CATALYTIC DEHYDRATION OF CASSAVA-DERIVED GLUCOSE INTO 5-HYDROXYMETHYL-FURAN (5-HMF) IN 1-BUTYL-3-METHYLIMIDAZOLIUM CHLORIDE ([BMIM]CL)

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ABSTRACT

Catalytic dehydration of glucose and fructose into 5-Hydroxymethylfuran (5-HMF) catalysed by sulfated zirconia in 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) ionic liquid was investigated by reactive vacuum distillation process. A 5-HMF yields of 82% and 65% were obtained using fructose and glucose substrates in 2 h reaction time at 180 °C. When the reaction time was increased beyond 2 h, a decreased in 5-HMF yield was observed. The ionic liquid and sulfated zirconia exhibited a constant activity when recycled for five successive trials. This process provided an avenue whereby the production of 5-HMF from cassava-derived carbohydrate is conducted and separated with minimal use of volatile solvents.

Keywords: Cassava, 5-Hydroxymethylfuran, reactive vacuum distillation

INTRODUCTION

Presently, the limit of fossil fuel reserves is quite clear, and the concerns over global warming are growing; hence, the catalytic transformation of biomass to value-added chemicals has come under intense focus from the scientific and industrial communities in recent years. Conversion of sugars to fine chemicals has attracted great (Huber *et al.*, 2006, Tong *et al.*, 2010a, Tong *et al.*, 2010c) deal of attention (Cao *et al.*, 2011). Fructose and glucose have been considered as exceptional carbohydrate compounds that can be used for the synthesis of furan-based chemicals (Chheda *et al.*, 2007, Roman-Leshkov *et al.*, 2006). For example, 5-Hydroxymethylfurfural (5-HMF) has been produced from the catalytic dehydration of fructose and sucrose (Moreau *et al.*, 2004, Moreau *et al.*, 2006). Therefore, 5-HMF has been proposed as a potential substrate for the production of nonpetroleum-derived building blocks of fine chemicals (Gallezot, 2012, Gandini, 2010, Gandini, 2011). Thus, 5-HMF has been referred to as a renewable furan-based platform chemical (Bicker *et al.*, 2003).

To achieve efficient transformation of fructose and glucose into 5-HMF, several catalytic systems has been developed. These includes liquid mineral acids (Kuster, 1990), solid acids (Moreau *et al.*, 1996, Qi *et al.*, 2011a, Qi *et al.*, 2008a) and a metallic compound (Ishida and Seri, 1996). For instance, dehydration of D-fructose was reported using H_2SO_4 as catalyst in sub-critical water at 250 °C (Antal *et al.*, 1990, Bicker *et al.*, 2003). The results indicate that 53% yield of HMF was obtained. Similarly, 78% yield was obtained at 180 °C when a sub-critical or supercritical acetone-water mixture was used as the reaction medium (Bicker *et al.*, 2003). Furthermore, glucose was reported to be hydrated using mineral acid such as H_3PO_4 at a temperature of 190 °C. The results indicate a low yield of 15.5% and was attributed to the stable ring structure of the glucose (Tong *et al.*, 2010b). Also, hydrated niobium pent oxide ($Nb_2O_5.nH_2O$) was reported to have shown high catalytic activity in the dehydration of carbohydrates to 5-HMF as a solid catalyst (Yang *et al.*, 2011) and from the results, 74% yield of 5-HMF was obtained. Other solid acids used in dehydration of carbohydrates are H-form mordenite (Moreau *et al.*, 1996), vanadyl phosphate (Carlini *et al.*, 2004), ion-exchange resins (Tong *et al.*, 2010b) and sulphated zirconia (Takagaki *et al.*, 2009). Although these catalysts could improve the dehydration of fructose, these systems suffer from the need for relatively high reaction temperatures, poor yields or low product selectivity. For example, a poor yield arose from the decomposition and polymerization of 5- HMF after its being produced, and the main by-products included levulinic acid, formic acid and humin, among other components (Corma, 1995, Kuster, 1990, Lewkowski, 2001). The production of 5-HMF in a high yield and by a cost-effective technique is still a challenge.

Sulfated zirconia has attracted much attention since it exhibited a promising catalytic activity in many reactions such as isomerization, hydrocracking, alkylation, condensations, and oligomerizations (Yadav and Nair, 1999). The use of sulfated zirconia as a solid catalyst was first reported elsewhere (Arata and Hino, 1984) and used in n-butane isomerization at moderate temperatures. The results showed that the reaction mechanism involved the formation of carbenium ions via protonation of the alkane, and this demonstrated the super acidity of sulfated zirconia. However, catalytic activity of sulfated zirconia is not only affected by acid strength alone, but also the type of the acid sites, Brønsted and Lewis acid sites, plays an important role in determining the catalytic properties. Sulfated zirconia was impregnated with H_2SO_4 used in dehydration of fructose as catalyst (Benvenuti *et al.*, 2000, Qi *et al.*, 2009b). From the results obtained, 72.8% yield of 5-HMF was reported at 180 °C at 93.6% fructose conversion in acetone-DMSO solvent mixtures. This suggests that sulfated zirconia is an effective solid catalyst that can catalysed fructose in non-aqueous solvents.

Recently, room temperature ionic liquids (ILs) have been employed in the dehydration of fructose to 5-HMF (Hsu *et al.*, 2011, Hu *et al.*, 2012, Hu *et al.*, 2009, Qi *et al.*, 2011a) because they are stable, have low vapour pressure and can be recycled (Sheldon, 2001, Yang *et al.*, 2008). These ILs can promote the

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dehydration reaction because of the enhanced dissolution of catalysts and substrates; for instance, it was reported that a 74.8% yield of 5-HMF was obtained from fructose dehydration at 90 °C using N-methyl-morpholinium methyl sulphonate as catalyst under a nitrogen atmosphere (Tong *et al.*, 2010c). Also, 88% yield of 5-HMF was reported using 1-ethyl-3-methylimidazolium hydrogen sulphate as catalyst at 30 min in MIKB as co-solvent (Tong *et al.*, 2010c). Therefore, catalytic synthesis of 5-HMF with ILs is considered a promising direction in chemical research and have been explored extensively in the dehydration of sugars (Hu *et al.*, 2009, Zhao *et al.*, 2007). In this work, we report the dehydration of glucose and fructose with a catalytic amount of sulfated zirconia in 1-butyl-3-methylimidazolium chloride as solvent via reactive vacuum distillation.

MATERIALS AND METHODS

Glucose (99.5%), fructose (99.5%), 1-butyl-3-methylimidazolium chloride (BMIMCl) (98%) and zirconium hydroxide (99.5%) were purchased from Sigma-Aldrich and 5-Hydroxymethylfurfural (99%) from Kosher. All chemicals were used as received. All ^1H and ^{13}C NMR were recorded using a Bruker AMX 300 MHz spectrometer and data were processed by ACD/NMR Processor Academic Edition. Samples were made as dilutions of CDCl$_3$ unless otherwise stated. All XRD data were collected using a Siemens D500 X-Ray Diffractometer using Cu K$_{\alpha 1}$ radiation with wavelength of 0.154056 nm. The diffractometer was operated at 40 kv and 30 mA. Scans began at a low angle of 2° and scanned to 25° of 2θ in 0.05° steps at 6 seconds per step. FTIR spectra obtained in this work were conducted with an ALPHA Bruker Optics FTIR spectrophotometer equipped with ZnSe ATR crystal. The samples were scanned from 400 – 4000 cm^{-1} wavenumber with a 32 scan per sample circle and a resolution of 4 (Halim *et al.*, 2013).

Synthesis of sulfated zirconia

Sulfated zirconia (SO$_4$$^{2-}$/ZrO$_2$) was prepared according to the method described by Qi *et al* (Qi *et al.*, 2011b, Qi *et al.*, 2009b). Briefly, 1 g of zirconium hydroxide was dissolved in 10 mL of 1M H$_2$SO$_4$ and stirred vigorously at room temperature for 3 h. The suspension was centrifuged using a Heraeus Biofuge Primo Centrifuge machine set at 3000 rpm for 15 minutes and the supernatant was discarded. The deposition at the bottom of the centrifuge tube was dried in a vacuum at 60 °C overnight. It was ground into a fine powder using pestle and mortar, and further calcined at 500 °C in a muffle furnace for 3 h. The catalyst was characterised by XRD and FT-IR.

Dehydration of glucose by vacuum distillation

Glucose (5.0 g, 0.028 mol) and BMIMCl (20.0 g, 0.11 mol) were heated in an oil bath at a temperature of 120 °C and stirred for 300 s to allow the dissolution of the glucose in the ionic liquid. The reaction was started by adding 10 mol. % of the following catalysts: CrCl$_3$.6H$_2$O, ZrO$_2$, and SO$_4$$^{2-}$/ZrO$_2$. After completion of the reaction, 5-HMF was collected by vacuum distillation at 180 °C, 2.7 kPa. The same procedure was used for fructose. ^1H NMR (300 MHz; CDCl$_3$) δ 9.57 (1H, s, CHO), 7.22 - 7.21 (1H, d, *J* = 3.0 Hz, 3-H), 6.50 (1H, d, *J* = 6.0 Hz, 4-H), 4.70 (2H, s, OCH$_2$); ^{13}C NMR (75 MHz; CDCl$_3$) δ 177.8 (C=O), 160.9 (C-5), 152.2 (C-2), 122.9 (C-3) 109.8 (C-4), 57.7 (OCH$_2$); FT-IR (cm^{-1}) 3377br, 1657s, 1250s, 1188s, 1160s.

Yield calculation of 5-HMF produced

The yield of 5-HMF produced was calculated from the following equation:

$$5\text{-HMF yield (mol. \%)} = \frac{\text{Moles of } 5-\text{HMF produced}}{\text{Moles of carbohydrate used}} \times 100\% \text{ -} \quad (1)$$

RESULTS

X-ray diffraction (XRD) patterns of Sulfated zirconia

The solid catalysts used in this work (was characterized by X-ray Diffractometer (XRD) and the results is presented in Figure 2 to illustrate the changes in the crystalline phase.
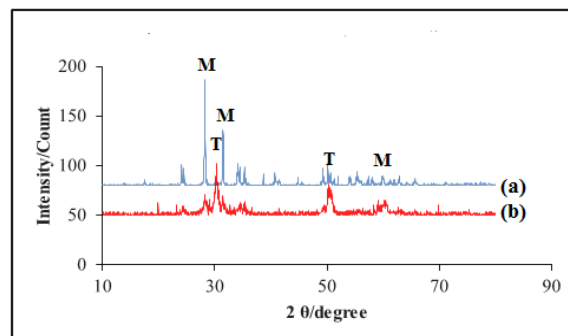

Fig. 2: XRD patterns of (a) ZrO$_2$ (b) SO$_4$$^{2-}$/ZrO$_2$ (M and T designate monoclinic and tetragonal phases)

Vapour pressure and Temperature of 5-HMF produced

The vapour pressure and temperature of 5-HMF was obtained from thermodynamic data to ascertain the actual boiling point of the product. These results are presented in Figures 3 and 4 which was used to find the boiling point of the product (5-HMF).
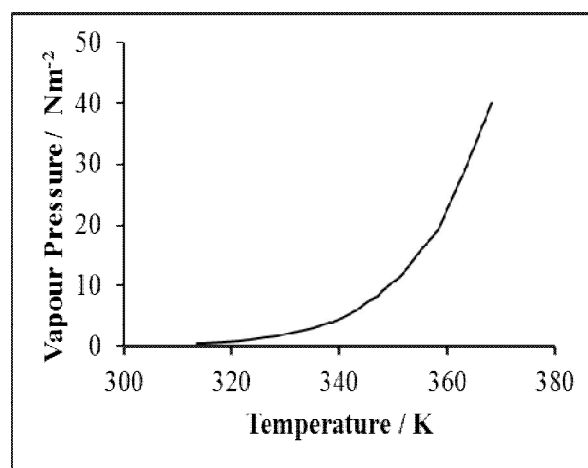

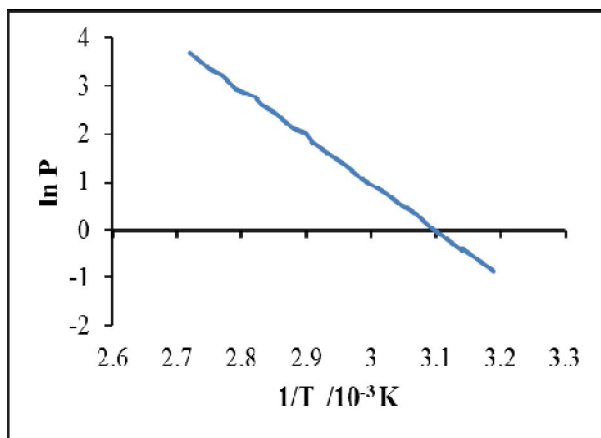**Fig. 3:** Plot of vapour pressure against temperature for 5-HMF (Verevkin *et al.*, 2009)

Fig. 4: Plot of ln P against reciprocal of temperature for 5-HMF (Verevkin *et al.,* 2009).

Dehydration of glucose and fructose

The results of the dehydration of glucose and fructose conducted under vacuum at 180 °C in 1-butyl-3-methylimidazolium chloride (BMIMCl) solvent with 10 mol.% of the catalysts, $CrCl_3.6H_2O$, ZrO_2 and SO_4^{2-}/ZrO_2 designated as Cr (III), Z and SZ respectively, are presented in Figure 5. From these results, it was observed that higher yields (82%, 75% and 55%) of 5-HMF were obtained using fructose as a substrate with catalysts SZ, Cr (III) and Z, respectively.
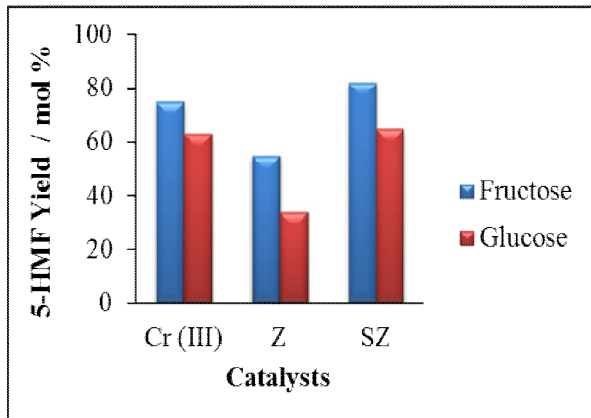

Fig. 5: Catalytic activity of the solid catalysts

Dehydration of glucose and fructose in different ionic liquids and 5-HMF yield

The results of the dehydration of glucose and fructose in various ionic liquids are presented in Figure 6. This is to show the optimisation 5-HMF yield in various ionic liquids.
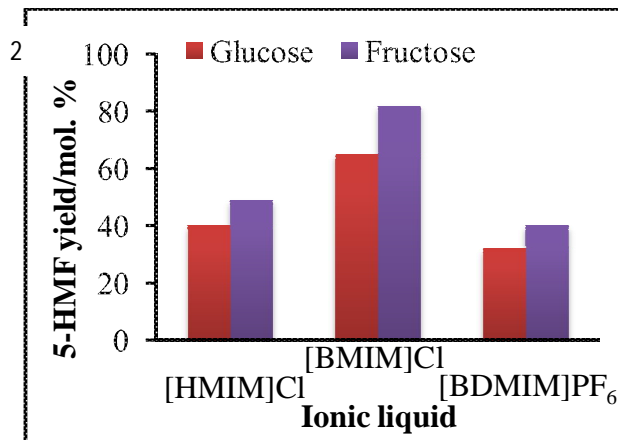

Fig. 6: 5-HMF yields in ionic liquids

Effect of reaction temperature with time on 5-HMF yield

The effect of reaction temperature with time on 5-HMF yield in the dehydration of fructose catalysed by sulfated zirconia (SZ) using [BMIM]Cl solvent was investigated and the results are presented in Figure 7.
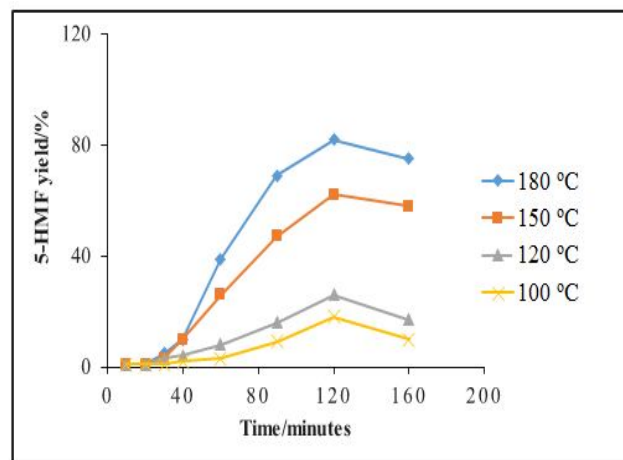

Fig. 7: Effect of reaction temperature and time on 5-HMF yield

Effect of catalyst dosage on 5-HMF synthesis

The effect of catalyst dosage on 5-HMF synthesis was investigated using fructose and glucose as substrates and the results are presented in Figure 8.

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Fig. 8: Effect of catalyst dosage on 5-HMF yield

Fig. 9: Recycling of sulfated zirconia and [BMIM]Cl

Sulfated zirconia and [BMIM]Cl recycling
Recycling of catalysts and solvents is very important based on the principles of green engineering (Anastas and Zimmerman, 2003) and therefore, recycling of sulfated zirconia catalyst and [BMIM]Cl ionic liquid was examined and the results are presented in Figure 9.

Characterization of 5-HMF
5-HMF was characterised by ^{1}H NMR, ^{13}C NMR and FT-IR and the results are presented in Figures 10, 11 and 12.

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Fig. 10: ¹H NMR spectra of 5-HMF synthesized

Fig. 11: ¹³C NMR of synthesised 5-HMF

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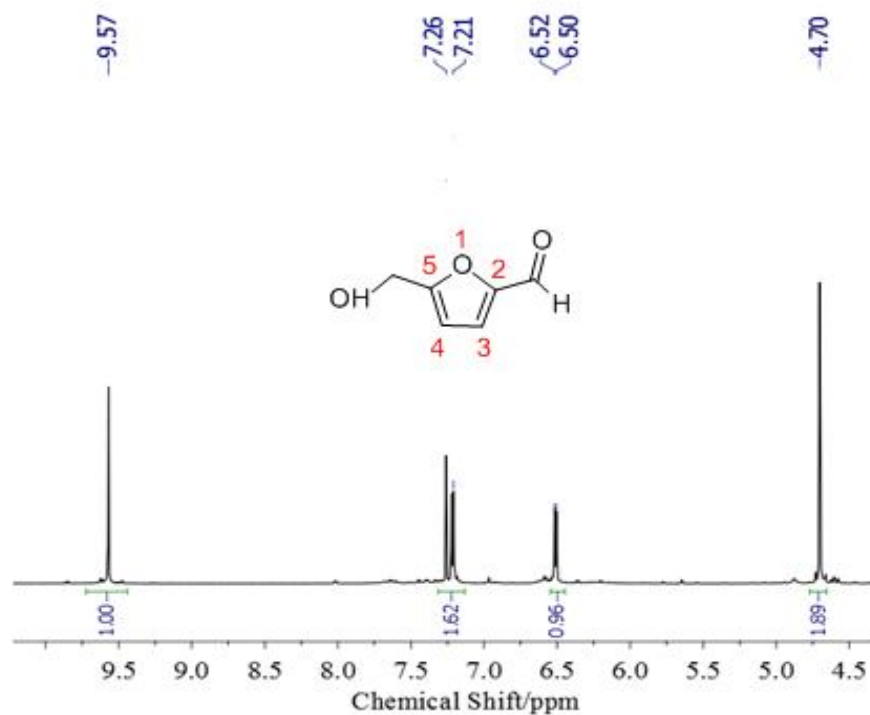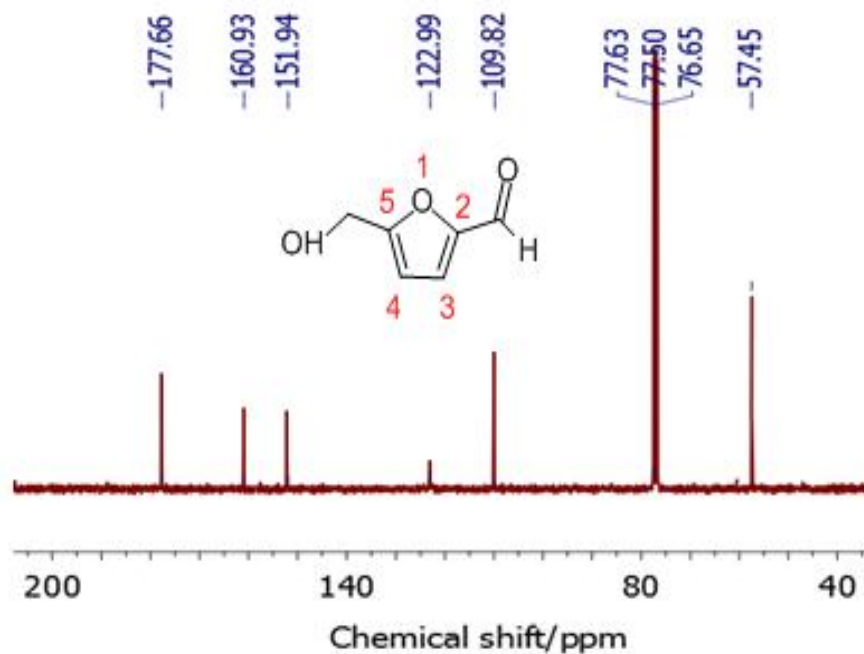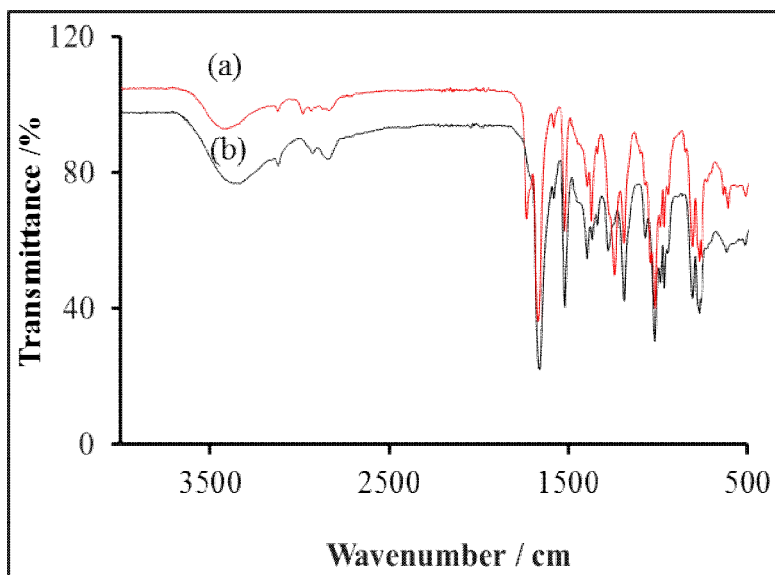**Fig. 12:** FT-IR spectra of (a) commercially sourced and (b) synthesized 5-HMF

DISCUSSION

Characterization of sulfated zirconia by XRD

XRD was used to elucidate the changes in the crystalline phase of zirconia before and after treatment with sulphuric acid. It was observed that the XRD patterns exhibited tetragonal–monoclinic phase transformation as revealed in Figure 2. From literature, it was revealed that sulfate treatment of zirconia retards its crystallization which leads to its transition from the tetragonal phase to the monoclinic phase occurs (Evans *et al.*, 1984). Furthermore, it was reported that during monoclinic–tetragonal phase transformation of zirconia, the tetragonal phase should be formed above 1170 °C (Qi *et al.*, 2011b), but in this experiment the zirconia prepared occurred as a tetragonal phase at lower temperature This might be that the transformation was hindered in fine SO_4^{2-}/ZrO_2 powders because of the sulfate treatment of pure zirconia. Moreover, this transformation of the tetragonal phase into the monoclinic phase was probably due to the lower surface energy of the tetragonal phase compared to monoclinic phase (Evans *et al.*, 1984).

Dehydration of glucose/fructose by vacuum distillation

The dehydration of glucose and fructose were investigated using a reactive vacuum distillation approach. This is to provide an avenue whereby the production of 5-HMF is conducted and separated with minimal use of volatile solvents: almost all reported literature on the synthesis of 5-HMF is based on solvent extraction (Chheda *et al.*, 2007, Qi *et al.*, 2009a, Qi *et al.*, 2011b, Qi *et al.*, 2008a, Qi *et al.*, 2008b, Qi *et al.*, 2009b). To date, only one paper reported the separation of 5-HMF under vacuum

distillation (Wei *et al.*, 2012).

Therefore, considering the boiling point of 5-HMF which is 114 - 116 °C at 1 mbar, a reactive vacuum distillation procedure involving both the chemical reaction and product separation steps within a single unit was applied for the production of 5-HMF from glucose dehydration. This reactive distillation method can have a wide range of industrial applications (Hasabnis and Mahajani, 2010, Noeres *et al.*, 2003, Taylor and Krishna, 2000). The process results in the evaporation of the most volatile component because when the pressure is reduced, the molecules are few and hence, it is possible for vaporization and distillation to take place. A continuous operation procedure could be envisaged.
The relationship between vapour pressure and temperature of 5-HMF from thermodynamic data reported (Verevkin *et al.*, 2009) was used to determine the actual boiling point of the 5-HMF at the pressure used (Figures 3 and 4).

The relationship between the temperature of a liquid and its vapour pressure is logarithmic and can be explained by the Clausius-Clapeyron equation as:

$$\frac{d\,lnP}{dT} = \frac{\Delta H_{vap}}{RT^2} \quad\text{--- (1)}$$

From the above equation, the rate at which the natural logarithm of the vapour pressure changes with temperature is determined by the molar enthalpy of vaporization ΔH_{vap}, the ideal gas constant R, and the temperature T (K) of the system.
Assuming that ΔH_{vap} does not change very much with

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temperature, equation (2) can be expressed in the following integrated form where C is a constant.

$$\ln P = \frac{RT}{\Delta H_{vap}} + C$$ ------------------------------------- (2)

This form of the Clausius-Clapeyron equation (3), is been used to measure the enthalpy of vaporization of the 5-HMF from plots of the natural logarithm of its vapour pressure versus temperature.

$$\ln P = -\frac{\Delta H_{vap}}{RT} + C$$ ------------------------------------- (3)

The logarithm of the vapour pressure increases as the temperature of the system increases. Thus the ln P vs 1/T plot shown in Figure 3 is linear as expected.

5-HMF yields from dehydration of glucose and fructose
From the results of the dehydration of glucose and fructose presented in Figure 5, it was observed that, when using glucose as a substrate, the yields were lower compared with those for fructose as substrate. This lower yield may be as a result of the glucose straight chain and pyranose ratio (63% β-glucopyranose and 37% α-glucopyranose) in water and hence, the enolisation rates might be slow (Kuster, 1990). Since fructose forms less stable ring structures, more open chains structures are likely to be present in BMIMCI and therefore the enolisation rates might be higher Fructose and glucose have been reported to exhibit different reaction mechanisms to form 5-HMF as glucose isomerizes to fructose on dehydration (Zhang *et al.*, 2011a), and this might account for the lower yield of 5-HMF from glucose as compared to that of fructose. This observation was also explained elsewhere (Tong and Li, 2010). The results of the 5-HMF yields from glucose (65 %, 63 % and 34%) using SZ, Z and Cr (III) catalysts in BMIMCI solvent was higher in this work as compared to 22%, 24% and 27% using the same solvent and catalysed by zeolite (H-ZMS-5) as reported from literature (Jadhav *et al.*, 2012). Therefore, this study revealed that SZ can effectively catalysed the dehydration of glucose to 5-HMF in higher yield as compared to zeolite even though both catalysts are environmentally benign.

Based on catalytic activity, it was observed that SZ exhibited a strong catalytic activity as can be seen (Figure 5) which gave almost 80 % and 65 % yields from fructose and glucose substrates. Also, the catalytic activity of SZ was compared with an untreated Z catalyst and lower yields were obtained from the latter. This increased catalytic activity of SZ may be attributed to the increased acid sites of SZ in comparison to Z.

5-HMF formation in other ionic liquids
In order to optimise 5-HMF yield, the use of other ionic liquids; 1-hexyl-3-methylimidazolium chloride [HMIM]CI and 1-butyl-2,3-dimethylimidazolium hexaflourophasphate ([BDMIM]PF$_6$) were used. The results compared to those when using [BMIM]CI ionic liquid are presented in Figure 6. Among the ionic liquids used in the synthesis of 5-HMF, [BMIM]CI clearly gave 5-HMF in higher yields.

Ionic liquids [BMIM]CI and [HMIM]CI media provided significant yields of 5-HMF in the dehydration reaction of fructose and glucose substrates. This may be due to the fact that the chloride ions form only weak ion pairs (El Seoud *et al.*, 2007), which leads more readily to the isomerization of carbohydrates (Zhao *et al.*, 2007) and the subsequent dehydration process . Furthermore, as a result of the weak coordination of the ionic liquid structures, they do not compete with sugar for the binding of metal chlorides; therefore it is more likely that a sugar-metal coordination complex will be formed (Zhang, 2006).

Effect of reaction temperature with time on 5-HMF yield
The effect of reaction temperature with time on 5-HMF yield in the dehydration of fructose catalysed by sulfated zirconia (SZ) using [BMIM]CI solvent was investigated and the results are presented in Figure 7. The reactions were conducted at 100 ºC, 120 ºC, 150 ºC and 180 ºC. As shown in Figure 7, it was observed that the reaction temperatures have a significant effect on the 5-HMF yield. When the reactions were conducted at 100 ºC, a lower yield (18 %) was obtained after 2 h and a maximum yield of 82 % was obtained at 180 ºC after the same time of 2 h. It was also observed that the yield tended to increase gradually with increasing reaction time up to 120 minutes. Beyond 120 minutes, a decrease in yield of 5-HMF was observed in these temperature regimes. These results indicate that the degradation of 5-HMF was significant at higher reaction time even though increase in temperature speeds up the reaction initially and this behaviour was also reported elsewhere (Antal *et al.*, 1990, Lewkowski, 2001, Rosatella *et al.*, 2011). Furthermore, it was reported that [BMIM]CI is known for its reaction with aldehyde functional group (Ebner *et al.*, 2008) and this decreased in yield might also be a side product formed reaction between 5-HMF and [BMIM]CI as reported in literature (Zhang *et al.*, 2011b).

Effect of catalyst dosage on 5-HMF synthesis
The effect of catalyst dosage on 5-HMF was investigated based on the dehydration of the substrates in BMIMCI ionic liquid solvent and sulphated zirconia catalyst at 180 ºC, where the highest yield of 5-HMF was obtained (Figure 7). When the catalyst dosage was increased from 2.5 mol. % to 10 mol. %, the yield of 5-HMF increased, at 180 ºC for a reaction time of 120 minutes, from 22 % to 82% with fructose as substrate and 16% to 65% when using glucose as substrate. However, when the amount of the sulfated zirconia was increase from 10 mol. % to 30 mol. %, there was a decrease in the 5-HMF yield with both fructose and glucose as substrates. Therefore, 10 mol. % of catalyst dosage was chosen as the most suitable condition.

Sulfated zirconia and [BMIM]CI recycling
Recycling of the catalyst and the ionic liquid was investigated and from the result of this study as presented in Figure 9 shows that the recycled catalyst and ionic liquid gave comparable results on 5-HMF yields. For instance, the catalyst and the solvent retained a very high activity up to the third cycle and tended to lose their activity slightly from fourth to fifth cycle. This might be due to the retention of some 5-HMF or unreacted substrates in these cycles.

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Characterization of 5-HMF

The synthesised 5-HMF was characterised by ^1H NMR, ^{13}C NMR and FT-IR and were identical to previous data reported (Wei *et al.*, 2012). From the analysis of the ^1H and ^{13}C NMR data as shown in Figures 10 and 11, only 5-HMF was present indicating a purity >95%. In addition, the FT-IR of the 5-HMF presented in Figure 12 showed that the absorption bands were in agreement with NMR data.

Conclusion

Sulfated zirconia catalyst was synthesis by treating zirconium hydroxide with H_2SO_4. This solid catalyst was used in the conversion of cassava-derived glucose to 5-HMF in ionic liquids. This catalyst was shown to have a higher catalytic activity over $CrCl_3.6H_2O$) and ZrO_2 catalysts with a 5-HMF yield of 82% at 180 oC for 2 h reaction time via reactive vacuum distillation, the ionic liquid and the catalyst could be recycled up to 6 times without loss of catalytic activity. This process can be employed for the synthesis of 5-HMF from cassava-derived glucose by vacuum distillation with minimal use of volatile solvents.

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