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Facile Acidic Choline Chloride-p-TSA DES Catalysed Dehydration of Fructose to 5-Hydroxymethylfurfural.

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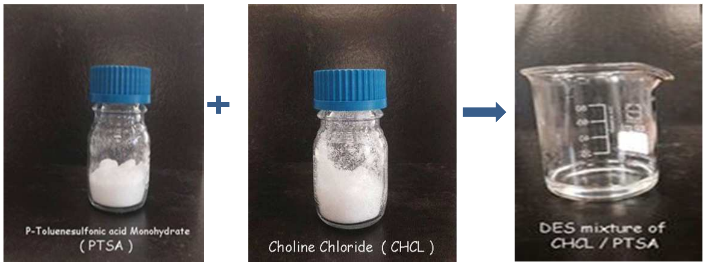
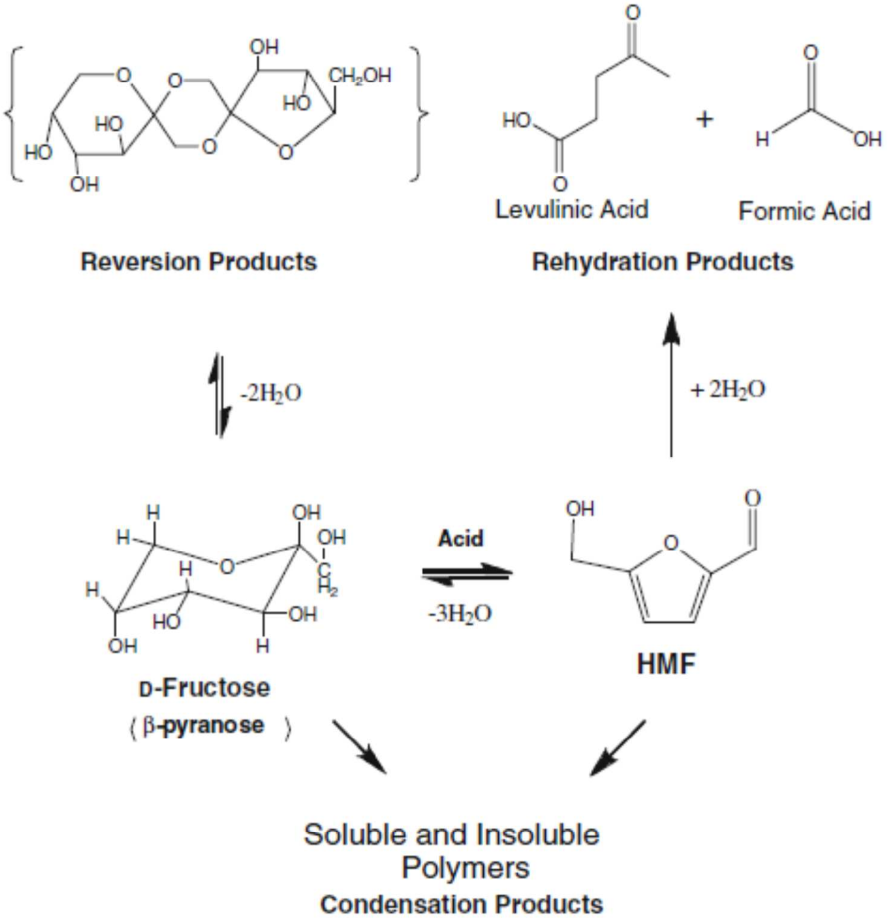


Abstract

The conversion of lignocellulosic biomass to biofuel precursors has recently been a focus of intensive research due to the essential role of biofuels in future transport fuels. Specifically, the conversion of fructose to 5-Hydroxymethylfurfural (5HMF) has gained momentum, as 5HMF is a versatile bio-based platform molecule leading to a plethora of high-value chemicals and biofuel molecules such as DMF. Herein, we report the use of an environmentally friendly Brønsted acidic deep-eutectic mixture consisting of Choline Chloride (ChCl) and p-TSA for the dehydration of fructose to 5HMF. Unlike previous systems, the use of ChCl-p-TSA played a dual role both as a hydrogen bond donor (HBD) and a catalyst for the dehydration reaction, thus obviating the addition of an external acid. The reaction was examined and optimised in a batch system, where it was found that fructose was readily dehydrated to 5-HMF. The best reaction conditions with the highest 5HMF yield of 90.7% was obtained at temperature of 80 ^{0}C using DES molar mixing ratio of 1:1, ChCl: p-TSA and feed ratio of 2.5%, reaction time of one hour.

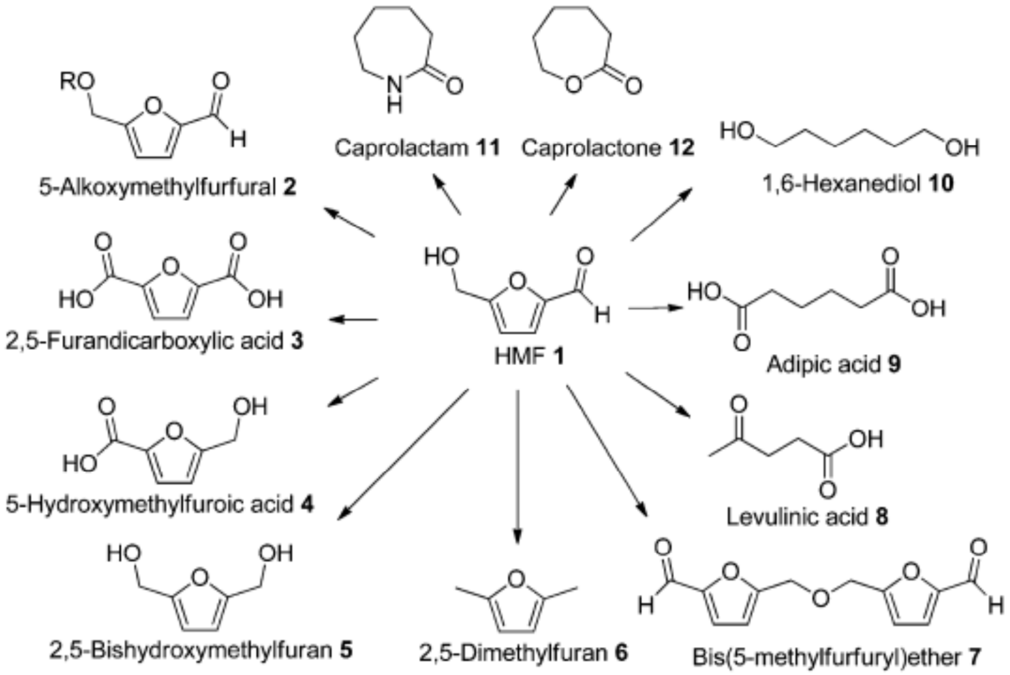
1. Introduction

Depletion of petroleum resources and subsequent changes in world economies; the increase in greenhouse gases emissions, and the associated climate change are a few of the issues that revealed the renewable and green energy resources to be urgently needed [1]. Among the different renewable resources, lignocellulosic biomass is a predominant renewable source for future bioenergy. It is low cost, abundant and does not compete with food resources. Fructose derived from lignocelulosic biomass was found to be among the best carbohydrate sources of furans [2].



Scheme 1 schematic diagram of acidic catalized fructose dehydration reaction and the possible sub reactions pathways [3].

One of the most important block intermediate materials obtained from the direct dehydration of fructose is 5HMF. The mechanism of fructose dehydration reaction and the possible side reactions are illustrated in Scheme 1. 5HMF is regarded as an important block material as it has many derivatives that can be used as biofuel precursors and useful chemicals[4-6]. The main derivatives of 5HMF are illustrated in scheme 2.



Scheme 1 Possible derivetives of 5HMF [7].

5HMF was first produced by Dull *et al* in the 19th century by pressurised heating of inulin in oxalic acid [8]. Subsequently, different acid catalysis systems consisted of mineral acids [9] [10], solid acids [11] [12], and metallic acids [10] were studied to improve the yields of 5HMF in aqueous medium by catalytic fructose dehydration reactions. The common drawback of these systems was the requirement for relatively high reaction temperatures which lead to low 5HMF yields because of the rehydration of the product 5HMF [4, 13, 14].

To overcome the drawbacks of aqueous systems, different organic solvents such as Dimethyl Sulfoxide (DMSO), Dimethylformamide (DMF), Acetic acid and Methanol were investigated. Despite a higher yield of 5HMF obtained with these solvents, some limitations were encountered. The poor solubility of sugars in many organic solvents, the difficult separation of 5HMF in high boiling point organic solvents and the poor extraction efficiency of low boiling point organic solvents, posed a barrier to utilize these systems. Similar challenges were faced with biphasic systems such as; Methyl isobutyl ketone (MIBK) and n-Butanol (BuOH) in water to extract produced 5HMF[7].

Recently the use of ionic liquids in fructose dehydration to 5HMF showed increased promise, because of their unique properties namely; the low vapour pressure, non-flammability, high chemical and thermal stability and ability to adjust solvent power [15].

Lansalot obtained 5HMF yield of 68%, when 5w% of fructose was solubilised in Dimethyl Sulfoxide (DMSO), and catalysed by PTSA in 1-butyl 3-methylimidazolium as ionic liquid solvent for 32 h [16].

Quan Cao studied the fructose dehydration to 5HMF in different imidazolium ionic liquids. He concluded that the acidic C-2 hydrogen of imidazolium cations acted as catalyst for the fructose dehydration reaction, even when no catalyst was used [17].

Although the use of ionic liquids highly improved the 5HMF yields obtained from fructose dehydration the elevated cost and the unclear environmental effect of the conventional ionic liquids would still pose a challenge for establishing a robust production process of 5HMF using ILs system.

Therefore research attention turned to room temperature ILs. Those liquids contain organic salts with melting point below 100 ^{0}C, namely choline chloride based ILs[18] and amino acid based[19].

In this matter, Suqin and others conducted fructose dehydration reaction to 5HMF using a biphasic system comprised renewable ionic liquid and ethyl acetate as extraction solvent[20].

The latest form of these solvents is Deep Eutectic Solvents (DES), which was discovered by Abbott [21]. DES are mixtures made of different ammonium salts such as choline chloride, and different space of hydrogen bond donors; namely amides, amines, alcohols and different acids [22]. Briefly the chemistry concept of these mixtures is an ionic interaction between the hydrogen bond donor (HBO) and the salt, lead to decrease in both melting and freezing points of the mixture[23, 24]. In addition to sharing similar properties with normal ionic liquids, DES mixtures retain superior advantages; they have low cost, are biodegradable and easy to prepare. Choline chloride/urea is the most common used DES mixture [25]; they have been widely used as solvents and co-solvents in many catalytic chemical synthesis applications [26, 27].

DES were found to be active catalytic mixtures in biomass hydrolysis [27]. Hayyan et al used a DES mixture of N, N-diethylenethanol ammonium chloride and p-TSA for free fatty acid esterification to biodiesel fuel [28], and a mixture of p-toluene sulfonic acid monohydrate (p-TSA) and allyltriphenylphosphonium bromide to produce biodiesel from low grade palm oil [29].

Liu reported the synthesis of 5HMF from concentrated solutions of fructose by using DES mixture formed from Choline Chloride and Carbon Dioxide, a yield of 62% was obtained [30].

In all of the above studies, a range of DES has previously been utilised for the hydrolysis of fructose to 5HMF, they require the addition of an acid catalyst, which is generally undesirable from processing view point.

This work investigates an acidic DES derived from choline chloride (ChCl) and P-toluene sulfonic acid monohydrate (p-TSA) to dehydrate fructose to 5HMF, which obviates the addition of acid catalyst. The selected DES was found to be highly efficient, where 90.7% yield of 5HMF was obtained. It has been produced from cheap and renewable materials rendering it environmentally friendly. The use of p-TSA as both HBO and catalyst would reduce the process cost.

2. Results and Discussion

2.1. The effect of feed ratio

As illustrated in section 5, the feed mass ratio was calculated as the percentage of fructose in the reaction mixture at the start. As shown in Figure 1, the 5HMF yield decreases with increasing the fructose mass ratio. This may be attributed to 5HMF being rehydrated by the presence of water produced from the dehydration reaction of fructose. The highest yield obtained was 90.7%, at mass ratio of 2.5%, after which, the yield sharply decreased to 52.3% at feed mass ratio of 10%. As the feed ratio increased from 20% to 100%, the 5HMF yield decreased gradually. The lowest yield was 20.5% at feed ratio of 100%. This can be attributed to the fact that increasing the initial fructose concentration could result subsequently in high 5HMF concentration, where the latter lead to the occurrence of unwanted side reactions[31]. These reactions are expected to produce insoluble humins and/or soluble polymers[32], which lead to decrease in 5HMF yield. The change of the sample colour to a darker brown by increasing fructose ratio is another sign for producing these undesirable by-products in the dehydration reaction. Self-polymerization of 5HMF and cross polymerization between fructose and 5HMF could produce polymers in fructose dehydration reactions[33]. It was mentioned that the increase of initial fructose concentration would encourage the occurrence of polymerization reactions, which would decrease the 5HMF selectivity[7] as illustrated in Figure 2. Despite the highest yield was obtained at feed ratio of 2.5%. It was found to be unstable, therefore a feed ration of 5% was chosen to for subsequent experiments.

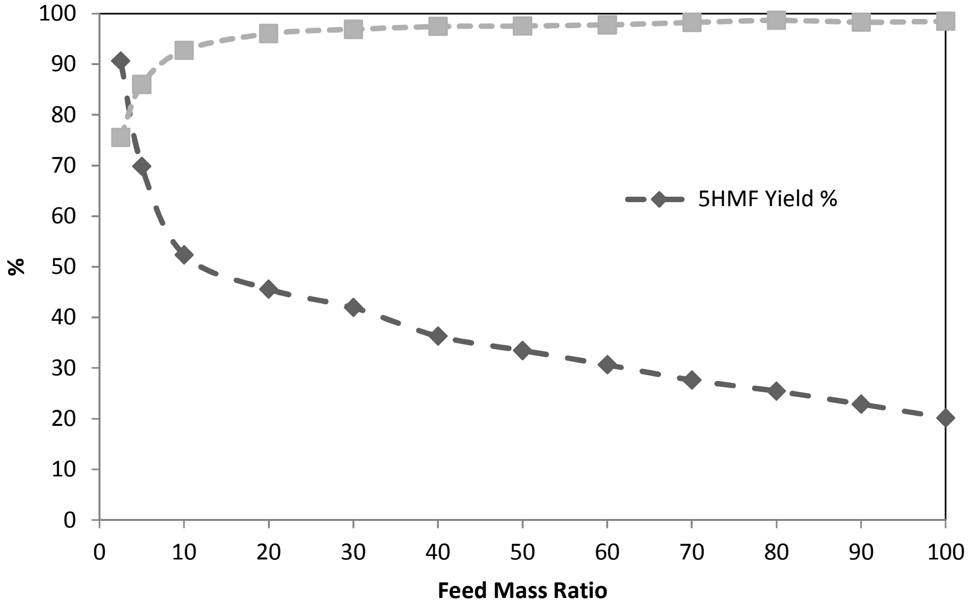


Figure 1 effect of feed ratio on 5HMF yield and fructose conversion

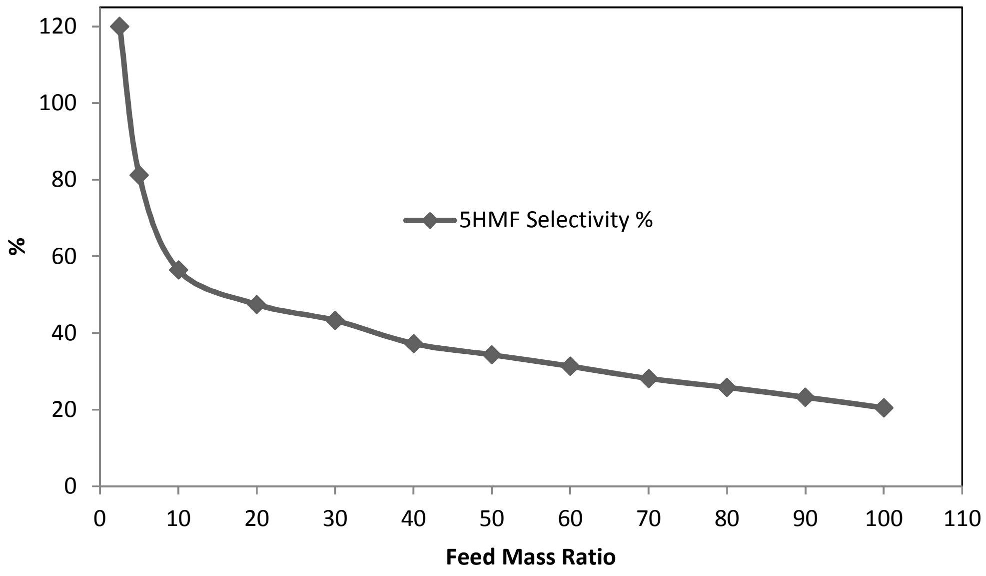


Figure 2 effect of feed ratio on 5HMF selectivity

2.2 The effect of reaction time

The effect of reaction time on fructose dehydration reaction was investigated using 10 minute intervals up to 120 minutes reaction time as shown in Figure 3.

Fructose conversion was almost steady for the whole reaction time scale. The yield and selectivity of 5HMF have shown almost similar trends. 5HMF yield of 57.5% was obtained at 10 minutes reaction time, and then increased to 63.7 % at 30 minutes. The selectivity showed slight increase from 65.5 % at 10 minutes to 68.3 % at 30 minutes. Over the course of 40 to 120 minutes reaction times the yield and selectivity did not show a definite trend, except for wavering around 70% yield ± 10%. This could be only attributed to the possible rehydration of 5HMF, the formation of side products by degradation [34]. For this reason, a reaction time of 1h was selected as optimum time.

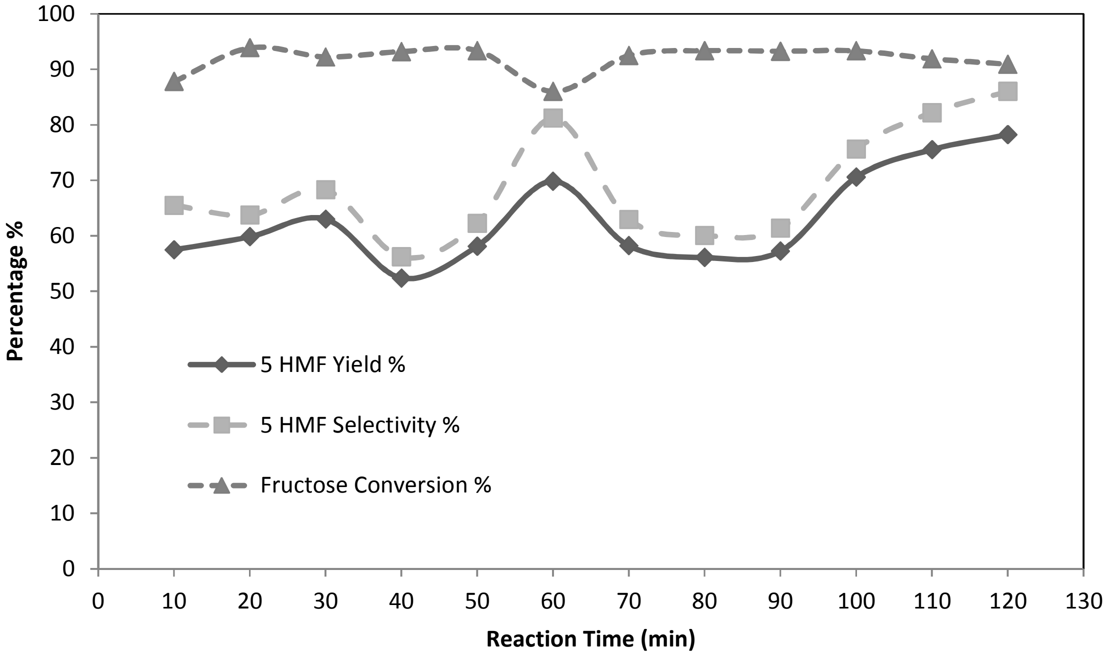


Figure 3 the effect of reaction time

2.3 effect of reaction temperature

The effect of reaction temperature on dehydration reactions was investigated, in temperatures range of 50 ^{0}C to 110 ^{0}C, as shown in Figure 4. Notably the recorded temperature was the oil bath temperature not the temperature inside the reaction beaker.

A DES mixture of 1:1 ChCl to p-TSA was used. Fructose conversion increased with temperature from 77.1% at 50 ^{0}C to 99% at 110 ^{0}C, keeping a generally high conversion over the whole temperature range.

On the other hand, 5HMF yield was almost steady at 65.0%, 65.2% and 63.8% when the reactions were conducted at 50 ^{0}C, 60 ^{0}C and 70 ^{0}C respectively. A highest yield of 70.6% was obtained at 80 ^{0}C, after which, the yield started to decrease with increasing the reaction temperature. The lowest yield recorded was 50.6% at 110 ^{0}C, where the sample colour was very dark. This might be due to thermal degradation to humins. Based on these results 80 ^{0}C was selected as the best reaction temperature.

As for the 5HMF selectivity, Figure 4 showed general decrease with increasing the reaction temperature, while remaining generally high. The highest 5HMF selectivity was 84.3% at 50

^{0}C and the lowest selectivity was 51.1% at 110 ^{0}C. On the other hand the highest fructose conversion was 99% at 110 ^{0}C while the lowest was 77.1% at 50 ^{0}C.

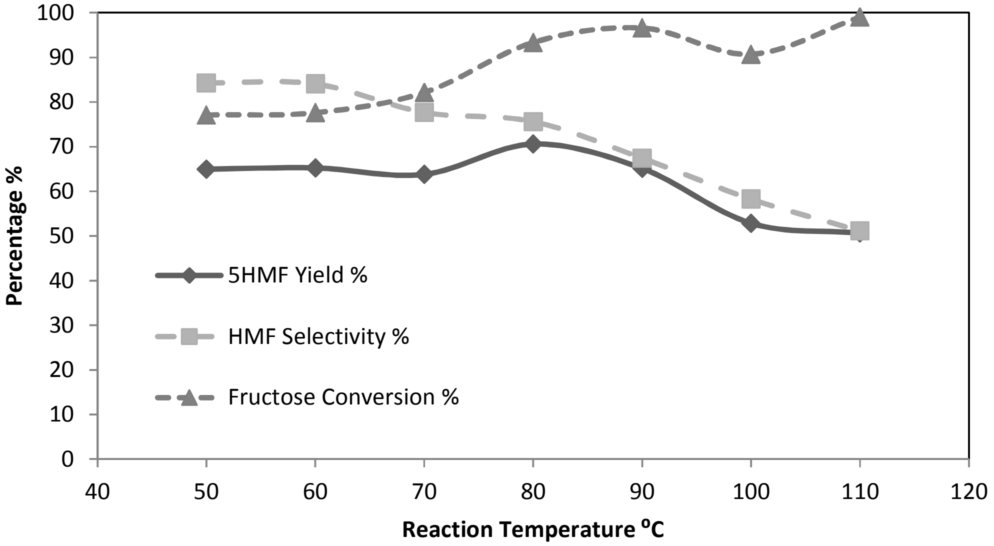


Figure 4 effect of reaction temperature

2.4 effect of DES mixing molar ratio

Deep Eutectic Solvent (DES) molar mixing ratio had great effect on the 5HMF yield and selectivity in fructose dehydration reactions, as DES plays a dual role as solvent and catalyst. In this work as shown in Figure 5, different DES mixing molar ratios were investigated as shown in table 1; at constant feed ratio of 5 w%, in order to have a clear assessment of the effect of the DES mixing ratio.

It was found that changing the ratio from 1:0.5% to 1:1.5% had a positive effect on 5HMF yield and selectivity. The yield increased from 53% at molar mixing ratio of 1:0.5 to 70% at 1:1 molar mixing ratio; reaching a value of 78.3% at molar mixing ratio of 1:1.5. On the other hand when the mixing molar ratio of DES increased to 1:2, severe decrease in the 5HMF yield down to 29.2% was observed.

Similar effect of the DES ratio on yield was seen on the 5HMF selectivity. The lowest selectivity of 33.9% was obtained at 1:2 molar mixing ratio, while a highest selectivity of 92.6% was obtained at 1:1.5 molar mixing ratio.

The effect of DES molar mixing ratio on fructose conversion was not prominent. It was steady around the range of 84.5% to 93.3% at molar mixing ratio of 1:1.5 and 1:1 respectively.

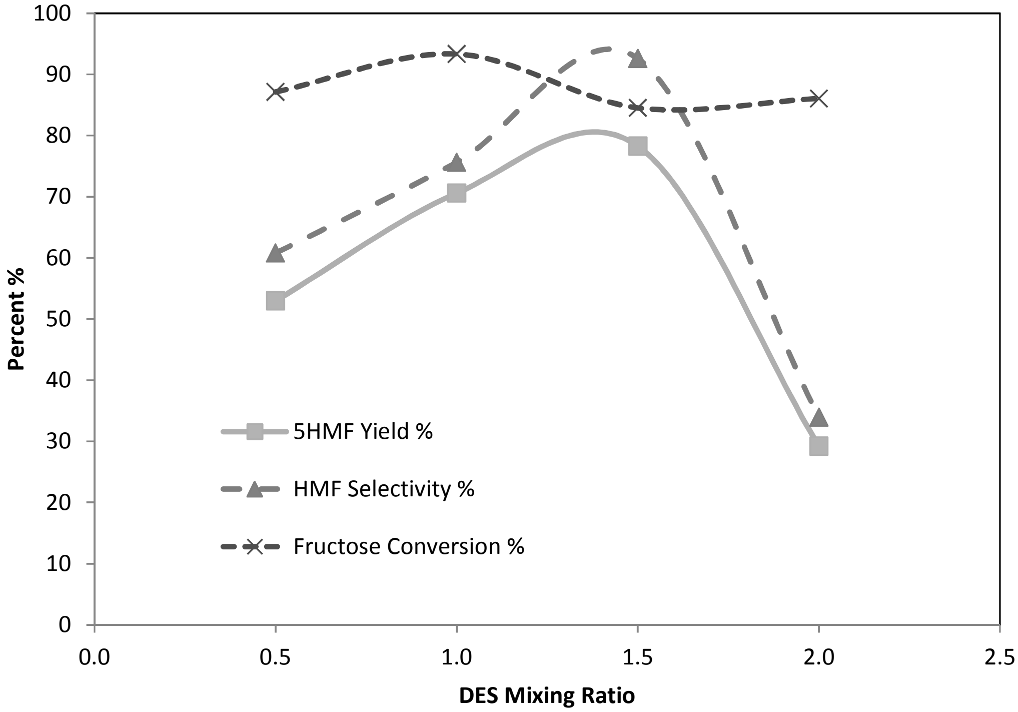


Figure 5 effect of DES mixing molar ratio

Other experiments were conducted, where 5HMF yield was investigated as function of DES ratio, keeping the feed ratio constant at 2.5 w%. Figure 6 shows that a maximum 5HMF yield of 90.7% was obtained at 1:1 DES molar mixing ratio. It decreased to 58.4% when the DES molar mixing ratio was increased to 1:1.5. This further proves that 2.5 w% feed ratio, 1:1 DES molar mixing ratio and 80 °C at 1 hour of reaction time are the best operating conditions for the investigated system.

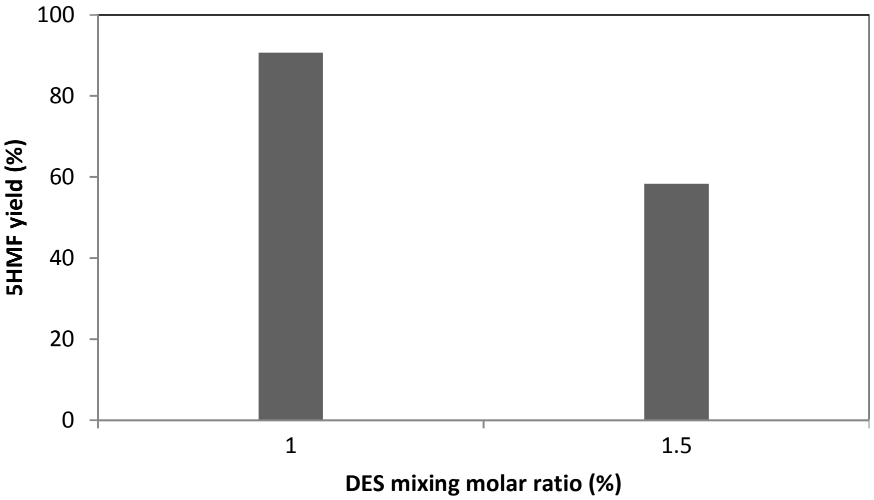


Figure 6 5HMF yield % Vs DES mixing ratio at feed ratio of 2.5%

3. Experimental

3.1. Materials

Fructose (99%), 5-Hydroxymthylfurfural (99%) and p-toluenesulfonic acid monohydrate (p-TSA) (98.5%) were ordered from Sigma Aldrich; Choline chloride (99%) from Acros., and Calcium hydroxide analytical reagent was ordered from Riedel-DeHaen. All materials were used with no further purification.

3.2 Preparation of Deep Eutectic Solvent (DES)

Choline chloride and p-toluenesulfonic acid (p-TSA) were dried under vacuum at 60 ^{0}C for 2 h prior to use, and then mixed together in different molar ratios at 80 ^{0}C, using oil bath and stirred by magnetic starrier at 300 rpm. After half an hour, colourless thick homogenous liquid mixture was obtained. The preparation was carried out in fume hood. Similar procedure was used by Hayyan to prepare DES of p-TSA and N, N-diethanol ammonium chloride to produce biodiesel from fatty acid [28].

3.3 Fructose Dehydration Reaction in DES Procedure

All the fructose dehydration reactions were carried out in 100 ml glass beaker clamped in oil bath, using magnetic stirrer at 300 rpm. Afterwards the required amount of fructose was added and stirred at 300 rpm for 1 hour at 80 ^{0}C. At the end of the reaction the thick dark brown reaction mixture was cooled down to room temperature, and then dissolved in 10 mL of HPLC grade water. Next the initial pH was measured by using pH meter, and then adjusted to neutral by using 2M of Calcium Hydroxide solution ($Ca(OH)_2$). The whole sample was poured in 100 mL calibration flask, then diluted by HPLC grade water up to 100 mL. 2 mL of the sample passed through a syringe filter and bottled in HPLC vials then shaken for HPLC analysis.

4. HPLC analysis

The reactant fructose and product 5HMF were analysed by HPLC 1100 Agilent series equipped with refractive index detector and Rezex RCM- Monosaccharide column (300×7.8 mm), ordered from Phenomenex. The analytical method was using 100% HPLC grade water from VWR as mobile phase at flow rate of 0.5 mL/min and column oven temperature of 75 ^{0}C, with injection volume of 20 μL and total time of 40 minutes.

5. Variables and Equations

The 5HMF yield, Selectivity and fructose conversion were calculated as following:

$$\text{5HMF yield \%} = \left(\frac{moles\ of\ 5HMF\ yield\ produced}{initial\ moles\ of\ fructose}\right) \times 100$$

$$\text{5HMF Selectivity \%} = \left(\frac{moles\ of\ 5HMF\ yield\ produced}{Converted\ moles\ of\ fructose}\right) \times 100$$

$$\text{Fructose Conversion \%} = \left(\frac{Total\ fructose\ moles\ converted}{initial\ fructose\ moles}\right) \times 100$$

$$\text{Feed Mass Ratio} = \frac{Fructose\ mass}{total\ mass\ of\ DES}$$

$$\text{DES Molar Mixing Ratio} = \left(\frac{pTSA\ moles}{ChCl\ moles}\right)$$

The experimental conditions and variables ranges investigated in this work are listed in table 1.

Variable	Range
Temperature ^{0}C	50, 60, 70, 80, 90, 100, and 110
Reaction Time (minute)	10 - 120
Feed Mass Ratio (%)	2.5 - 100
DES Mixing Molar Ratio (%) ChCl : PTSA	1:0.5, 1:1, 1:1.5 and 1:2

Table 1 parameters studied and their ranges.

6. Conclusion

Deep Eutectic Solvent mixture of ChCl/ p-TSA was found to be a highly promising catalytic solvent mixture for the reactions of fructose dehydration to 5HMF, giving a high yields and selectivity. The dehydration process using such mixture was found to be efficient; as the DES mixture comprised renewable, non-toxic and cheap materials. The process did not require severe reaction conditions as 80 ^{0}C was found to be the best reaction temperature. There was no need to use external catalyst as the p-TSA serves as both hydrogen bond donor (HBD) and acid catalyst for the dehydration reaction. The DES mixture was easy to prepare and had no contamination effect, as it is not reactive. The best yield was obtained 90.7%; at feed ratio of 2.5w%, DES mixing molar ratio of 1:1, 80 ^{0}C and 1h. Further investigations are required for efficient separation process for the final product 5HMF. Also superior analytical technique is required to identify the by-products obtained from the occurred side reactions.

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