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1,1,3,3-Tetramethylguanidinium hydrogen sulphate (TMG·HSO$_4$) ionic liquid in carbon dioxide enriched water: a highly efficient acidic catalytic system for the hydrolysis of cellulose†

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1,1,3,3-tetramethylguanidinium hydrogen sulphate (TMG·HSO$_4$) ionic liquid was used for the hydrolysis of cellulose using water enriched with carbon dioxide as the reaction media. The addition of carbon dioxide enhanced the reaction rates significantly and afforded glucose and total reducing sugars in 26 and 72% yields, respectively. The addition of carbon dioxide might play a dual role, it reduces the viscosity of the medium for better mass transfer and also reacts with water to give carbonic acid which subsequently dissociates to the hydronium ion and enhances the acidity of the medium. The developed ionic liquid was easily recovered and reused for a subsequent four runs without any significant change in the catalytic efficiency.

Depleting petroleum resources and the increasing demand and price of the petroleum products, has forced researchers to utilize sustainable natural resources for the production of alternative fuels (bio-ethanol, biofuels). One such important renewable resource is cellulose which is an abundantly underutilized biomass polysaccharide component consisting of a chain of β-(1,4)-linked glucose residues. For the commercial production of bio-ethanol, efficient and economical cellulose depolymerisation to produce glucose is an essential step to achieve the high conversion of cellulose to bio-ethanol through fermentation. The first important obstacle encountered in hydrolysis, processing, fusibility, and functionalization of cellulose is the insolubility of the cellulose in water and in common traditional organic solvents except under extreme conditions due to its molecular and supra molecular rigid structure as a consequence of hydrogen bonding. A second important drawback is the need for severe conditions such as the use of dilute sulphuric acid at high temperatures. To combat these issues, many solvent systems and catalytic strategies have been reported for the hydrolysis of cellulose. Solid acid catalysts have been found to be advantageous and economical due to their reduced or even no corrosion, milder reaction conditions and ease of catalyst recovery. Conventional strong solid acid catalysts such as H-form zeolites, transition-metal oxides, cation-exchange resins, supported solid acids and heteropoly compounds, niobic acid, H-mordenite, Nafion and amberlist have been tried but showed poor efficiency[1,2] then amorphous carbon materials bearing SO$_3$H, COOH and OH functions were used but the glucose yield only reached up to 4%.[3] Nanostructured solid acid catalysts were also developed.[4] The main drawback of these methods is the generation of lots of waste during the synthesis of these catalysts. Recently graphene oxide, a two-dimensional carbon lattice decorated by abundant oxygen functionalities, is demonstrated to be an efficient green catalyst towards selective hydrolysis of cellulose to glucose.[5] Hydrolysis of cellulose into saccharides was also done utilizing magnetically separable functionalized graphene. It was observed that complete hydrolysis of cellulose takes place into glucose and small (4–5 unit size) oligomers using low (1 : 1) catalyst to cellulose ratio.[6] As a consequence of the excellent work done by Rogers *et al.*[7,8] who showed that the ionic liquid (IL) 1-butyl-3-methylimidazolium chloride ([C$_4$mim]$^+$Cl$^-$) is a powerful solvent for cellulose to make homogeneous solution, many efforts have been done to use the ionic liquids for the cellulose hydrolysis. Acidic catalyst in ionic liquid was demonstrated as an efficient system for hydrolysis of cellulosic with improved total reducing sugars yield under mild conditions.[9] Li and Zhao summarizes the hydrolysis conditions and yields of model substrate Sigma cell cellulose in solvent [C$_4$mim]$^+$Cl$^-$ with H$_2$SO$_4$ as the catalyst.[10] To increase the efficiency of solid acid catalysts, the hydrolysis reaction was also performed in ionic liquids. In this regard, the macroporous styrene divinylbenzene resins functionalized with sulfonic groups (–SO$_3$H) proves to be powerful catalyst for the selective depolymerisation of cellulose dissolved in ionic liquids.[11–13] However, due to higher cost and higher consumption of solid acid catalyst with ionic liquid makes this process unfeasible for the commercial production. Also the high activity of IL leads to further degradation of the reducing sugars and thus making their isolation

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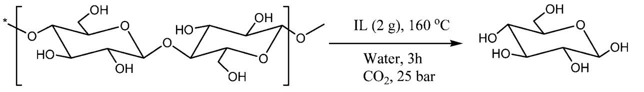
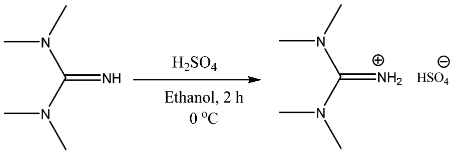


Scheme 1 Acidic hydrolysis of cellulose.



Scheme 2 Synthesis of TMG·HSO_4 ionic liquid.

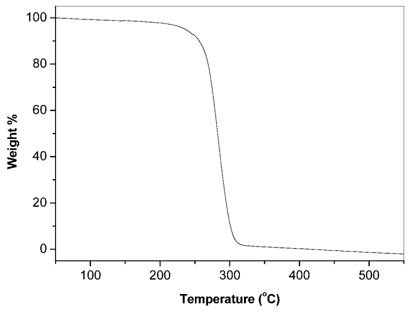


Fig. 1 TGA of TMG·HSO_4 ionic liquid.

tough. In addition to that some work on the acidic ionic liquid grafted over the nanoporous polymeric material was also reported.[14] Mellvaine *et al.*[15] reported the use of 1-methylimidazolium-3-ethylsulfonic acid triflate as catalyst for the depolymerisation of cellulose in an ionic liquid. Combination of solid acid catalyst, Amberlyst 15 DRY in ionic liquid (1-butyl-3-methylimidazolium chloride) and microwave irradiation provides a quite effective method which is useful for depolymerisation of natural polymers such as cellulose. However this solid catalyst is not really heterogeneous as acidity is being leached from it into IL.[16] Nowadays the efforts are going to tune the activity of the ionic liquid which can work as efficient catalyst for the cellulose hydrolysis. Therefore, the development of highly active, selective and low cost new ionic liquids would be an emerging field for the conversion of cellulose into alternative fuels.

Protic ionic liquids, especially those based on the 1,1,3,3-tetramethylguanidine (TMG) are synthesized through simple neutralizing of equimolar TMG with acids have been found to be useful as catalysts for various organic transformations including Henry reaction,[17] one-pot synthesis of pyran,[18] synthesis of 3,4-dihydropyridin-2-(1*H*)-ones[19] and direct Aldol reaction.[20]

Inspired by literature reports on acid catalyzed reactions in CO_2 enriched high temperature liquid water[21] and study on the viscosity of CO_2–ionic liquid system[22] herein we report an efficient acidic catalytic system including 1,1,3,3-tetramethylguanidinium hydrogen sulphate ionic liquid (TMG·HSO_4) prepared from the reaction of 1,1,3,3,-tetramethylguanidine and sulphuric acid in 1 : 1 molar ratio for hydrolysis of cellulose in water using CO_2 as additive at higher temperature (Scheme 1).

Synthesis and characterization of TMG·HSO_4 ionic liquid

In a typical experiment, TMG (20 mmol) was added in 100 mL of ethanol followed by the drop wise addition of H_2SO_4 (20 mmol in 30 mL of ethanol) at 0 °C under stirring. The stirring was continued for another 2 h. A white semi-solid material was isolated by decantation and washed thoroughly with ethanol, dried under vacuum for 6 h and then characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopy (Scheme 2).

Elemental analysis of the 1,1,3,3-tetramethylguanidinium hydrogen sulphate ionic liquid (TMG·HSO_4) reveals $C = 35.71\%$, $H = 6.59\%$, $N = 14.12\%$, $S = 9.53\%$, which was found to be in good agreement with the calculated values: $C = 32.79\%$, $H = 7.57\%$, $N = 14.46\%$, $S = 10.51\%$. Thermal stability of the catalyst was determined by thermo gravimetric analysis (TGA) under nitrogen atmosphere at 10 °C min^{-1} of heating rate. As shown in Fig. 1, the 1,1,3,3-tetramethylguanidinium hydrogen sulphate ionic liquid (TMG·HSO_4) was found to be stable up to 250 °C and then degraded between 250–300 °C temperature range.

Furthermore, successful synthesis and identity of the synthesized ionic liquid were confirmed by ^1H and ^{13}C NMR spectroscopy (Fig. S1†).

TMG·HSO_4 ionic liquid catalyzed hydrolysis of cellulose

Effect of CO_2 on cellulose hydrolysis

At first, the reaction of cellulose was carried out in water using TMG·HSO_4 as catalyst without adding CO_2. At 160 °C for 3 h the yield of total reducing sugar and glucose was found to be 48% and 14% respectively. However using CO_2 under 25 bar pressure to the reaction mixture, the yield of TRS and glucose was significantly increased and reached up to 72% and 26% respectively. As suggested in the literature,[21,22] addition of CO_2 might be reducing the viscosity of reaction medium for better mass transfer and also it reacts with water at high temperature to yield carbonic acid, which subsequently dissociates to increase the hydronium ion concentration and in turn acidity of the medium.

To see the effect of pressure, the reaction was performed under different CO_2 pressure conditions. It is evident from Fig. 2 that beyond 25 bar pressure of CO_2 the yield of glucose unchanged. This is most likely due to the saturation of the reaction medium with carbon dioxide.

To ascertain the effect of CO_2 on the acidity of reaction medium, we also determined the acidity of the ionic liquid in water at higher temperature before and after the addition of CO_2 taking 4-nitroaniline as an indicator by using UV-visible spectroscopy (Fig. 3). The absorption spectra of IL having 4-nitroaniline in water with or without adding CO_2 is shown in Fig. 3. It is evident that absorbance of 4-nitroaniline is

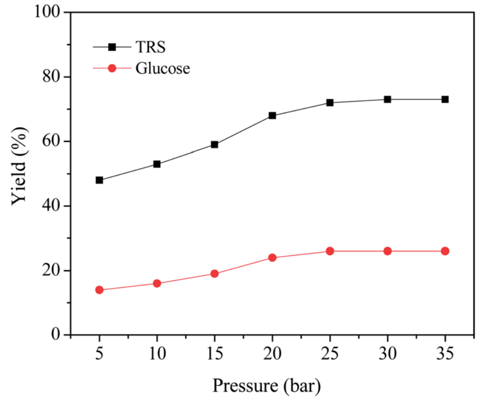


Fig. 2 Effect of CO_2 pressure on TRS and glucose yield.

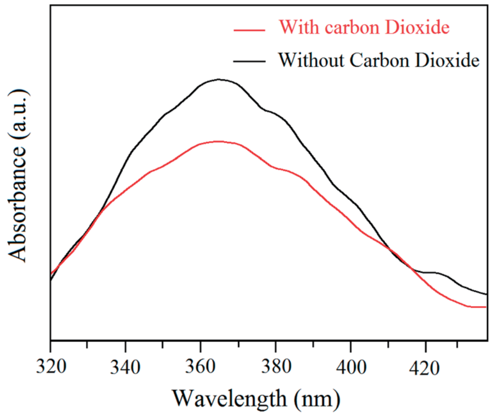


Fig. 3 UV-vis spectra of ionic liquid in water.

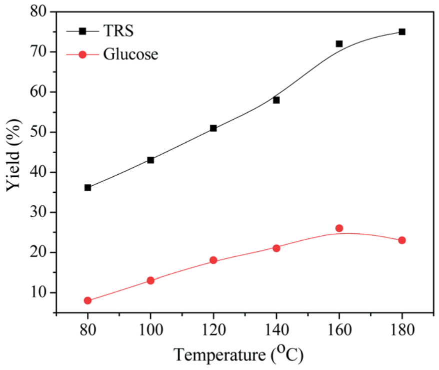


Fig. 4 Effect of temperature on TRS and glucose yield.

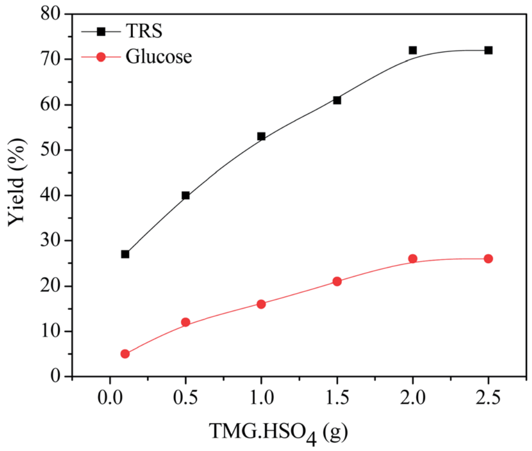


Fig. 5 Effect of TMG·HSO_4 concentration on TRS and glucose yield.

decreased because of protonation of 4-nitroaniline, indicating the higher acidity of the reaction mixture in presence of CO_2.

Effect of temperature

The effect of reaction temperature was studied to obtain the optimum temperature condition for the hydrolysis of cellulose in synthesized acidic ionic liquid as catalyst. To confirm the effect of hydrolysis temperature on the yield of TRS, we studied the hydrolysis of cellulose at different temperature *i.e.* 80, 100, 120, 140, 160 and 180 °C (Fig. 4). The hydrolysis rate at 160 °C was highest than the rate at other temperatures. The yield of TRS was found to be 72% in 3 h at 160 °C. While 58% of TRS yield was produced at 140 °C. At 80 °C the yield of TRS was found to be very low *i.e.* 36.2%. There is no doubt that reaction temperature has a great effect on the hydrolysis of cellulose. A higher hydrolysis temperature can shorten the reaction time and produced higher TRS yield. Meanwhile, the degradation of glucose begins earlier as shown in Fig. 4.

Effect of the TMG·HSO_4 ionic liquid concentration

The effect of acidic ionic liquid concentration on the hydrolysis of cellulose was studied. The amount of IL used was 0.1 g, 0.5 g, 1.0 g, 1.5 g, 2.0 g and 2.5 g respectively. As it was depicted in Fig. 5, when the dosage of IL is increased, TRS yield also increases at a certain point. Beyond this point, the yield of TRS becomes independent on the ionic liquid. Based on these results, the optimum conditions for hydrolysis of cellulose to produce maximum yield of TRS with effective yield of glucose was as follows: amount of ionic liquid (2.0 g), temperature 160 °C, CO_2 pressure 25 bar and reaction time 3 h.

Effect of reaction time

The TRS yields kept nearly constant and had a slowly decrease from the 4th hour due to the dehydration of monosaccharide such as glucose. It also observed that longer heating times produced excessive charring of the sample, giving black residues, and thus lowering the TRS and glucose yields (Fig. 6).

Reuse of the catalyst

The reusability of the catalyst was tested by using the same catalyst sample in four catalytic cycles using 2.0 g of catalyst at 160 °C applying 25 bar pressure of CO_2 for 3 h, and the results of these experiments are shown in Fig. 7. The yield of glucose and TRS in these recycling experiments are obtained as 26% and 72% (first run), 26% and 71.5% (second run), 25% and 71%

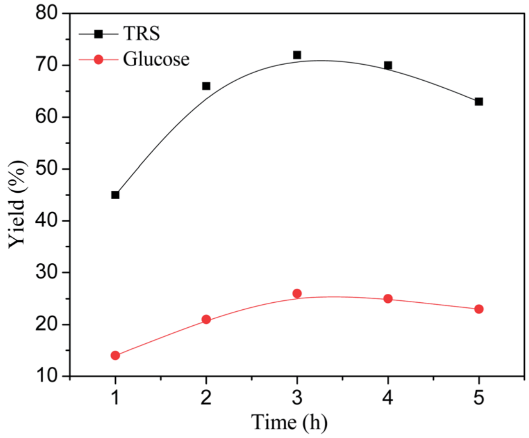


Fig. 6 Effect of time on TRS and glucose yield.

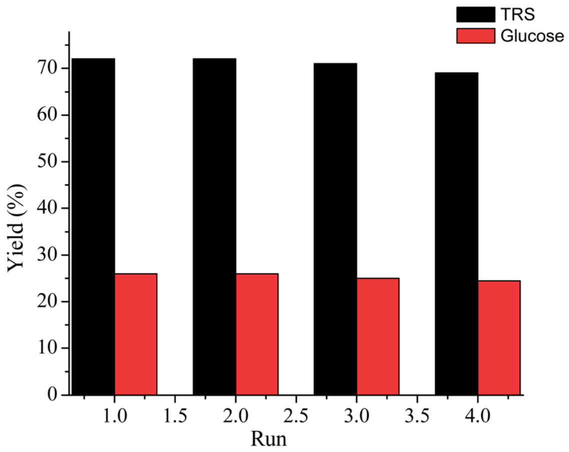


Fig. 7 Recyclability of TMG·HSO_4 ionic liquid.

(third run), 24.5% and 69% (fourth run) respectively. These results suggested that the recovered catalyst exhibited almost similar activity and can be reused at least for four runs without significant loss in catalytic activity.

In summary, we have demonstrated the significance enhancement in reaction rates by using CO_2 as additive in TMG·HSO_4 ionic liquid catalyzed hydrolysis of cellulose in water. The addition of CO_2 exhibited remarkable enhancement in product yield and afforded maximum TRS yields 72% with 26% glucose. In addition, the amount of catalyst used had great effect on the hydrolysis products. When the dosage of TMG·HSO_4 was higher, the dehydration rate of monosaccharide increased, which led to less accumulation of TRS and the increase of further dehydration products. The developed ionic liquid was found to be easily recoverable and recyclable for subsequent four runs without any significant loss in efficiency.

Typical experimental procedure for the hydrolysis of cellulose

Cellulose (0.25 g) and ionic liquid (2.0 g) was mixed in 5 mL of water. The resulting mixture was then transferred to the 15 mL of Parr reactor. The reactor is then pressurized by carbon dioxide up to 25 bar and heated at 160 °C for 3 h. After being cooled the reaction mixture at room temperature, the CO_2 is vented out and the mixture was concentrated under reduced pressure. The resulting residue was diluted with methanol and the solid material which was settled down was separated by filtration. The methanol layer was concentrated under reduced pressure to recover the ionic liquid. The recovered ionic liquid was reused for subsequent runs. The solid thus obtained was mixed with water to dissolve the reducing sugars. The yield of total reducing sugars (TRS) was found to be 72% and the selectivity towards glucose was found to be 26%. Yield and selectivity is calculated with the help of calibration curves generated with commercially available standards using HPLC. Detailed information on the analytical method used to quantify glucose and TRS has been given in the ESI† file.

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