## **CHEMSUSCHEM**

DOI: 10.1002/cssc.201000162

### Acid-Catalyzed Dehydration of Fructose and Inulin with Glycerol or Glycerol Carbonate as Renewably Sourced Co-Solvent

Maud Benoit, Yoan Brissonnet, Erwan Guélou, Karine De Oliveira Vigier, Joël Barrault, and François Jérôme<sup>\*[a]</sup>

lonic liquids (ILs) can be partially substituted by glycerol or glycerol carbonate as cheap, safe, and renewably sourced cosolvents in the acid-catalyzed dehydration of fructose and inulin to 5-hydroxymethylfurfural (HMF). In the particular case of glycerol, we found that HMF can be conveniently extracted from the IL/glycerol (65:35) mixture with methylisobutylketone, limiting the reactivity of glycerol with HMF and allowing the

erol with HMF and allowing the I

### Introduction

Since fossil carbon reserves are predicted to disappear and with growing concerns about global warming, the use of biomass as raw material for energy and fine chemistry has in recent years emerged as a fascinating and promising approach.<sup>[1]</sup> In this context, interest in the acid-catalyzed dehydration of hexoses to 5-hydroxymethylfurfural (HMF) has grown. Indeed, from HMF a new generation of biofuels (e.g., dimethylfuran) and a wide range of fine chemicals can be obtained. Several comprehensive review articles on the use of HMF can be found in the literature.<sup>[2]</sup>

In the acid-catalyzed dehydration of hexoses, the nature of the solvent is of prime importance. For economical and environmental reasons, the use of water as solvent for the production of HMF has been widely explored.<sup>[3]</sup> Although very good works have been reported, aqueous processes still suffer from a lack of selectivity due to the possible side rehydration of HMF to levulinic and formic acid. Dimethylsulfoxide (DMSO) and dimethylformamide (DMF) have also been reported as solvents for the acid-catalyzed dehydration of hexoses to HMF.<sup>[4]</sup> These solvents have the property to dissolve hexoses while being capable of diluting the released water, thus limiting the HMF rehydration side reaction. However, even though HMF yields higher than 90% have been achieved in these solvents, the extraction of HMF, the toxicity of DMF, and the possible formation of sulfurized products (with DMSO) remain some major drawbacks.

lonic liquids (ILs) are widely used in carbohydrate chemistry owing to their unique ability to dissolve a large number of different mono-, oligo-, and polysaccharides.<sup>[5]</sup> In this context, their use as solvent for the acid-catalyzed dehydration of hexoses has been extensively investigated.<sup>[6]</sup> Compared to DMSO and DMF, a few ILs are known to be poorly miscible with methylisobutylketone (MIBK), a recognized green solvent,<sup>[7]</sup> thus offering a convenient way to selectively extract HMF from recovery of HMF with a high purity (95%). Influences of the fructose content, temperature, and the nature of the ionic liquid are also discussed. The possible use of industrial-grade glycerin is also investigated. We demonstrate that by using glycerol carbonate, up to 90wt% of the IL can be successfully substituted, decreasing the environmental costs of traditional IL-based processes.

the IL phases with high purity. Although these IL-based processes have allowed the isolation of HMF with high yields, the toxicity hazards and high prices of ILs are currently major obstacles, that have to be circumvented.

One of the possible solutions for decreasing the environmental and economical impact of IL-based processes involves substituting a reasonable amount of the IL by a cheap and renewably sourced co-solvent. For the success of this strategy, it is clear that a few issues need to be addressed. In particular the choice of the renewably sourced co-solvent is crucial, because it should be (1) capable of dissolving large amounts of carbohydrates, (2) very cheap and safe, and (3) miscible with ILs. Obviously, the addition of a co-solvent should not have a detrimental effect on the reaction selectivity and the catalyst activity.

Recently, we and others have shown that glycerol can be used as a cheap  $(0.5 \in kg^{-1})$  and renewable solvent for catalysis and organic chemistry.<sup>[8]</sup> In recent reports, glycerol has been proved to have a beneficial effect on the rate of various organic reactions, making this natural liquid polyol an attractive candidate for our study. Inspired by these preliminary works, we show here that glycerol and glycerol carbonate can be used as renewably sourced co-solvents for the acid-catalyzed dehydration of fructose and inulin into HMF. In particular, we found that up to 90 wt% of the ILs can be substituted by glycerol carbonate without significant alterations of the HMF yield, thus decreasing the cost and the environmental impact of traditional IL-based processes. The possible extraction of HMF from IL/

<sup>[</sup>a] M. Benoit, Y. Brissonnet, Dr. E. Guélou, Dr. K. De Oliveira Vigier, Dr. J. Barrault, Dr. F. Jérôme Laboratoire de Catalyse en Chimie Organique, Université de Poitiers-CNRS 40 avenue du recteur Pineau, 86022 Poitiers (France) Fax: (+ 33) 05 49 45 33 49 E-mail: francois.jerome@univ-poitiers.fr

### **FULL PAPERS**

glycerol and IL/glycerol carbonate mixtures with MIBK is also discussed.

### **Results and Discussion**

In a first set of experiments, we investigated the acid-catalyzed dehydration of fructose in 1-butyl-3-methyl imidazolium chloride ([BMIM]Cl), which is known to be an efficient medium for the production of HMF.<sup>[6]</sup> In a typical procedure, 1 g of fructose was dissolved in 2.5 g of neat [BMIM]Cl and heated at 110 °C in the presence of Amberlyst 70 (A70; 0.1 equiv H<sup>+</sup>). In agreement with existing literature, HMF was produced in a yield of 94% after 15 min of reaction (Table 1, entry 1). Then, [BMIM]Cl was partially substituted by glycerol. From the results present-



ed in Table 1, it appears that substituting [BMIM]Cl by glycerol leads to a faster fructose conversion rate, but lowers the HMF yield. The HMF yield remained acceptable up to a glycerol-for-[BMIM]Cl substitution level of 35 wt%, (70%; entry 3); however, when using a higher glycerol content the HMF yield dropped to unacceptable levels (entries 8–9). More details about the reactivity of glycerol in our reaction are provided in the following paragraphs. On the basis of these first results, the 65:35 [BMIM]Cl/glycerol mixture was selected as medium for the experiments described in this manuscript.

With the aim of minimizing the energy consumption of our process, we then decreased the reaction temperature. As expected, a decrease of the reaction temperature from 110 °C to 90 °C required an increase of the reaction time, from 10 to 40 min. In this case, the selectivity of the process slightly decreased: HMF was produced in a yield of 60% yield (vs 70% at 110 °C, Table 1, entries 3 and 5). The reaction could even be carried out at 70 °C, but at the expense of the reaction selectivity as a maximum HMF yield of 52% was obtained after 210 min (entry 6).

We next checked the catalytic activity of various Brønsted acids in different 65:35 IL/glycerol mixtures. The reactions were performed by starting from 1 g of fructose, dissolved in 2.5 g of solvent mixture. Regardless of which homo- or heterogeneous Brønsted acid was used in the [BMIM]Cl/glycerol mixture, similar HMF yields (60–70%) were obtained after nearly 10 min of reaction at 110°C (Table 2, entries 1–6). These results are in



[a] Conditions: 1 g fructose dissolved in 2.5 g of solvent mixture (65:35), 110 °C, 10 mol% of H<sup>+</sup>. [b] Time required to reach the maximum HMF yield. [c] Determined by HPLC. [d] H<sup>+</sup>-exchange capacity 4.70 mmol g<sup>-1</sup>. [e] Vulcan was used as carbonaceous support; H<sup>+</sup>-exchange capacity 0.58 mmol g<sup>-1</sup>. [f] Reused in a second catalytic cycle. [g] Reused after reactivation with HCl.

perfect agreement with recent reports by Schüth et al. and Corma et al., who independently reported that a release of protons occurs when using [BMIM]Cl and Brønsted acids (i.e., cation exchange between the imidazolium moiety and the proton, leading to the liberation of HCl in the reaction medium).<sup>[10]</sup> This hypothesis was further confirmed by recycling the A70 catalyst. Indeed, when A70 was reused in a fresh [BMIM]Cl/glycerol mixture, a HMF yield of less than 10% was obtained (Table 2, entry 7). After treatment of the used A70 with a solution of HCl the A70 recovered its initial activity, further evidencing the leaching of protons during the catalytic process (entry 8).

In the literature, [BMIM]Cl is considered as one of the best solvents for the acid-catalyzed dehydration of hexoses, but never in the presence of a co-solvent such as glycerol. We selected other ILs in combination with glycerol as a co-solvent in this study: 1-methyl-3-dodecyl imidazolium hexafluorophosphate ([MDIM]PF6), hexylpyridinium chloride ([HPYR]Cl), and hexylpyridinium bromide ([HPYR]Br). As reported in the literature, chloride-based ILs gave the highest HMF yields (Table 2, entries 1 and 10). In the [HPYR]Br/glycerol and [MDIM]PF<sub>6</sub>/glycerol mixtures, the HMF yields dropped to 41% and less than 5%, respectively (entries 9 and 11). These lower yields are consistent with a release of protons in the reaction medium. Indeed, HBr and HPF<sub>6</sub> are more acidic than is HCl; therefore,

### **CHEMSUS**CHEM

cation exchange between imidazolium and the supported proton is much less favorable with  $PF_{6}$ - and bromide-based ILs than with chloride-based ILs. Thus, it is reasonable to conclude that our reaction is mainly catalyzed by the released HCl.

We also performed viscosity measurements because, like [BMIM]Cl, glycerol is a highly viscous liquid and mass-transfer problems may occur. The results are shown in Figure 1. Inter-



**Figure 1.** Viscosity of a) neat glycerol, b) neat [BMIM]Cl, c) [BMIM]Cl/glycerol (65:35), d) [BMIM]Cl/glycerol (65/35)+1 g of fructose, and e) [BMIM]Cl/glycerol (65/35)+1 g of fructose after 8 min of reaction in the presence of A70. Viscosity measurements were performed at 110 °C.

estingly, it appears that the viscosity of glycerol (99.9% purity) at 110°C is five times lower than that of neat [BMIM]Cl (41.7 MPas for [BMIM]Cl vs. 7.5 MPas for glycerol). The substitution of 35 wt% of [BMIM]Cl by glycerol decreased the viscosity of the reaction medium at 110°C from 41.7 to 31.8 MPas.

When 1 g of fructose was dissolved in 2.5 g [BMIM]Cl/glycerol (65:35), the viscosity of the reaction medium increased from 31.8 to 53.0 MPas. Even if at 110 °C the viscosity of the reaction medium is initially high, it does not really impact the reaction progress because during the reaction the viscosity rapidly drops due to the release of water (3 mol water per fructose), which rapidly makes the reaction medium more "fluid." For example, after addition of the Amberlyst 70 resin the viscosity of the reaction medium dropped from 53.0 to 18.0 MPas within 8 min (corresponding to the time required to reach the maximum HMF yield; Table 1, entry 3).

Because glycerol is capable of dissolving large amounts of fructose, we investigated the influence of the fructose content on the HMF yield. As shown in Figure 2, at 110 °C, a decrease of the amount of fructose dissolved in 2.5 g of [BMIM]Cl/glycerol (65:35), from 1 g to 0.5 and 0.25 g, did not affect the HMF yield. However, an increase of the fructose content from 1 g to 5 g led to a drop of the HMF yield, from 67% to 50%. A highly concentrated solution of fructose can be used in the 65:35 [BMIM]Cl/glycerol mixture (up to 9 g in 2.5 g). However, with 7 and 9 g of fructose the selectivity of the process dropped owing to the formation of insoluble black material (presumably humins), and in these cases the maximum HMF yields was 35% and 27%, respectively.

We next investigated the reactivity of glycerol in our process, in order to clarify why a high glycerol content (>35 wt%) is detrimental to the selectivity of the reaction. Whatever the



Figure 2. Influence of the fructose content on the HMF yield. Conditions: 2.5 g of [BMIM]Cl/glycerol (65:35), 110  $^\circ$ C, and A70 (0.1 equiv H<sup>+</sup>).

initial amount of fructose, analysis of the reaction progress by HPLC clearly showed that nearly 20 mol% of glycerol was consumed within 10 min (Figure 2). Like fructose, glycerol is a natural polyol that can be dehydrated under acidic conditions, or can react either with fructose, HMF, or intermediates. Indeed, compared to neat [BMIM]Cl the formation of few unidentified secondary products was detected by HPLC. The presence of these secondary products made the purification of HMF at the end of the reaction rather complex.

To get more insight on the reactivity of glycerol a few counter experiments were undertaken. First, a [BMIM]Cl/glycerol mixture (65:35) was heated, without fructose and Amberlyst 70, to 110°C. Glycerol was not consumed in these conditions, confirming the stability of glycerol in [BMIM]Cl. Next, a [BMIM]Cl/glycerol (65:35) mixture was heated to 110°C in the presence of Amberlyst 70, but without fructose, for 60 min. Again, no reaction took place since 100% of the glycerol was recovered, showing that glycerol is stable in these conditions. It should be noted that when Amberlyst 70 is used as solid catalyst oligomerization or dehydration of glycerol may occur, but only after a prolonged reaction time or at a reaction temperature higher than 110°C. Therefore, any consumption of glycerol at this stage can be ascribed to a side reaction with fructose or HMF, or intermediates.

Similar to [BMIM]Cl, glycerol is not miscible with MIBK. Therefore, we explored the possibility of converting fructose into HMF in biphasic [BMIM]Cl/glycerol (65:35)–MIBK. Such a methodology is expected to (1) limit the possible reactivity of glycerol with HMF, and (2) allow the convenient and selective recovery of HMF from the [BMIM]Cl/glycerol (65:35) mixture. Such a strategy has proved to be efficient especially for the acid-catalyzed dehydration of fructose to HMF in water.<sup>[9]</sup>

As shown in Figure 3, a continuous extraction of HMF with MIBK suppressed the consumption of glycerol. Whereas glycerol was continuously consumed without assistance of MIBK, we found that no glycerol was consumed in biphasic [BMIM]Cl/ glycerol–MIBK (Figure 3). This result shows that (1) the side consumption of glycerol can be ascribed to its reaction with HMF, and (2) side reactions between glycerol and fructose are negligible. It should be also noted that the HMF yields obtained with or without assistance of MIBK are similar, showing that the side reaction between glycerol and HMF is not a dom-

## **FULL PAPERS**



Figure 3. Conversion of glycerol in [BMIM]Cl/glycerol (65:35) and in biphasic [BMIM]Cl/glycerol-MIBK [results collected from 5 g fructose, 2.5 g [BMIM]Cl/glycerol (65:35), 110  $^{\circ}$ C, and A70 (0.1 equiv H<sup>+</sup>)].

inating reaction (at the initial stage of our process) as compared to the dehydration of fructose to HMF (Table 1, entries 3 and 4).

It should be noted that, starting from 5, 7, and 9 g of fructose, the use of MIBK as an extraction solvent not only allowed to inhibit the reactivity of glycerol, but also the recovery of HMF with a very high purity (95%), thereby considerably simplifying the work-up procedure. Figure 4 shows <sup>1</sup>HNMR spectra



**Figure 4.** <sup>1</sup>HNMR spectra (300 MHz, 25 °C, CDCl<sub>3</sub>) of HMF recovered with MIBK from [BMIM]Cl/glycerol (65:35) [obtained from 5, 7, or 9 g of fructose dissolved in 2.5 g of [BMIM]Cl/glycerol (65:35)].

of the recovered HMF and confirms the purity of the recovered HMF (only the remaining MIBK was detected as a contaminant). Considering that chloride-based ILs provide better results, [BMIM]Cl is more attractive than [HPYR]Cl because of its very low solubility in MIBK, allowing the isolation of high-purity HMF. Indeed, when using [HPYR]Cl a significant contamination of HMF with this IL occurred during the extraction stage with MIBK.

The glycerol used in this study has a purity of 99.9% (pharmaceutical grade). However, glycerol produced from the manufacture of biodiesel (named glycerin) is actually a mixture of glycerol, water, and soap (stemming from the catalyst neutralization step). Even though pharmaceutical-grade glycerol is cheap  $(0.5 \in kg^{-1})$ , the purification of industrially produced glycerin is a costly and energy-consuming process. Therefore,

it is clear that the direct use of glycerin is much more desirable from the viewpoint of green chemistry. To this end, we investigated the acid-catalyzed dehydration of fructose to HMF in a [BMIM]Cl/glycerin 65:35 mixture. Typically, 1 g of fructose was dissolved in 2.5 g of [BMIM]Cl/glycerin 65:35 and heated to 110 °C in the presence of A70 (0.1 equiv H<sup>+</sup>). The glycerin used here was kindly provided by Valagro and comes from a biodiesel unit located in the western part of France (Chalandray). This glycerin ( $0.3 \in kg^{-1}$ ) is brown-colored and contains 80 wt% glycerol, 15 wt% water, and 5 wt% of soap. Using glycerin, we found that a 72% yield of HMF was produced after 12 min of reaction, showing that glycerin is also eligible for use in our process (Table 1, entry 7).

Although the use of glycerin as a renewably sourced co-solvent is indeed attractive, the extraction of HMF is more problematic. Indeed, when the catalytic reaction was performed in biphasic [BMIM]Cl/glycerin (65:35)–MIBK, the purity of the recovered HMF was lower compared to the use of pharmaceutical-grade glycerol, owing to the concomitant extraction of impurities initially present in glycerin.

With the aim of further limiting the dependency of our process on [BMIM]Cl, we moved on to the possible utilization of glycerol carbonate as a renewably sourced co-solvent. Glycerol carbonate is readily available from glycerol by reaction with other renewable raw materials, such as  $CO_2^{[11]}$  or urea.<sup>[12]</sup> Glycerol carbonate can be also prepared by transcarbonatation with diethylcarbonate, an ecofriendly carbonatation agent.<sup>[13]</sup> Like glycerol, glycerol carbonate is cheap and recognized as a green solvent, but to date examples of its use as a green solvent for catalysis remain scarce. As compared to glycerol, the presence of only one hydroxyl group was expected to limit its reactivity with HMF.

Similar to the experiments described above with glycerol, [BMIM]Cl was partially substituted by glycerol carbonate and the yield of HMF was monitored by HPLC. As expected, up to 80 wt% of [BMIM]Cl could be substituted. In these conditions, HMF was produced with a yield higher than 75% (Table 3, entries 1-4). When the catalytic process was performed in the presence of MIBK, the glycerol carbonate content could be further increased from 80 to 90 wt%. For example, in biphasic [BMIM]Cl/glycerol carbonate (10:90)-MIBK, the HMF yield was increased from 60% to 70% (Table 3, entries 5 and 6).<sup>[14]</sup> Similarly, when the amount of fructose was decreased from 1 g to 0.5 g, a HMF yield of 72% was obtained in [BMIM]Cl/glycerol carbonate (10:90) (Table 3, entry 7). These last experiments show that 90 wt% of the [BMIM]Cl could be replaced by glycerol carbonate without a dramatic effect on the HMF yield, thus considerably limiting the dependence of our process on [BMIM]Cl.

In addition, whereas after total consumption of fructose HMF was consumed in the [BMIM]Cl/glycerol (65:35) mixture, mainly due to side reactions with glycerol, the HMF yield remained stable in the [BMIM]Cl/glycerol carbonate mixture (65:35), demonstrating the greater stability of HMF in glycerol carbonate (Figure 5). All attempts to dehydrate fructose to HMF in neat glycerol carbonate failed, and only a 10% yield of HMF was obtained in these conditions (Table 3, entry 8).

# CHEMSUSCHEM

<b>Table 3.</b> Acid-catalyzed dehydration of fructose in [BMIM]Cl/glycerol carbonate mixtures. <sup>[a]</sup> HO $\rightarrow OH$				
Entry	Amount of [BMIM]Cl [wt%]	Amount of glycerol carbonate [wt %]	t <sup>ib]</sup> [min]	HMF <sup>[c]</sup> [%]
1	100	0	15	95
2	65	35	35	98
3	50	50	30	91
4	20	80	25	75
5	10	90	20	60
6 <sup>[d]</sup>	10	90	30	70
7 <sup>[e]</sup>	10	90	40	72
8	0	100	20	10
[a] 1 a of fructose dissolved in 2.5 a of a [RMIM]CL/alycerol carbonate mix-				

[a] 1 g of fructose dissolved in 2.5 g of a [BMIM]Cl/glycerol carbonate mixture. [b] Time required to reach the maximum HMF yield. [c] Determined by HPLC. [d] In the presence of MIBK. [e] Starting from 0.5 g of fructose dissolved in 2.5 g of a [BMIM]Cl/glycerol carbonate mixture.



**Figure 5.** Acid-catalyzed dehydration of fructose to HMF in [BMIM]Cl/glycerol (65:35) and [BMIM]Cl/glycerol carbonate (65:35).

Finally, we investigated the acid-catalyzed dehydration of inulin in [BMIM]Cl/glycerol carbonate (10:90) to show the versatility of our approach (Scheme 1). Inulin is a biopolymer of fructose, extracted from chicory or dahlia tubers. Direct production of HMF from inulin is even more complex and first requires a hydrolysis of inulin to fructose, followed by dehydration of fructose to HMF.<sup>[15,16]</sup> The catalyst Amberlyst 70 contains 54–59 wt% of water and was used here without any drying in order to promote the hydrolysis of inulin to fructose. Using the same procedure as that described above for the acid-catalyzed dehydration of fructose, a 60% yield of HMF was obtained at 110 °C from inulin in [BMIM]Cl/glycerol carbonate (10:90), showing the convenience of our methodology.<sup>[17]</sup>

### Conclusions

We have shown that glycerol and glycerol carbonate can be used as cheap and renewably sourced co-solvents for the acidcatalyzed dehydration of fructose and inulin into HMF. In particular, when using glycerol carbonate we found that up to 90 wt% of [BMIM]Cl can be substituted without affecting the HMF yield, thus considerably limiting the costs and environmental impact of traditional IL-based processes. In the particu-





**Scheme 1.** Acid-catalyzed production of HMF from inulin in [BMIM]Cl/glycerol carbonate (10:90): 0.5 g inuline, Amberlyst 70 (0.1 equiv H<sup>+</sup>), 2.5 g [BMIM]Cl/glycerol carbonate (10:90), 110 °C.

lar case of glycerol, its reactivity with HMF can be circumvented by the addition of MIBK. In this case side reactions involving glycerol are not only suppressed but HMF can be also conveniently recovered with a purity close to 95%, considerably simplifying the work-up procedure.

### **Experimental Section**

#### Chemicals

Fructose was purchased from Sigma-Aldrich. Glycerol (purity 99.9%) was kindly provided by Stéarinerie-Dubois. Glycerol carbonate and [BMIM]Cl were synthesized as described in Refs. [13] and [18], respectively. Amberlyst 70 was provided by Rohm&Haas and used as-received. Amberlyst 70 is a macroporous polystyrenic-type resin containing 2.55 mmolg<sup>-1</sup> sulfonic groups, has a water content of 53–59 wt%, a surface area of 36 m<sup>2</sup>g<sup>-1</sup>, and a particle size of 0.5 mm. Viscosity measurements were collected on a Rotational Viscometer "VISCO ELITE L" from Fungilab S.A.

#### Analysis

The amounts of HMF were calculated by external calibration at 25 °C using a HPLC equipped with a nucleosil 100–5 C18 column (250×4.6 mm), a Varian Prostar UV detector (320 nm), Varian Prostar pumps (model 210), using acetonitrile/water (10:90) as mobile phase (0.8 mLmin<sup>-1</sup>). Fructose and glycerol were quantified by external calibration at 25 °C using a HPLC equipped with a Varian NH<sub>2</sub>-column, a Shimadzu LC-20AT pump, a Shimadzu RID-10A detector, and acetonitrile/water (80:20) as mobile phase at 0.8 mLmin<sup>-1</sup>.

#### General procedure for acid-catalyzed dehydration

Fructose (0.5 or 1 g) was dissolved in 2.5 g of a mixture [BMIM]Cl/ glycerol or [BMIM]Cl/glycerol carbonate. Then the mixture was heated under air at 110 °C in the presence of Amberlyst 70 (0.1 equiv H<sup>+</sup>). All attempts to recycle the [BMIM]Cl/glycerol or [BMIM]Cl/glycerol carbonate medium failed. Indeed, even if an HMF yield of nearly 70% was produced in such media, the remaining 30% was mainly composed of black soluble and insoluble materials, making the recycling of the medium almost impossible. The same phenomenon was encountered in neat [BMIM]CI, for which cumbersome and energy-consuming purification processes were required.

*Note*: In the mixture [BMIM]Cl/glycerol (65:35), the reaction could be scaled up without significant change of yield. For example, starting from 8 g of fructose dissolved in 20 g of [BMIM]Cl/glycerol (65:35), a 69% yield of HMF was obtained after 15 min of reaction at 110 °C in the presence of Amberlyst 70 (0.1 equiv H<sup>+</sup>).

## General procedure for the acid-catalyzed dehydration of fructose in biphasic [BMIM]Cl/glycerol (65:35)-MIBK

10 mL of MIBK was added to the reaction mixture. Below 10 mL of MIBK, the HMF extraction from the glycerol phase was not complete (e.g., isolated yield of HMF with only 5 mL of MIBK=30%). The HMF/MIBK phase was then recovered by simple phase decantation, and MIBK was separated from HMF by distillation using a rotary evaporator. Because the extraction with MIBK is highly selective to HMF, the distilled MIBK could be recycled for other extraction cycles. It should be noted that because glycerol is insoluble in most volatile organic solvents, we also tried to use ethyl acetate for the extraction of HMF from the [BMIM]Cl/glycerol phase. However, in this case the extraction was much less selective than with MIBK and HMF was recovered with a lower purity.

## General procedure for the acid-catalyzed conversion of inulin in [BMIM]Cl/glycerol carbonate (10:90)

0.5 g of inulin was dissolved in 2.5 g [BMIM]Cl/glycerol carbonate (10:90). The resulting solution was heated in air at 110  $^\circ$ C in the presence of A70 (0.1 equiv H^+).

### Acknowledgements

The authors are grateful to the CNRS and the French Ministry of Research for financial support. M.B. also thanks the "Agence Nationale de la Recherche" (ANR-09-CP2D-18–01) for the funding of her PhD. The authors acknowledge Rodolphe De Sousa for providing the glycerol carbonate used in this study.

**Keywords:** carbohydrates · catalysis · ionic liquids · renewable resources · solvent effects

- a) A. Corma, S. Iborra, A. Velty, Chem. Rev. 2007, 107, 2411–2502;
  b) G. W. Huber, S. Iborra, A. Corma, Chem. Rev. 2006, 106, 4044–4098;
  c) J. H. Clark, Green Chem. 2006, 8, 17–21; d) R. Rinaldi, F. Schüth, Chem-SusChem 2009, 2, 1096–1107; e) P. Gallezot, ChemSusChem 2008, 1, 734–737; f) J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen, Chem. Rev. 2010, 110, 3552–3599; g) J. J. Bozell, G. R. Petersen, Green Chem. 2010, 12, 539–554.
- [2] Selected reviews: a) J. Lewkowski, Arkivoc 2001, 17–54; b) K. De Oliveira Vigier, F. Jérôme, Top. Curr. Chem. 2010, 1–30.
- [3] a) X. Qi, M. Watanabe, T. M. Aida, R. L. Smith, Green Chem. 2008, 10, 799–805; b) F. S. Asghari, H. Yoshida, Carbohydr. Res. 2006, 341, 2379–2387; c) F. S. Asghari, H. Yoshida, Ind. Eng. Chem. Res. 2006, 45, 2163–2173; d) X. Qi, M. Watanabe, T. M. Aida, R. L. Smith, Catal. Commun. 2008, 9, 2244–2249; e) J. N. Chheda, Y. Roman-Leshkov, J. A. Dumesic, Green Chem. 2007, 9, 342–350.

- [4] a) A. Takagaki, M. Ohara, S. Nishimura, K. Ebitani, *Chem. Commun.* 2009, 6276–6278; b) A. S. Amarasekara, L. D. Williams, C. C. Ebede, *Carbohydr. Res.* 2008, 343, 3021–3024; c) X. Qi, M. Watanabe, T. M. Aida, R. L. Smith, *Ind. Eng. Chem. Res.* 2008, 47, 9234–9239; d) X. Tong, Y. Li, *Chem-SusChem* 2010, 3, 350–355.
- [5] a) Q. Liu, M. H. A. Janssen, F. van Rantwijk, R. A. Sheldon, *Green Chem.* 2005, 7, 39–42; b) O. A. El Seoud, A. Koschella, L. C. Fidale, S. Dorn, T. Heinze, *Biomacromolecules* 2007, *8*, 2629–2647; c) S. Murugesan, R. J. Linhardt, *Curr. Org. Synth.* 2005, *2*, 437–451.
- [6] a) G. Yong, Y. Zhang, J. Y. Ying, Angew. Chem. 2008, 120, 9485–9488; Angew. Chem. Int. Ed. 2008, 47, 9345–9348; b) H. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, Science 2007, 316, 1597–1599; c) X. Qi, M. Watanabe, T. M. Aida, R. L. Smith, ChemSusChem 2009, 2, 944–946; d) S. Hu, Z. Zhang, Y. Zhou, B. Han, H. Fan, W. Li, J. Song, Y. Xie, Green Chem. 2008, 10, 1280–1283; e) C. Moreau, A. Finiels, L. Vanoye, J. Mol. Catal. A: Chem. 2006, 253, 165–169; f) X. Qi, M. Watanabe, T. M. Aida, R. L. Smith, Green Chem. 2009, 11, 1327–1331; g) T. S. Ståhlberg, M. G. Sorensen, A. Riisager, Green Chem. 2010, 12, 321–325; h) S. Hu, Z. Zhang, J. Song, Y. Zhou, B. Han, Green Chem. 2009, 11, 1746–1749; j) Q. Bao, K. Qiao, D. Tomida, C. Yokoyama, Catal. Commun. 2008, 9, 1383–1388; j) C. Lansalot-Matras, C. Moreau, Catal. Commun. 2003, 4, 517–520.
- [7] The European Medicines Agency has classified MIBK as a solvent with low toxic potential, in the same range as ethanol. Document reference: CVMP/VICH/502–99/FINAL. Available from http://www.emea.europa.eu/ pdfs/vet/vich/050299en.pdf (accessed September 2010).
- [8] For a recent review, see Y. Gu, F. Jérôme, Green Chem. 2010, 12, 1127– 1138, and references cited therein.
- [9] a) C. Carlini, M. Giuttari, A. M. Raspolli Galletti, G. Sbrana, T. Armaroli, G. Busca, *Appl. Catal. A: Gen.* **1999**, *183*, 295 302; b) F. Benvenuti, C. Carlini, P. Patrono, A. M. Raspolli Galletti, G. Sbrana, M. A. Massucci, P. Galli, *Appl. Catal. A: Gen* **2000**, *193*, 147–153; c) C. Moreau, R. Durand, S. Razigade, J. Duhamet, P. Faugeras, P. Rivalier, P. Ros, G. Avignon, *Appl. Catal. A: Gen.* **1996**, *145*, 211–224; d) C. Moreau, R. Durand, C. Pourcheron, S. Razigade, *Ind. Crops Prod.* **1994**, *3*, 85–90.
- [10] a) R. Rinaldi, N. Meine, J. vom Stein, R. Palkovits, F. Schüth, *ChemSuschem* 2010, *2*, 266–276, b) N. Villandier, A. Corma, *Chem. Commun.* 2010, *46*, 4408–4410.
- [11] a) J. George, Y. Patel, M. Pillai, P. Munshi, J. Mol. Catal. A: Chem. 2009, 304, 1; b) M. Aresta, A. Dibenedetto, F. Nocito, C. Pastore, J. Mol. Catal. A: Chem. 2006, 257, 149.
- [12] a) J. W. Yoo, Z. Mouloungui, *Stud. Surf. Sci. Catal.* 2003, *146*, 75; b) S. Claude, Z. Mouloungui, J.-W. Yoo, A. Gaset, US Pat. US6025504, 2000; c) M. J. Climent, A. Corma, P. De Frutos, S. Iborra, M. Noy, A. Velty, P. Conception, *J. Catal.* 2010, *269*, 140–149; d) M. Aresta, A. Dibenedetto, F. Nocito, C. Ferragina, *J. Catal.* 2009, *268*, 106–114.
- [13] a) Y. Patel, J. George, S. Muthukumaru, P. Munshi, *Green Chem.* 2009, *11*, 1056 1060; b) N. Pasquier, H. Keul, E. Heine, M. Moeller, *Biomacromolecules* 2007, *40*, 2874–2882; c) N. Fricke, H. Keul, M. Möller, *Macromol. Chem. Phys.* 2009, *210*, 242–255; d) H. R. Pfaendler, F. X. Muller, *Synthesis* 1992, 350.
- [14] Contrary to what was observed in the [BMIM]Cl/glycerol, the HMF recovered by extraction with MIBK was, in this case, contaminated with glycerol carbonate.
- [15] F. Ilgen, D. Ott, D. Kralisch, C. Reil, A. Palmberger, B. König, Green Chem. 2009, 11, 1948–1954.
- [16] For a selected recent example, seea) S. Hu, Z. Zhang, Y. Zhou, J. Song, H. Fan, B. Han, *Green Chem.* 2009, *11*, 873–877.
- [17] In agreement with previous works, a very low HMF yield (<5%) was observed starting from glucose.
- [18] J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser, R. D. Rogers, Chem. Commun. 1998, 1765 – 1766.

Received: June 10, 2010 Revised: July 15, 2010 Published online on September 30, 2010