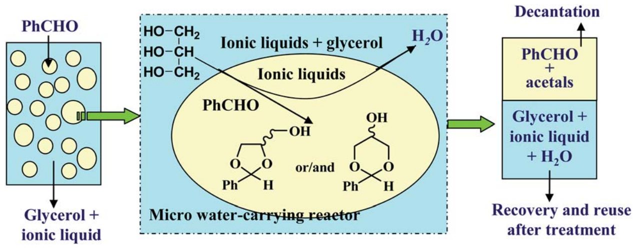

Fig. 8 Mass transfer mechanism of acetalization of glycerol with PhCHO catalyzed by [BPy]$HSO_4$ in the micro water-removing reactor.

Table 1 Acetalization of several carbonyl compounds in [BPy]$HSO_4$ ionic liquid[a]

| | Yield of acetals (%) | Yield of 1.3-dioxolane (%) | Yield of 1.3-dioxane (%) |
|---|---|---|---|
| Acetaldehyde | 95.6 | 39.4 | 56.2 |
| Butyraldehyde | 96.8 | 38.7 | 58.1 |
| Furfural | 92.5 | 28.2 | 64.3 |
| Acetone | 76.7 | 33.5 | 43.2 |

[a] Reaction condition, [BPy]$HSO_4$ 20 mol% based on carbonyl compound, 25 °C, 2 h, molar ratio of glycerol to carbonyl compound is 1 : 2.

## 4. Conclusion

Glycerol, a platform chemical from renewable materials, has been used as the starting material for the preparation of cyclic glycerol acetals catalyzed by acidic ionic liquids. The probe reaction carried out using PhCHO as reactant has indicated that acidic ionic liquids gave the satisfactory yields (66.1–73.4%) which derived from their relative special structures, and the yield of 99.8% for total cyclic glycerol acetals was obtained under the optimized conditions catalyzed by [BPy]$HSO_4$. It was probably attributed to the micro water-removing system constituted by ionic liquid in virtue of its special solubility, in which the water could be transferred out from the organic phase in time to shift the condensation equilibrium to products side. In addition, the acetalization of bio-based aldehydes such as furfural and acetaldehyde with glycerol also indicated the applicability of [BPy]$HSO_4$ ionic liquid.

The product mixture **A** and **B** were identified as *cis* and *trans* two stereo-isomer for each one checked by $^1$H NMR. The acetal **A** and **B** could constitute the excellent compound for the additives of gasoline, diesel and biodiesel fuels. **B** is of particular interest as precursor for 1,3-propanediol derivatives. In the catalyst-free condition, **A** (**A**-*cis* and **A**-*trans*) was formed dominantly, and **A**-*trans* was produced more than **A**-*cis*. In contrast, **B** took part in the majority catalyzed by acidic catalysts, in which, **B**-*trans* was given less than **B**-*cis*. Higher temperature could be benefit for the acetalization of glycerol with PhCHO and lower temperature was in favour of the transformation of **A** to **B**. Unlike the previous studies on the acetalization of glycerol, this reaction proceeded in a clean and simple system without water-carrying agent or reactive evaporation device in the absence of organic solvents. Because [BPy]$HSO_4$ ionic liquid has combined the advantages of friendly benign acidic catalyst with an excellent product separation methodology, as well as the cost efficiency and green aspect, which are in line with the demand of sustainable chemistry.

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## References

1 (*a*) A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**(6), 2411–2502; (*b*) L. Petrus and M. A. Noordermeer, *Green Chem.*, 2006, **8**, 861–867.

2 F. Motasemi and F. N. Ani, *Renewable Sustainable Energy Rev.*, 2012, **16**(7), 4719–4733.

3 (*a*) S. P. Singh and D. Singh, *Renewable Sustainable Energy Rev.*, 2009, **14**, 200–216; (*b*) J. M. Marchetti, V. U. Mguel and A. F. Errazu, *Renewable Sustainable Energy Rev.*, 2007, **11**, 1300–1311.

4 A. Behr, J. Eilting, K. Irawadi, J. Leschinski and F. Lindner, *Green Chem.*, 2008, **10**(1), 13–30.

5 (*a*) Y. G. Zheng, X. L. Chen and Y. C. Shen, *Chem. Rev.*, 2008, **108**, 5253–5277; (*b*) L. A. Lucia, D. S. Argyropoulos, L. Adamopoulos and A. R. Gaspar, *Materials, Chemicals, and Energy from Forest Biomass*, ACS Symposium Series, 16 April 2007, vol. 954, ch. 1.

6 C. H. Zhou, J. N. Beltramini, Y. X. Fan and G. Q. Lu, *Chem. Soc. Rev.*, 2008, **37**, 527–549.

7 (*a*) M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi and C. D. Pina, *Angew. Chem., Int. Ed.*, 2007, **46**, 4434–4440; (*b*) C. H. Zhou, H. Zhao, D. S. Tong, L. M. Wu and W. H. Yu, *Catal. Rev.*, 2013, **55**(4), 369–453.

8 (*a*) J. A. Melero, G. Vicente, G. Morales, M. Paniagua and J. Bustamante, *Fuel*, 2010, **89**, 2011–2018; (*b*) X. Hong, O. McGiveron, A. K. Kolah, A. Orjuela, L. Peereboom, C. T. Lira and D. J. Miller, *Chem. Eng. J.*, 2013, **222**, 374–381.

9 M. J. Climent, A. Corma and A. Veltry, *Appl. Catal., A*, 2004, **263**, 155–161.

10 P. Sari, M. Razzak and I. G. Tucker, *Pharm. Dev. Technol.*, 2004, **9**, 97–106.

11 M. Akiyama, S. Sato, R. Takahashi, K. Inui and M. Yokota, *Appl. Catal., A*, 2009, **371**, 60–66.

12 P. H. J. Carlsen, K. Sørbye, T. Ulven and K. Aasbø, *Acta Chem. Scand.*, 1996, **50**, 185–187.

13 K. Y. Wang, M. C. Hawley and S. J. DeAthos, *Ind. Eng. Chem. Res.*, 2003, **42**, 2913–2923.

14 (*a*) P. H. R. Silva, V. L. C. Goncalves and C. J. A. Mota, *Bioresour. Technol.*, 2010, **101**, 6225–6229; (*b*) M. D. Torres, G. Jiménez-osés, J. A. Mayoral, E. Pires and M. de los Santos, *Fuel*, 2012, **94**, 614–616.

15 C. X. A. da Silva and C. J. A. Mota, *Biomass Bioenergy*, 2011, **35**, 3541–3551.

16 E. GarcÍa, M. Laca, E. Pérez, A. Garrido and J. Peinado, *Energy Fuels*, 2008, **22**, 4274–4280.

17 B. M. Smith, T. M. Kubczyk and A. E. Graham, *RSC Adv.*, 2012, **2**, 2702–2706.

18 (*a*) G. S. Nair, E. Adrijanto, A. Alsalme, I. V. Kozhevnikov, D. J. Cooke, D. R. Brown and N. R. Shiju, *Catal. Sci. Technol.*, 2012, **2**, 1173–1179; (*b*) P. S. Reddy, P. Sudarsanam, B. Mallesham, G. Raju and B. M. Reddy, *Ind. Eng. Chem.*, 2011, **17**, 377–381.

19 G. Aksnes, P. Albriktsen and P. Juvvik, *Acta Chem. Scand.*, 1965, **19**, 920–930.

20 C. J. A. Mota, C. X. A. Silva, Jr, N. Rosenbach, J. Costa and F. Silva, *Energy Fuels*, 2010, **24**, 2733–2736.

21 (*a*) S. B. Umbarkar, T. V. Kotbagi, A. V. Biradar, R. Pasricha, J. Chanale, M. K. Dongare, A. S. Mamede, C. Lancelot and E. Payen, *J. Mol. Catal. A: Chem.*, 2009, **310**, 150–158; (*b*) C. Piantadosi, C. E. Anderson, E. A. Brecht and C. L. Yarbro, *J. Am. Chem. Soc.*, 1958, **80**(24), 6613–6317.

22 G. Vicente, J. A. Melero, G. Morales, M. Paniagua and E. Martín, *Green Chem.*, 2010, **12**, 899–907.

23 I. Dosuna-Rodríguez and E. M. Gaigneaux, *Catal. Today*, 2012, **195**, 14–21.

24 P. Ferreira, I. M. Fonseca, A. M. Ramos, J. Vital and J. E. Castanheiro, *Appl. Catal., B*, 2010, **98**, 94–99.

25 (*a*) C. X. A. da Silva, V. L. C. Goncalves and C. J. A. Mota, *Green Chem.*, 2009, **11**, 38–41; (*b*) H. Serafim, I. M. Fonseca, A. M. Ramos, J. Vital and J. E. Castanheiro, *Chem. Eng. J.*, 2011, **178**, 291–296.

26 L. Wang, J. Zhang, S. Yang, Q. Sun, L. F. Zhu, Q. M. Wu, H. Y. Zhang, X. J. Meng and F. S. Xiao, *J. Mater. Chem. A*, 2013, **1**, 9422–9426.

27 (*a*) M. B. Güemez, J. Requies, I. Agirre, P. L. Arias, V. L. Barrio and J. F. Cambra, *Chem. Eng. J.*, 2013, **228**, 300–307; (*b*) R. P. V. Faria, C. S. M. Pereira, V. M. T. M. Silva, J. M. Loureiro and A. E. Rodrigues, *Ind. Eng. Chem. Res.*, 2013, **52**, 1538–1547; (*c*) I. Agirre, M. B. Güemez, A. Ugarte, J. Requies, V. L. Barrio, J. F. Cambra and P. L. Arias, *Fuel Process. Technol.*, 2013, **116**, 182–188.

28 B. L. Wegenhart, S. Liu, M. Thom, D. Stanley and M. M. Abu-Omar, *ACS Catal.*, 2012, **2**, 2524–2530.

29 S. Y. T. Suzie and D. R. MacFarlane, *Top. Curr. Chem.*, 2009, **290**, 311–339.

30 B. Wang, S. Zhou, Y. Sun, F. Xu and R. Sun, *Curr. Org. Chem.*, 2011, **15**, 1392–1422.

31 J. J. Peng, F. Shi, Y. L. Gu and Y. Q. Deng, *Green Chem.*, 2003, **5**, 224–226.

32 E. Janus, *Pol. J. Chem. Technol.*, 2013, **15**(3), 1–120.

33 W. X. Luo and J. B. Wang, *Hans J.Chem. Eng. Technol.*, 2012, **2**(3), 73–74.

34 M. Yoshizawa, M. Hirao, K. Ito-Akita and H. Ohno, *J. Mater. Chem.*, 2001, **11**, 1057–1062.

35 W. Leitner, *Green Chem.*, 2011, **13**, 1379.

36 B. Wang, J. He and R. Sun, *Chin. Chem. Lett.*, 2010, **21**, 794–797.

37 J. Requies, M. B. Güemez, P. Maireles, A. Iriondo, V. L. Barrio, J. F. Cambra and P. L. Arias, *Appl. Catal., A*, 2012, **423–424**, 185–191.

38 Y. Li, H. Liu, C. H. Song, X. M. Gu, H. M. Li, W. S. Zhu, S. Yin and C. R. Han, *Bioresour. Technol.*, 2013, **133**, 347–353.