

Preparation of 5-hydroxymethyl- furfural from glucose and fructose in ionic liquids by reactive vacuum distillation over a solid catalyst

M.B. Nasirudeen, H.C. Hailes, J.R.G. Evans

Department of Chemistry, University College London, 20 Gordon Street London WC1H 0AJ, UK

Abstract: Dehydration of glucose and fructose to 5-hydroxymethylfurfural (5-HMF) on a commercial scale would benefit from a separable and reusable catalyst, a low volatility solvent and ease of separation of products. For these reactions, we use a sulfated zirconia (SZ) catalyst in 1-butyl-3-methylimidazolium chloride [BMIM]Cl ionic liquid as solvent and separate the product by reactive vacuum distillation. The results are of particular relevance to sub-Saharan Africa with an emerging agricultural resource of cassava and the use of industrial solar power. Yields for 5-HMF of 82% and 65% were obtained at a 5 g experimental scale using fructose and glucose substrates in 2 h reaction time at 180 °C. The ionic liquid and SZ exhibited high activity when recycled for five successive trials.

Keywords: 5-hydroxymethyl-furfural (5-HMF), catalysis, ionic liquids, cassava

1. INTRODUCTION

The limits on readily extractable fossil fuel reserves have encouraged the exploration of biomass for value-added chemicals [1, 2]. This is particularly relevant for sub-Saharan Africa which has potential for agricultural development, particularly of cassava [3, 4], the tuber of which is capable of producing food, fuel and chemical feedstocks [5, 6]. The region benefits from high insolation which can be harnessed, *inter alia*, for solar-powered chemical plant [7]. Conversion of sugars to fine chemicals has attracted a great deal of attention especially in the last two years as shown in Table 1. Fructose and glucose in particular are viewed as principal carbohydrate compounds that can be used for the synthesis of furan-based chemicals [8-10]. As can be seen from Table 1, reaction temperatures for this transformation are in the region 80-200 °C. Acid catalysts are preferred and for commercial viability, solid or supported catalysts capable of separation and re-use are needed. Sulfated oxides such as ZrO₂ produce yields of 5-hydroxymethylfurfural (5-HMF) from 20-100% depending on conditions. 5-HMF derived from the catalytic dehydration of fructose, glucose and sucrose [11, 12], is proposed as a potential substrate for the production of nonpetroleum-derived building blocks for fine chemicals [13-15]. It is a renewable furan-based platform chemical [16]. 5-HMF and its derivative 2,5-furandicarboxylic acid are described more poetically, as the ‘sleeping giants’ of chemical intermediates derived from renewable sources [16].

To achieve efficient transformation of fructose and glucose into 5-HMF, several catalytic systems have been developed. These include liquid mineral acids [17], solid acids [18-20] and lanthanides [21]. For instance, dehydration of D-fructose using H₂SO₄ as catalyst in sub-critical water at 250 °C [16, 22] gave a 53% 5-HMF yield. Similarly, a 78% 5-HMF yield was obtained at 180 °C when a sub-critical or supercritical acetone-water mixture was used as the reaction medium [16]. Glucose has been dehydrated using mineral acids such as H₃PO₄ at a temperature of 190 °C with a lower yield of 16% attributed to the more stable ring structure of glucose [23]. Hydrated niobium pentoxide

($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) was also reported to have shown high catalytic activity in the dehydration of carbohydrates to 5-HMF as a solid catalyst [24] with a 74% yield of 5-HMF. Furthermore, high yields of 5-HMF have been obtained from 34% to 82% with 12-molybdophosphoric acid catalyst dissolved in ionic liquids [24]. Other solid acids used in the dehydration of carbohydrates are H-form mordenite [20], vanadyl phosphate [25], ion-exchange resins²³ and sulfated zirconia [26]. Although these catalysts could improve the dehydration of fructose, these systems suffer from the need for relatively high reaction temperatures, low yields or product selectivity. For example, a poor yield arose during the dehydration reaction from 70% to 33% at 4 hours reaction time due to the decomposition and polymerization of 5-HMF and the main by-products included levulinic acid, formic acid and humin, among other components [27-29]. Simeonov et al. [30] used tetraethyl- and tetrapropyl ammonium bromide as solvent with Amberlyst-15 catalyst to obtain yields up to 97% such that the solvent could be separated by crystallization. The production of 5-HMF in high yield and using a cost-effective will benefit from the use of a robust, reusable catalyst, the avoidance of VOCs where possible and continuous separation of product.

SZ exhibits promising catalytic activity in many reactions such as isomerization, hydrocracking, alkylation, condensations, and oligomerizations [31]. Its efficacy as a solid catalyst was first reported for the isomerization of *n*-butane at moderate temperatures [32]. The reaction mechanism involved the formation of carbocations via protonation of the alkane, demonstrating its 'super acidity'. The catalytic activity of SZ is not only affected by acid strength but by the type of acid site: Brønsted and Lewis acid sites play an important role in determining the catalytic properties. Zirconia impregnated with sulfuric acid has been used as a catalyst for the dehydration of fructose [33, 34] in acetone-dimethylsulfoxide mixtures and a 73% yield of 5-HMF was reported by HPLC analysis at 180 °C with microwave heating at 2 MPa N_2 pressure. This suggested that SZ is an effective solid catalyst that can catalyse fructose dehydration in non-aqueous solvents.

Recently, room temperature ionic liquids (ILs) have been employed in the dehydration of fructose to 5-HMF [18, 35-37]: they are also stable, have low vapour pressure and can be recycled [38, 39]. Such ILs promote the dehydration reaction of carbohydrates to furans because of the enhanced dissolution of catalysts and substrates. A 75% yield of 5-HMF was obtained from fructose dehydration at 90 °C using *N*-methylmorpholinium methyl sulfonate as catalyst under a nitrogen atmosphere [1]. Also an 88% yield of 5-HMF was reported using 1-ethyl-3-methylimidazolium hydrogen sulphate [EMIM]HSO₄ as catalyst in 30 min in methyl isobutyl ketone as co-solvent [40]. Furthermore Hu et al. [36] obtained a 61% yield of 5-HMF from glucose using SnCl₄ in 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM]BF₄ IL. Therefore, the catalytic synthesis of 5-HMF with ILs is considered a promising strategy and is beginning to be explored in the dehydration of other sugars [35, 41]. There is however less interest in the use of chromium, iridium or tin salts because of the toxicity and problems of disposal of waste. It can be argued that the cost of ILs is high but there is the prospect that as their use becomes more widespread, this will change.

The conversion of starch derived from cassava to sugars is established [42] but the preference for enzymatic over acid catalysis is emerging [43]. In this work, with an eye to the commercial realization of this important process, we combine, for the first time, the features needed for a scaled-up operation drawing upon the agricultural source of cassava and the use of industrial solar power by reporting the dehydration of glucose and fructose with a SZ catalyst in 1-butyl-3-methylimidazolium chloride [BMIM]Cl ionic liquid as solvent and reactive vacuum distillation of the product.

| Sugar F/G | Catalyst | Solvent | Temp. /°C | Cat./Subst. mass ratio | Scale/g | Separation / analysis | Yield of 5-HMF % | Reference |
|-------------|---|--------------------------------|-----------------------------|------------------------|----------------------|---|---------------------|-----------|
| F&G | zeolite | MIBK + H ₂ O | 165 | 0.29 | 3.5 | MIBK | 34% (conv x select) | 44 |
| G | Lanthanide Cl (homogeneous) | H ₂ O | 140 (10atm.N ₂) | 0.7 | 0.8 | benzene | | 21 |
| F | H-mordenite | MIBK + H ₂ O | 165 | 0.29 | 3.5 | MIBK continuous | 34% (conv x select) | 20 |
| F | H ₂ SO ₄ (homogeneous) | Acetone-H ₂ O (9:1) | 180 | 0.05 | 0.02 | HPLC | 75% | 16 |
| F | VOPO ₄ ·2H ₂ O (Fe-doped) | H ₂ O | 80 | 0.59 | 6.0 | GC-MS | 60% | 25 |
| F | HCl or PK-216 (homogeneous) | DMSO | 180 | 1.0 (resin) | 0.75 | MIBK continuous | 72% (conv x select) | 45 |
| F&G | HCl (homogeneous) | DMSO-H ₂ O | 170 | 0.36 | 0.5 | MIBK-2 butanol or CH ₂ Cl ₂ | - | 9 |
| F&G | HCl +NaCl (homogeneous) | Acetone/H ₂ O | 165-180 | 0.003 | Flow | 78% | - | 46 |
| F&G | H ₃ BO ₃ (homogeneous) | [EMIm]Cl | 120 | 0.35 | 0.1 | HPLC | 41%(G) 80%(F) | 47 |
| F | H ₃ PO ₄ (and other acids) (homogeneous) | H ₂ O | 200-320 | 0.54 | 0.05 | HPLC | 65% | 48 |
| F & others | H ₃ PO ₄ and acetic (homogeneous) | H ₂ O | 240 | 0.09 | 250 g/h Flow reactor | EtOAc & LGC | 40% | 49 |
| F | DOWEX 50WX8-100 | Acetone-DMSO | 150 2MPa N ₂ | 1.0 | 0.2 | HPLC | 82% | 50 |
| F&G | Amberlyst-15 hydrotalcite | DMF | 100 | 1.0 | 0.1 | HPLC | 73% (F) 42%(G) | 26 |
| F | FePW ₁₂ O ₄₀ | DMSO | 120 | 0.07 | 0.31 | HPLC | 97% | 51 |
| F | [NMM]+[CH ₃ SO ₃]- | DMF-LiBr | 90 | 0.104 | 1 | EtOAc | 75% | 1 |
| F&G | Nb ₂ O ₅ -nH ₂ O | Butanol-H ₂ O | 160 | 0.08 | 1.2 | HPLC | 89% | 52 |
| F,G & other | SbCl ₃ (homogeneous) | THF-H ₂ O | 120 | 0.1 | 1 | EtOAc | 84 | 53 |
| F | Cr-HA-Fe ₂ O ₃ | DMSO | 120 | 0.56 | 0.18 | HPLC | 89% | 54 |
| F | CPL-HSO ₄ +metal halide | PGME+H ₂ O | 105 | 1.5g/8.6 mmol | 1.5 | EtOAc | 81% | 55 |
| F | MLC-SO ₃ H | DMSO | 130 | 0.5 | 0.1 | HPLC | 81% | 56 |
| F | TPA on Ta ₂ O ₅ | DMSO | 120 | 0.14 | 0.36 | HPLC | 85% | 57 |
| F | HO ₂ CMMImCl | Propan-2-ol | 110 | 1.0 | 0.1 | HPLC | 91% | 58 |
| F | ZrO ₂ -SO ₄ TiO ₂ -SiO ₂ -SO ₄ | DMSO | 110 | 0.83 | 0.6 | HPLC | 100% | 59 |
| F&G | ZrO ₂ , TiO ₂ | H ₂ O | 200 | 0.5 | 0.1 | HPLC | 38%(F) | 34 |
| G | SO ₄ ²⁻ /ZrO ₂ and SO ₄ ²⁻ /ZrO ₂ -Al ₂ O ₃ | DMSO | 130 | 0.4 | 0.045 | Et ₂ O | 48% | 60 |
| F | ZrO ₂ -SO ₄ | Acetone- DMSO | 180 2MPa N ₂ | 0.2 | 0.1 | HPLC | 73% | 34 |
| F&G | ZrO ₂ -SO ₄ | H ₂ O | 100 | 1.0 | 0.1 | HPLC | 20% | 61 |
| F&G | Porous ZrO ₂ -SO ₄ | H ₂ O | 100 | 1.0 | 0.1 | HPLC | - | 62 |
| F | Cellulose -SO ₄ | DMSO | 100 | 0.28 | 0.18 | Centrifuge +HPLC | 94% | 63 |
| G | CrCl ₃ ·6H ₂ O | TEAC | 130 | 0.1 | 1.0 | UV-Vis | 71% | 35 |
| F | CrCl ₃ ·6H ₂ O, H ₂ SO ₄ | [EMIM][HSO ₄] | 100 | 0.1 | 1.0 | HPLC | 88% | 40 |

| | | | | | | | | |
|----------------|--|---|-----|---------------------|-------|-----------------------|---------------------------|-----------|
| F | CrCl ₃ ·6H ₂ O | [C ₄ C ₁ IM][HSO ₄] | 100 | 0.1 | 1.0 | NMR | 96 | 64 |
| F | HMIM ₄ Cl- | [HMIM]Cl- | 90 | 2.8 (incs. solvent) | 0.13 | Et ₂ O | 92% | 11 |
| F&G | NHC-CrCl ₂ | [BMIM]Cl | 100 | 0.06 | 0.1 | Et ₂ O | 99%(F) 81%(G) | 65 |
| F,G, others | H ₂ SO ₄ (homogeneous) | [BMIM]Cl | 120 | 0.07 | 1.0 | HPLC | 98% | 66 |
| G | 12-MPA | Imidazolium ionic liquid | 120 | 0.1 | 0.18 | EtOAc | 100% | 24 |
| F&G | CrCl ₃ or H ₂ SO ₄ | Imidazolium ionic liquid | 100 | 0.054 | 0.5 | HPLC | 75% (F) 67% (G @120°C) | 8 |
| F&G | IrCl ₃ , CrCl ₃ | [OMIM]Cl | 180 | 0.08/0.04 | 0.48 | Vacuum reactive dist. | 93%(F), 88%(G) | 67 |
| F,G, others | IrCl ₃ / AuCl ₃ ·HCl | [BMIM]Cl [Et ₃ NH][HSO ₄] | 120 | 0.11 | 0.2 | HPLC | 89% | 68 |
| F | AlCl ₃ +acids | [BMIM]Cl +DMF | 120 | 0.34 | 125 | Dist | 93% | 69 |
| F | Pd/Si,Ru/Si + acids + light | DMSO/H ₂ O | 80 | 1 | 0.040 | HPLC | 97% | 70 |
| F | H ₃ PW ₁₂ O ₄₀ | [BMIM]Cl | 80 | 0.57 | 0.5 | HPLC | 99% | 71 |
| G | CrCl ₂ | [EMIM]Cl | 100 | 0.6 | 1.0 | HPLC | 70% | 41 |
| F | (NH ₄) ₂ S ₂ O ₃ (homogeneous) | [BMIM]Cl | 130 | 0.5 | 0.1 | HPLC | 82% | 72 |
| F | ZrO ₂ -SO ₄ | [BMIM]Cl | 100 | 0.4 | 0.05 | EtOAc | 88% | 18 |
| F & others | Amberlyst-15 | TEAB/TPAB | 100 | 0.1 | 20 | Crsytallization | 97% | 30 |
| F | Amberlyst-15 | BMIM ⁺ BF ₄ ⁻ BMIM ⁺ PF ₆ ⁻ +DMSO | 80 | 2.0 | 0.07 | HPLC | 87% | 73 |
| F&G | ZrO ₂ -SO ₄ | [BMIM]Cl | 180 | 0.1 | 5.0 | Vacuum distillation | 82%(F) 65%(G) | This work |

Table 1. Summary of key developments in catalytic dehydrogenation of fructose and glucose to give 5-HMF. The use of ionic liquids can also be treated homogeneous systems unless a heterogeneous catalyst is present. (MIBK methyl isobutyl ketone; DMSO dimethyl sulfoxide; EtOAc ethyl acetate; [BMIM]Cl 1-butyl-3-methylimidazolium chloride; PGME propylene glycol methyl ether; DMF dimethyl formamide; [OMIM]Cl 1-methyl-3-octyl imidazolium chloride); TEAB, TPAB tetraethyl- and tetrapropyl ammonium bromide. CPL caprolactam; HA hydroxyapatite; NMM N-methylmorpholinium; TPA tungstophosphoric acid; MLC magnetic lignin-derived amorphous carbon; NHC N-heterocyclic carbene; MPA 12-molybdophosphoric acid.

2. MATERIALS AND METHODS

2.1 Materials

Glucose (99.5%), fructose (99.5%), 1-butyl-3-methylimidazolium chloride [BMIM]Cl (98%), zirconium hydroxide (99.5%) and 5-hydroxymethylfurfural (99%) were purchased from Sigma-Aldrich. All chemicals were used as received. All ¹H and ¹³C NMR were recorded in CDCl₃ using a Bruker AMX 300 MHz spectrometer and data were processed by ACD/NMR Processor (Academic Edition). All XRD data were collected using a Siemens D500 X-Ray diffractometer using Cu K_{α1} radiation with wavelength of 0.154056 nm. The diffractometer was operated at 40 kV and 30 mA from 10 to 80° of 2θ in 0.05° steps at 6 seconds per step. FTIR spectra were obtained 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 cm^{-1} [41, 74].

2.2 Synthesis of sulfated zirconia

SZ ($\text{SO}_4^{2-}/\text{ZrO}_2$) was prepared according to the method described by Qi *et al.* [18, 75]. Thus 1 g of zirconium hydroxide was dissolved in 10 mL of 1 M H_2SO_4 and stirred vigorously at room temperature for 3 h. The suspension was centrifuged (Heraeus Biofuge Primo at 3000 rpm for 15 min.) and the supernatant was discarded. The sediment was dried under vacuum at 60 °C overnight. It was ground into a fine powder using a pestle and mortar, and calcined at 500 °C in a muffle furnace for 3 h. The catalyst was characterised by XRD and FT-IR.

2.3 Dehydration of glucose

Glucose (5.0 g, 0.028 mol) and [BMIM]Cl (20.0 g, 0.11 mol) were heated in an oil bath at 120 °C and stirred for 5 min. The reaction was started by adding one of the following catalysts: $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (0.74 g, 2.8 mmol), ZrO_2 , (0.35 g, 10 mol%) or $\text{SO}_4^{2-}/\text{ZrO}_2$ (0.8 g, 10 mol%). After completion of the reaction, 5-HMF was collected by vacuum distillation at 180 °C, 2.7 kPa (20 mm Hg) using N_2 as an entrainer. The same procedure was used for fructose. Isolated yields are detailed throughout the results and discussion section. ^1H NMR data for 5-HMF (300 MHz; CDCl_3) δ 9.57 (1H, s, CHO), 7.22 (1H, d, $J = 4.5$ Hz, 3-H), 6.50 (1H, d, $J = 4.5$ 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.

3. RESULTS AND DISCUSSION

3.1 Characterization of sulfated zirconia

XRD was used to measure phase purity of zirconia with and without sulfuric acid treatment. In general, zirconia undergoes a tetragonal to monoclinic transformation around 1170 °C but in fine powders, surface effects preserve the tetragonal phase below this temperature. Figure 1 shows that without sulfation, monoclinic is the major phase and, using the (111) peaks, it is possible to calculate [76] the monoclinic fraction as ~70%. Sulfate treatment of zirconia reversed this composition and the tetragonal phase was present at 70%. Similar XRD traces were obtained by Qi *et al.* [18] who also found that sulphate treatment stabilised tetragonal and obtained nearly fully tetragonal zirconia.

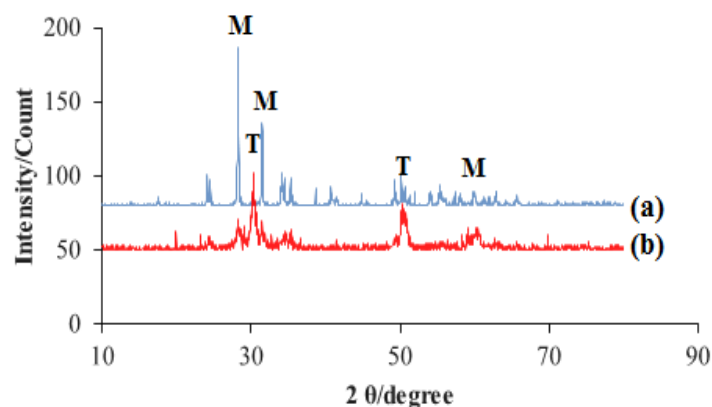


Figure 1. XRD patterns of (a) ZrO_2 (b) $\text{SO}_4^{2-}/\text{ZrO}_2$ (M and T designate monoclinic and tetragonal phases).

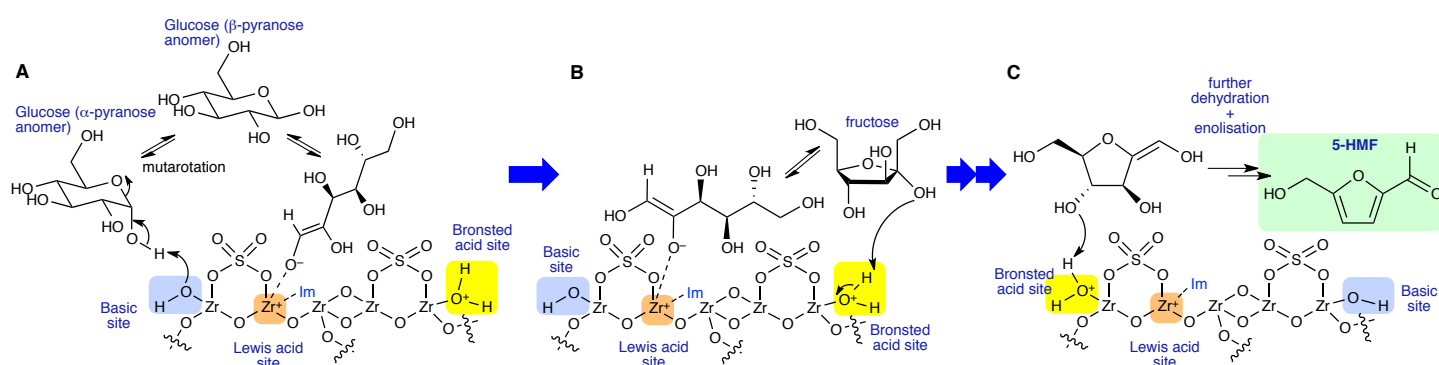
3.2 Dehydration of glucose/fructose and separation

Almost all reported literature on the synthesis of 5-HMF is based on solvent extraction [9, 18, 19, 35, 50, 75]: only one paper reported the separation of 5-HMF under vacuum distillation conditions [67]. To emphasize the applicability of the method, in particular because many methods reported are on a small scale with analysis via HPLC or GC conversion yields, in this work all reactions were performed on a 5 g scale and yields reported are for isolated 5-HMF obtained by vacuum distillation, the envisaged goal being a continuous reactor. The dehydration of glucose and fructose were therefore investigated using a reactive vacuum distillation approach to provide an avenue whereby the production of 5-HMF is accompanied by separation with the minimal use of volatile solvents. The boiling point of 5-HMF is 292 °C at atmospheric pressure but 114 -116 °C at 130 Pa [67] so a reactive vacuum distillation procedure involving concurrent chemical reaction and product separation steps within a single unit should be possible for production of 5-HMF from glucose and fructose dehydration. Reactive distillation can have a wide range of industrial applications [77-79] and would make continuous operation possible. The vapour pressure of 5-HMF measured by a transpiration method is available for the temperature range 313-368 K [80] to guide the vacuum distillation system. The deviation from Raoultian behaviour is needed for each ionic liquid used. The particular value of reactive vacuum distillation is that it avoids the costs and disposal issues/recovery methods required with solvent extraction.

3.3 5-HMF yields from dehydration of glucose and fructose

Ionic liquids have played a prominent part in carbohydrate chemistry for over 15 years as reviewed by Murugesan and Linhardt [81] who demonstrate a bibliometric transition in 2001. Here, the results of the dehydration of glucose and fructose conducted under vacuum at 180 °C in [BMIM]Cl IL solvent with 10 mol % of the catalysts, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, ZrO_2 and $\text{SO}_4^{2-}/\text{ZrO}_2$ designated as Cr (III), Z and SZ respectively, are presented in Figure 2. Water was used as solvent in a control reaction and no 5-HMF was obtained. The synthesised 5-HMF was characterised by IR and NMR spectroscopies and was identical to previous data reported [67]. Higher yields (82%, 75% and 55%) of 5-HMF were obtained using fructose as a substrate compared to glucose with catalysts SZ, Cr (III) and Z, respectively. The lower yields when using glucose may be as a result of the glucose non-cyclic and pyranose ratio (63% β -glucopyranose and 37% α -glucopyranose) in water and hence, the enolisation rates may be slower [27]. Fructose and glucose are reported

to exhibit different reaction mechanisms to form 5-HMF as glucose isomerizes to fructose [82] and this might also account for the lower yield of 5-HMF from glucose and has been noted elsewhere [76]. A proposed overview of the mechanism, in which for clarity not every step is included, is indicated in Scheme 1. It highlights the role of SZ and [BMIM]Cl where they can catalyse the mutarotation, ring opening and isomerisation of glucose to fructose which is then dehydrated to 5-HMF [7, 41]. The bifunctional catalytic surface possessing basic and acidic site [5] and complexation of Zr^{4+} (or Cr^{3+} when using Cr(III)) to the imidazolium ring of BMIM) can account for the high conversion levels observed and is consistent with other reports [41,59].



Scheme 1. Proposed overview of the mechanism for the formation of 5-HMF from glucose and fructose. Im represents the BMIM imidazolium ring. **A)** Mutarotation of α -anomer of glucose in SZ and [BMIM]Cl and isomerisation to the enolate; **B)** Tautomerisation of the enolate and isomerisation to fructose. **C)** Dehydration and enolisation at the acid sites [41,61]

The amount of 5-HMF generated from glucose (65%, 63% and 34%) using SZ, Z and Cr (III) catalysts in [BMIM]Cl solvent was higher in this work compared to 22%, 24% and 27% using the same solvent and catalysed by zeolite (H-ZMS-5) reported elsewhere [82]. Also the catalytic activity of SZ was compared to untreated Z catalyst and gave lower yields. Therefore, even though both catalysts are environmentally benign, SZ can more effectively catalyse the dehydration of glucose to 5-HMF compared to zeolite. This increased catalytic activity of SZ may be attributed to the increased acid sites of SZ in comparison to Z. Overall, SZ exhibited strong catalytic activity (Figure 2) giving almost 80% and 65% yields from fructose and glucose substrates.

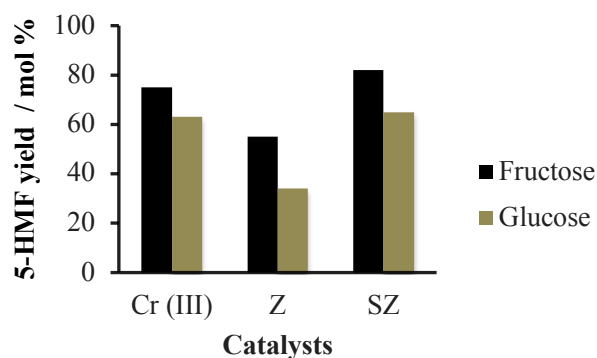


Figure 2. Catalytic activity of the solid catalysts: isolated yield after 2 hours at 180 °C in [BMIM]Cl solvent. (Conditions: Glucose = 5.0 g (0.028 mol), fructose = 5.0 g (0.028 mol), Z = 0.35 g (0.0028 mol), SZ = 0.8 g, (0.0028 mol) and Cr (III) = 0.74 g (0.0028 mol).

3.4 5-HMF formation in other ionic liquids

In order to optimise the 5-HMF yield, other ionic liquids; 1-hexyl-3-methylimidazolium chloride [HMIM]Cl and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate [BDMIM]PF₆ were tested with SZ. The results are compared to those obtained when using [BMIM]Cl ionic liquid in Figure 3; [BMIM]Cl clearly produced 5-HMF in higher yields. Nevertheless, [BMIM]Cl and [HMIM]Cl both provided significant yields of 5-HMF for both substrates and this may be due to the fact that the chloride ions form only weak ion pairs [83] which leads more readily to the isomerization of carbohydrates [39] and the subsequent dehydration process. Furthermore, as a result of the weak coordination of the ionic liquid structures, they do not compete with the sugars for the binding of metal chlorides; therefore it is more likely that a sugar-metal coordination complex will be formed [84].

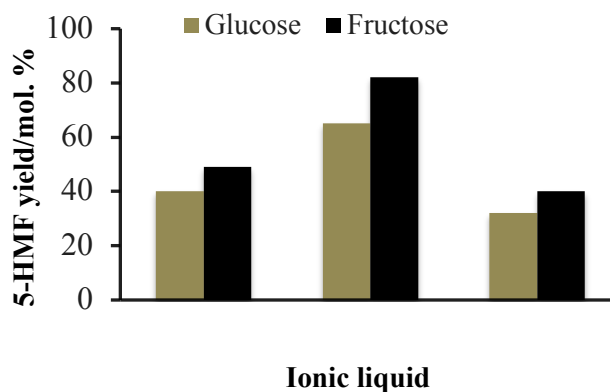


Figure 3. 5-HMF yields in ionic liquids after 2 hours at 180 °C with sulphated zirconia catalyst. (Conditions: Glucose = 5.0 g (0.028 mol), fructose = 5.0 g (0.028 mol), Z = 0.35g (0.0028 mol), SZ = 0.8 g, (0.0028 mol) and Cr (III) = 0.74 g (0.0028 mol)

3.5 Effect of reaction temperature with time on 5-HMF yield

The combined effect of reaction temperature and time on the 5-HMF yield in the dehydration of fructose catalysed by SZ using [BMIM]Cl solvent was investigated at 100 °C, 120 °C, 150 °C and 180 °C. As shown in Figure 4, these

reaction temperatures have a significant effect on the 5-HMF yield. At 100 °C, a lower yield (18%) was obtained after 2 h and at 180 °C a maximum isolated yield of 82% was obtained after the same time of 2 h. The yield increased over time up to 120 minutes and beyond this, a decrease was observed in these temperature regimes. These results indicate that the degradation of 5-HMF was significant at higher reaction times even though an increased reaction temperature enhances the reaction initially: the degradation of 5-HMF has been noted elsewhere in the presence of ILs [22, 28, 85]. Furthermore, it has been observed that [BMIM]Cl can react with aldehyde functional groups [86] and this decrease in yield might also be due to side products formed from the reaction between 5-HMF and [BMIM]Cl as previously described [87]. It can be argued that high yields are obtained with sulphated zirconia solid catalysts at lower temperatures such as 110 °C in DMSO as solvent [59] but even high boiling point organic solvents such as DMSO make it more difficult to use reactive vacuum distillation as a separation stage.

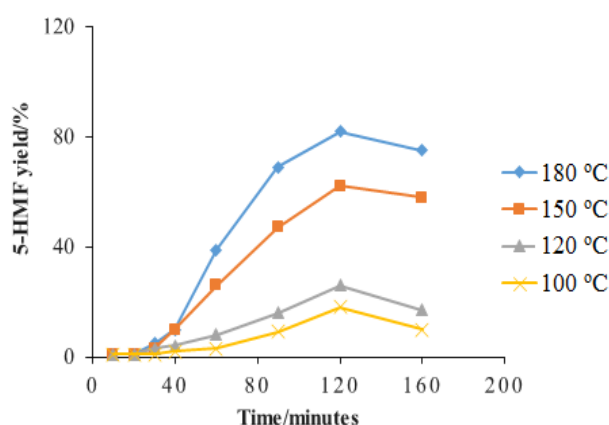


Figure 4. Effect of reaction temperature and time on 5-HMF yield for fructose as substrate with sulfated zirconia catalyst in 20.0 g [BMIM]Cl solvent. [67] (Conditions: Glucose = 5.0 g (0.028 mol), fructose = 5.0 g (0.028 mol), Z = 0.35 g (0.0028 mol), SZ = 0.8 g, (0.0028 mol) and Cr (III) = 0.74 g (0.0028 mol).

3.6. Effect of catalyst dosage on 5-HMF synthesis

The effect of catalyst dosage on 5-HMF synthesis using fructose and glucose in [BMIM]Cl and SZ catalyst at 180 °C is presented in Figure 5 using conditions where the highest yield of 5-HMF was obtained (Figure 4). When the catalyst dosage was increased from 0.09 g (2.5 mol %) to 0.35 g (10 mol%), the yield of 5-HMF increased, from 22% to 82% with fructose as substrate and 16% to 65% when using glucose as substrate. However, when the amount of the SZ was increased from 0.35 g (10 mol%) to 1.5 g (30 mol%), there was a decrease in the 5-HMF yield with both fructose and glucose as substrates. When no catalyst was used the yields were 1-2%. Therefore, 10 mol % of catalyst was selected as the optimal amount of catalyst required.

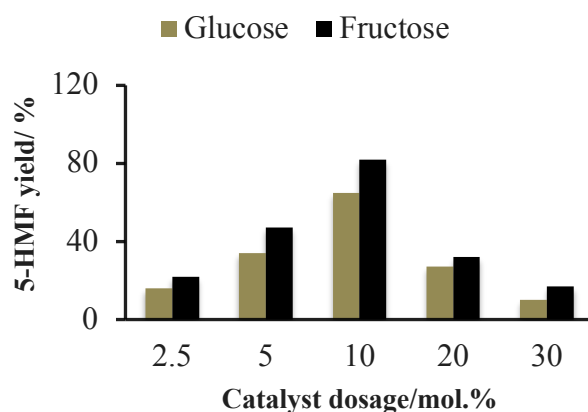


Figure 5. Effect of SZ catalyst dosage on 5-HMF yield after 2 hours at 180 °C in [BMIM]Cl solvent. (Conditions: Glucose = 5.0 g (0.028 mol), fructose = 5.0 g (0.028 mol), Z=0.35 g (0.0028 mol), SZ = 0.8 g, (0.0028 mol) and Cr (III) = 0.74 g (0.0028 mol)

3.7 Sulfated zirconia and [BMIM]Cl recycling

The recycling of catalysts and solvents is an essential principle of green engineering [88] and may be decisive in determining economic viability of a process. The recycling of SZ catalyst and [BMIM]Cl ionic liquid is presented in Figure 6 which shows that the recycled catalyst and ionic liquid gave comparable results with respect to 5-HMF isolated yields obtained, retaining very high activity up to the third cycle and tending to lose activity slightly from fourth to fifth cycle. In this process, the catalyst remained in the reaction flask with the ionic liquid and was not washed between cycles. The aim is ultimately for a continuous process. As the reaction proceeded, products were collected and more substrate added at intervals: the catalyst was reused in that manner for five consecutive cycles. The loss of yield over this period might be due to the retention of some 5-HMF or unreacted substrates in these cycles. Certainly it is possible to conceive a semi-continuous process in which the solid catalyst is filtered off and washed for subsequent reuse after several cycles in the manner described here.

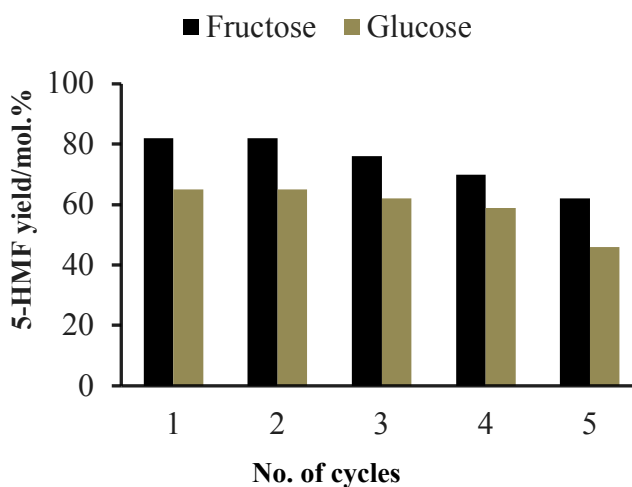


Figure 6. Recycling of sulfated zirconia and [BMIM]Cl. (Conditions: Glucose = 5.0 g (0.028 mol), fructose = 5.0 g (0.028 mol), Z=0.35 g (0.0028 mol), SZ = 0.8 g,(0.0028 mol) and Cr (III) = 0.74 g (0.0028 mol)

CONCLUSIONS

Sulfated zirconia solid catalyst was synthesised by treating zirconium hydroxide with H₂SO₄ and used in the conversion of glucose which itself can be derived from cassava to 5-HMF in ionic liquids. This catalyst (give catalyst loading) was shown to have a higher activity than CrCl₃.6H₂O which presents issues of toxicity producing a 5-HMF yield of 82% from fructose and 65% from glucose at 180 °C for a 2 h reaction time via reactive vacuum distillation. This is the first time that a heterogeneous catalyst has been used with ILs with reactive distillation for this application. The reactions were performed on 5 g scale to demonstrate the feasibility of carrying out larger scale preparations and product isolation. The ionic liquid and the catalyst could be recycled up to 6 times without significant loss of catalytic activity. The solid catalyst can be filtered and in operation might be supported. This integrated ionic liquid heterogeneous catalyst method with simultaneous product isolation 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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