



Original Research Paper

Efficient Conversion of Carbohydrates to 5-Hydroxymethylfurfural (HMF) Using ZrCl₄ Catalyst in Nitromethane

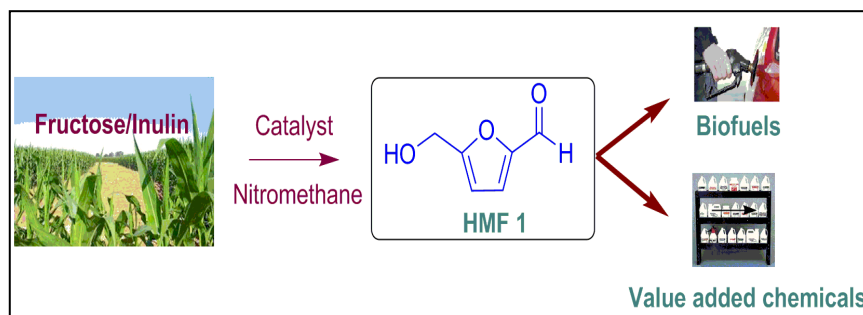
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HIGHLIGHTS

- A promising process for 5-Hydroxymethyl furfural (HMF) formation from biomass.
- Efficient synthesis HMF from carbohydrates by ZrCl₄ in nitromethane
- Fructose and inulin led to highest HMF yield of > 70% with 100% selectivity

GRAPHICAL ABSTRACT



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ABSTRACT

Solvent nitromethane along with a variety of metal chloride and mineral acids as catalyst were studied for the synthesis of 5-Hydroxymethylfurfural (HMF), a key precursor in the formation of alternative fuel 2,5-dimethylfuran (DMF) and other value added chemicals. Reaction time, temperature and catalyst concentration were also systematically studied to achieve highest HMF formation. Among the carbohydrates studied for HMF synthesis, D-fructose and inulin were found particularly most productive yielding >70% and with 100% selectivity using ZrCl₄ in nitromethane at 100 °C during 3h. Readily available reagents, solvents, and simple reaction conditions could mark this process promising for HMF formation from biomass.

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1. Introduction

Non renewable fossil sources such as natural gas, oil and coal meet around 85% of the world's energy demands today. With increase in world's population, there are growing concerns about diminishing fossil fuel resources, global warming, and environmental pollution; hence, there is a

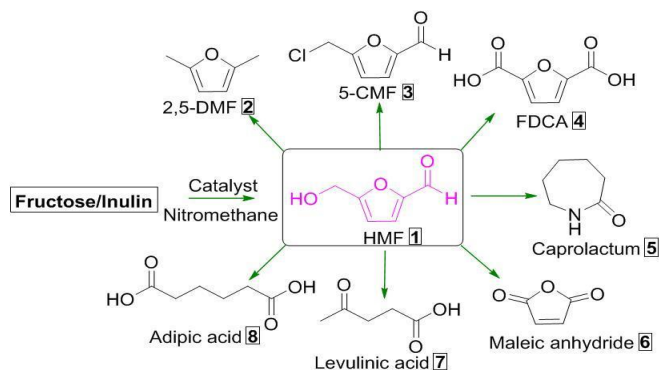
need to search for renewable resources to bridge the gap between the supply and demand of energy and chemicals. In this respect, biomass is the only widespread, abundant, inexpensive, and sustainable resource which can be an ideal substitute for fossil-based resources. Carbohydrates comprise about 75% of the annual renewable biomass (Roper., 2007). Hence, there is need to

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develop efficient and environmentally and ecofriendly methods to convert carbohydrates into useful chemicals e.g. alternative fuels.

5-Hydroxymethylfurfural (HMF) is a valuable biomass-derived platform chemical. HMF is a versatile intermediate between biomass-based carbohydrate chemistry and petroleum-based organic chemistry. HMF and its derivatives could replace petroleum-based building blocks and could also be used to make polymers and valuable chemicals (Sutton et al., 2013). As presented in Figure 1, HMF can be a common intermediate for 2,5-dimethyl furan (DMF), which is proposed to be an alternative for petroleum-based liquid fuels (Román-Leshkov et al., 2007). It also could be used for the production of 5-chloromethylfurfural, a precursor to 5-ethoxymethylfurfural (potential bio-diesel candidate) (Mascal and Nikitin, 2008), 2,5-furan dicarboxylic acid (FDCA) (Pan et al., 2013), caprolactum (Buntara et al., 2011), maleic anhydride (Du et al., 2011), levulinic acid (Alonso et al., 2013), adipic acid (Arias et al., 2013) and many other value added chemicals (Huber et al., 2005).



Scheme 1. HMF serves a key precursor for a number of fuels and value-added chemicals. 1: HMF; 2: 2,5-dimethyl furan (DMF); 3: 5-chloromethylfurfural (CMF); 4: 2,5-furan dicarboxylic acid (FDCA); 5: Caprolactum; 6: Maleic anhydride; 7: Levulinic acid and 8: Adipic acid.

As for HMF production, achieving a high yielding and highly selective process is still a challenge. In fact, high production cost currently limits the availability and use of HMF industrially. Hence the challenge faced by chemists/engineers is to develop an economically feasible process for synthesis of HMF from biomass. To date, numbers of methods have been developed for synthesis of HMF from various sustainable reactants (Yang et al., 2011). As reported in the literature, many acidic catalysts have been used for the HMF synthesis from D-fructose. Homogeneous acids such as HCl (Román-Leshkov et al., 2006) and H₂SO₄ (Binder et al., 2009) were used to catalyze the dehydration of D-fructose which resulted in 40–85% yield of HMF in solvents like dimethyl sulfoxide (DMSO), dimethylacetamide (DMA), and 2,5-dimethylfuran (DMF). Solvent systems studied for dehydration of D-fructose include organic solvents (DMSO, DMF, DMA, Sulfolane, γ -Valerolactone (GVL) (Van Putten et al., 2013), ionic liquids (Zhao et al., 2007), aqueous systems (Rosatella et al., 2011), nitromethane-water system (Karimi and Mirzaei, 2013) and biphasic mixtures (Pagan-Torres et al., 2012). The high boiling point and the instability of DMF, DMSO, DMA solvents at high temperatures limits their use in synthesis of HMF. Raines and co-workers (Caes and Raines, 2011) reported sulfolane as a solvent for synthesis of HMF, while recently Dumesic and co-workers reported GVL as a solvent for synthesis of HMF (Gallo et al., 2013). Ionic liquids are also used extensively in synthesis of HMF, but they suffer drawbacks of being expensive and are deactivated in presence of small amounts of water. Use of aqueous systems favor formation of more by-products i.e., decomposition of HMF to levulinic acid and formic acid (Girisuta et al., 2006). Biphasic mixtures are hard to handle for separation. The fact still remains that for the production of HMF to be made commercial for the purpose of biofuel production, economic and readily available

solvents, as well as economic acid catalysts (capable of quick conversions of D-fructose to HMF with limited side reactions leading to HMF degradation) are to be addressed.

From this point of view, we strived to use nitromethane as solvent and metal chlorides/mineral acids as catalyst as a superior combination for HMF formation from biomass. Nitromethane is polar, protic (bp. 101 °C) solvent and is used in variety of industrial applications (Deshpande et al., 1998). The lower boiling point serves as an additional advantage leading to its easy removal from the reaction medium. Nitromethane is found stable at higher temperatures and acidic conditions. Herein, we report the formation of HMF from D-fructose in high yields using the combination of an efficient solvent; nitromethane in presence of different acid catalysts.

2. Experimental

2.1. Materials

D-Fructose, D-glucose, starch, sucrose and inulin were purchased from Sigma Aldrich Chemicals. Metal chlorides, acids, and nitromethane were purchased from a local manufacturer. 5-Hydroxymethylfurfural (99%) was purchased from Aldrich Chemicals and was used establishing the calibration curve. 5-Chloromethylfurfural was synthesized based on the literature suggested by Kumari et al. (2011).

2.2. Experimental procedure

In a typical reaction protocol for the dehydration of carbohydrates, a 10 wt% carbohydrate/nitromethane solution containing carbohydrates (1 g) was charged into a 50 mL flask, followed by the addition of 3 different concentrations (10, 50 and 100 mol%) of different catalysts. The carbohydrates investigated included D-fructose, starch, sucrose, inulin, glucose, and cellulose. The catalyst investigated included chlorides (i.e. ZrCl₄, SnCl₂, CrCl₃, FeCl₃, BiCl₃, CuCl₂, CaCl₂, CeCl₃, MgCl₂, LaCl₃.7H₂O, HgCl₂, NH₄Cl, ZnCl₂, AlCl₃, CrCl₂, SnCl₂.2H₂O, CoCl₂.6H₂O, LiCl.Anh, CuCl, BaCl₂.2H₂O, NiCl₂, TiCl₄, ZrO₂Cl₂, and RuCl₃) and mineral (HCl, HBr, H₂SO₄, TFA, and H₃PO₄) acid catalysts. The reaction was then heated at different temperatures (60, 80 and 100 °C) for a specific time (1-5 h, with measurements performed in 30 min intervals), while stirred with a magnetic stirrer. The reaction mixtures were diluted with a known mass of deionized water, stirred for 5 min to remove any insoluble products and were analyzed to determine the amounts of HMF and CMF by a gas chromatography (Agilent 6890N) equipped with a HP-5 5% phenyl methyl column (I.D: 320 mm, length 30 m, film thickness 1 mm) and a flame ionisation detector (280 °C max.). Furfuraldehyde was used as the internal standard. The temperature was initially set at 100 °C (1 min) and was then increased with a rate of 20 °C/min (10 min) upto 280 °C. Moreover, different carbohydrate sources including starch, sucrose, inulin, glucose and cellulose were investigated using the most efficient catalyst.

3. Results and Discussion

A variety of acid catalysts for HMF formation from D-fructose in solvent nitromethane was investigated and the reaction conditions i.e. reaction time, temperature and catalyst concentration were optimized. In fact, reaction time and temperature are very crucial factors for HMF formation for under un-optimized conditions, HMF decomposition occurs. It was observed that for all the catalysts investigated the reaction proceeded at lower rates at 60 and 80 °C in comparison with that of 100 °C. Figures 2 presents the effect of temperature and time on the rate of reaction or in another word, HMF yield in presence of D- Fructose using ZrCl₄ as catalyst.

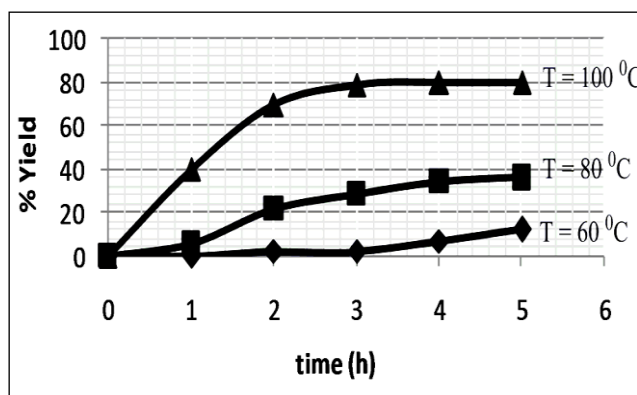


Figure 2. HMF formation from D- Fructose using ZrCl₄ as catalyst at different temperatures.

The catalyst concentration resulting in maximal HMF formation was also investigated. Catalyst concentration of 10 mol% was shown to lead to the highest HMF yield for all the catalysts tested i.e. both the chlorides and mineral acid catalysts. As an example, Figure 3 compares the impact of catalyst concentration on HMF yield in case of CrCl₃ as catalyst. As shown, the HMF yield is negatively correlated with catalyst concentration. More specifically, it was found that by increasing the concentration of catalysts, HMF yield decreased while CMF concentration increased and also the formation of some by-products was detected. Hence, to achieve highest HMF yields, catalyst concentration of 10 mol% was found. The same trend was also observed for all the catalysts investigated (data not shown).

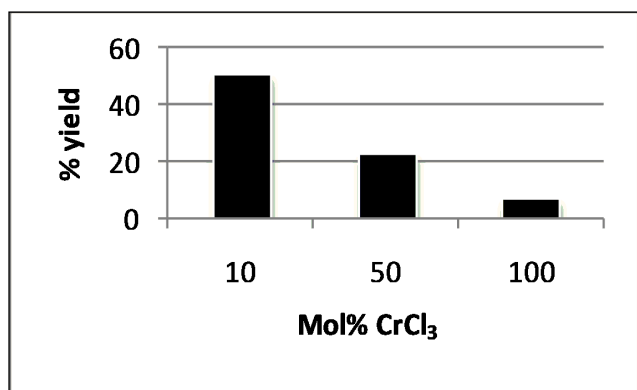


Fig.3. HMF formation from D- Fructose using CrCl₃ as catalyst at different catalyst concentration (Mol%).

As for time, HMF formation reached its maximum value after 3 and 1.5 h for metal chloride and mineral acid catalysts, respectively. Tables 1 and 2, tabulates HMF and CMF yields from D-Fructose (10 wt %) in presence of chloride and mineral acid catalysts under optimal conditions, respectively

Among the chloride catalysts investigated, ZrCl₄ resulted in highest HMF yield of 82% with 100% selectivity of HMF. This catalyst was followed by CeCl₃ which achieved an HMF yield of 73% ZrCl₄. The same order was also obtained when HMF was isolated and yields were compared with ZrCl₄ and CeCl₃ ranking first and second (73 and 65% HMF yield). RuCl₃ also yielded moderately at about 53% (GC-based yield) and 48% (after isolation) with 100% selectivity but it was advantageous for only traces of levulinic acid and formic acid were formed during the reaction. As shown in Table 1. HMF isolation was only performed when GC-based HMF yield was above 15%.

Table 1. HMF synthesis from D-Fructose (10 wt %) using metal chlorides as catalyst in nitromethane.

No.	Catalyst Type ^a	HMF yield (%) ^b	CMF yield (%) ^b	HMF yield (%) ^c
1	ZrCl ₄	82	-	73
2	SnCl ₂	15	-	-
3	CrCl ₃	55	5	43
4	FeCl ₃	7	-	-
5	BiCl ₃	3	-	-
6	CuCl ₂	56	10	44
7	CaCl ₂	0	-	-
8	CeCl ₃	73	6	65
9	MgCl ₂	3	-	-
10	LaCl ₃ ·7H ₂ O	10	-	-
11	HgCl ₂	6	-	-
12	NH ₄ Cl	15	-	-
13	ZnCl ₂	0	-	-
14	AlCl ₃	26	-	18
15	CrCl ₂	25	3	20
16	SnCl ₂ ·2H ₂ O	6	-	-
17	CoCl ₂ ·6H ₂ O	4	-	-
18	LiCl·Anh	0	-	-
19	CuCl	8	-	-
20	BaCl ₂ ·2H ₂ O	0	-	-
21	NiCl ₂	19	-	11
22	TiCl ₄	39	21	13
23	ZrO ₂ Cl ₂	56	6	44
24	RuCl ₃	53	-	48

^a Catalyst concentration was set at the optimum value of 10 mol.%.

(Optimum reaction time and temperature were at 3 h and 100 °C, respectively)

^b Yields are based on GC analysis.

^c Isolated yields.

Table 2. HMF synthesis from D-Fructose (10 wt %) using mineral acids catalysts in nitromethane.

No.	Catalyst Type ^a	HMF yield (%) ^b	CMF yield (%) ^b	HMF yield (%) ^c
1	HCl	83	8	72
2	HBr	49	-	40
3	H ₂ SO ₄	80	7	70
4	TFA	10	-	-
5	H ₃ PO ₄	64	-	56

^a Catalyst concentration was set at the optimum value of 10 mol.%.

(Optimum reaction time and temperature were at 1.5 h and 100 °C, respectively)

^b Yields are based on GC analysis.

^c Isolated Yields.

As for mineral acid-catalyzed conversion of D-fructose into HMF in nitromethane solvent, the optimal conditions were determined as 100 °C and 90 min reaction time. As tabulated in Table 2, under the optimized conditions, HCl and H₂SO₄ led to the highest yields of about 72% and 70%, respectively. Moreover, they resulted in the formation of only small traces of levulinic acid, formic acids, and other by-products during the reaction. To achieve further improvements in HMF yield, different combinations of metal chlorides, and also combinations of metal chlorides and mineral acids were also studied. More specifically, the catalysts which highest yield and selectivity were considered in the combination experiments. But no significant increase in yields of HMF was observed (Table 3).

Table 3.

HMF synthesis from D-Fructose (10 wt %) using various combination patterns of metal chlorides catalysts as well as metal chlorides/mineral acids as catalyst in Nitromethane.

No. ^a	catalyst (1:1)	HMF yield (%) ^a
1	ZrCl ₄ /CrCl ₃	70
2	ZrCl ₄ /CeCl ₃	74
3	CrCl ₃ /CeCl ₃	65
4	ZrCl ₄ .H ₂ SO ₄	76
5	CeCl ₃ .H ₂ SO ₄	68

^a Catalyst concentration was set at the optimum value of 10 mol.% (Optimum reaction time and temperature were at 3 h and 100 °C, respectively)

Having achieved efficient synthesis of HMF from D-fructose, different carbohydrates which could be obtained from biomass i.e. starch, sucrose, inulin, glucose, and cellulose were also investigated for HMF production.

Since, the combination of ZrCl₄ catalyst in nitromethane as solvent was proven to result in the maximum yield and selectivity in HMF formation from D-fructose, hence, the other carbohydrates were also reacted under the same conditions with ZrCl₄ as catalyst in nitromethane as solvent (Table 4). Inulin which is a constituent of biomass led to the highest HMF yield of about 85% (74% after isolation). Sucrose ranked second on the list producing about 14% HMF after isolation. Glucose and cellulose resulted in only traces of HMF formation. This could be ascribed to the fact that the conversion of cellulose into HMF requires the initial hydrolysis of the β-1,4 linkages present in cellulose to form glucose units. Moreover further glucose isomerisation to fructose is also needed. The hydrolysis and isomerisation processes were not found feasible using acid catalysts in nitromethane as solvent.

Table 4. HMF Synthesis from different sources of carbohydrates (10 wt %) using ZrCl₄ Catalyst in Nitromethane.

No. ^a	Carbohydrate	Time (h)	HMF yield (%) ^a	HMF yield (%) ^b
1	Starch	1.5	0	-
2	Sucrose	1.5	20	14
3	Inulin	1.5	85	74
4	Glucose	4	<1	-
5	Cellulose	4	<1	-

^a Catalyst concentration was set at the optimum value of 10 mol.% (Optimum reaction temperature was 100 °C)

4. Conclusion

In conclusion, we have demonstrated that ZrCl₄ and nitromethane is an excellent catalyst/solvent combination for conversion of D-fructose and inulin into HMF with yields standing at 73% and 74%, respectively, and with almost 100% selectivity. Finally, the inexpensive catalyst and solvent system, efficient and eco-friendly reaction conditions, and the easy procedure offered in the present study for the formation of HMF, seems like a promising strategy for the production of HMF as a key precursor in the formation of alternative fuel 2,5-dimethylfuran (DMF) and other value added chemicals from biomass.

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