Review Paper

Synthesis of 2, 5-Dimethyl Furan from Renewable Lignocellulosic Biomass

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ABSTRACT

Renewable biomass resources could reduce the dependency on the fossil fuels by conversion of its lignocellulose into bio-fuels and other valuable chemicals. Depolymerisation of lignocellulose, hydrolysis of cellulose to monomer glucose and its subsequent dehydration results 5-hydroxymethyl furfural (HMF). HMF is an important platform chemical for fuels and various other applications. The hydrogenation of HMF results 2, 5-dimethylfuran (DMF), which may be a biofuel with 40 per cent greater energy density than that of ethanol. The homogeneous catalytic method is preferred for lignocellulosic biomass conversion to cellulose, its hydrolysis and further dehydration to HMF. The Cu-Ru/C and related catalysts are preferred for hydrogenation of HMD to 2, 5-dimethylfuran. This review is an attempt to summarise the current research and developments in the field of lignocellulose derived HMF and further conversion to DMF as a potential biofuel.

Keywords: Bio-fuel; Lignocellulose; 2,5-Dimethylfuran; Hydroxymethyl furfural; Cellulose; Catalysts.

1. INTRODUCTION

The fossil fuel reserves of the world are limited to sustain modern effective civilisation. As per a recent estimate[1], in 2017, the global petroleum reserves is approximately 1700 billion barrel which is sufficient to meet global demand for next 50 years. The research and development is focused globally on alternative feedstock for fuels and industrial chemical. Lignocellulosic biomass obtained from agricultural and forestry waste and residue is a renewable option and that may serve as alternative feedstock to the fossils fuels. Generally, biomass is made up of three major components i.e. cellulose, hemicelluloses and lignin. Among these, cellulose is having potential to form chemicals and fuels. Cellulose is a straight chain polymer of glucose and depending upon the biomass its percentage usually ranges from 30 to 40 per cent. Carbohydrates may serve as feedstock for 5-hydroxymethyl furfural (HMF). Hydrogenation of HMF results 2, 5-dimethylfuran (DMF) which is a potential bio-fuels. DMF has an energy density 40 per cent greater than that of ethanol with boiling point 14 °C higher i.e. 92 °C in comparison to 78 °C of ethanol. It is also chemically stable, non-hygroscopic, less volatile and may be blended with gasoline.

2. HMF SYNTHESIS

The synthesis of HMF from cellulose involves three steps namely, hydrolysis of polymeric cellulose to monosaccharides,

followed by isomerisation of glucose to fructose and finally dehydrartion of fructose. The reaction step of hexoses sugar to 5-HMF followed by 2-5 DMF as illustrated in Fig. 1[2]. The HMF is a platform chemical for levulinic acid, 2,5-furandicarboxylic acid (FDA), 2,5-diformylfuran (DFF), dihydroxymethylfuran and 5-hydroxy-4-keto-2-pentenoic acid as depicted in Fig. 2[3]. Isolation of HMF from aqueous phase is complex process, since the distribution coefficient between the organic and the aqueous phase is not favourable. Zhang[4], *et al.* reported isolations of HMF by the use of organic solvents such as methyl isobutyl ketone, diethyl ether and acetone. Moreover, Musau and Munavu[5] reported that polar organic solvents, such as DMSO (dimethyl sulfoxide) or dimethyl formamide have a high boiling point. While Chheda[6], *et al.* studied the reactivity of HMF at high temperature distillation and found it to be undesirable. It has been possible to isolate HMF by extraction with a low-boiling point solvent in the presence of ionic liquids.

2.1 Synthesis of HMF using Homogeneous Catalyst

The dehydration of glucose was studied by Chheda[4], *et al.* with using HCl as catalyst in an aqueous phase with DMSO as co-solvent with extracting phase methyl isobutyl ketone resulting 53 per cent of HMF. In the same study, the best conditions were further achieved by adjusting the pH and adding DMSO during dehydration of glucose and other saccharides such as inulin (a polyfructan), starch (a polyglucan), cellobiose (a glucose dimer) and sucrose (a disaccharide of glucose and fructose). The main constraint with DMSO, the separation of HMF from
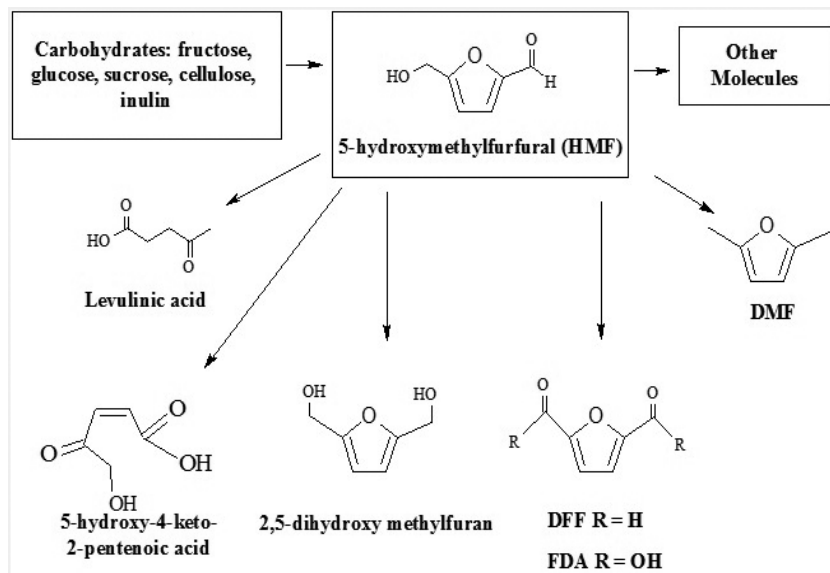
Figure 1. The reaction step of hexoses sugar to 5-HMF followed by 2-5 DMF.
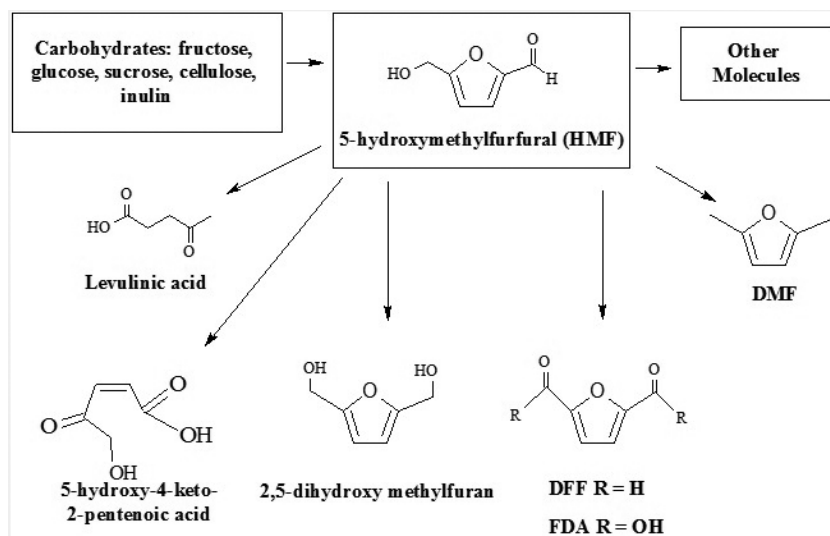

Figure 2. HMF as intermediate to fuels and chemicals such as levulinic acid, 2,5-furandicarboxylic acid (FDA), 2,5-diformylfuran (DFF), dihydroxymethylfuran and 5-hydroxy-4-keto-2-pentenoic acid.

organic phase is mandatory requirements. Recently, Bhanja[7], *et al.* have described the microwave assisted conversion of fructose using 2D-hexagonal bifunctionalised mesoporous SBA-15 with mesoporous bifunctionalised organosilica in DMSO and achieved 74 per cent yield of HMF.

The glucose or fructose conversion in aqueous media depends on pH. The maximum yield of HMF is 38-43 per cent at pH range of 1.5 - 2.15 from glucose or fructose. A narrow acidic pH range 2.7-3.9 prevents the successive conversion of 5-HMF to levulinic and formic acid[8]. The glucose conversion to HMF in aqueous media is also dependent on temperature. The complete transformation of glucose to HMF is accomplished at temperature between 150 °C - 200 °C with pH range 1-11. The complete transformation of glucose into soluble oligomers has been reported at 200 °C in either acid or basic aqueous solutions, the slight degradation of glucose occurs under basic conditions at 180 °C, while yield of HMF is 17 per cent, slightly converted in acidic conditions at 150 °C.

Li[9], *et al.* reported the high conversion of glucose to 5-hydroxymethylfurfural using hydrochloric acid as a catalyst and sodium chloride as a promoter in a water/γ-valerolactone system. The optimal reaction conditions were 0.2 M HCl and 0.1 M NaCl at 140 °C with a residence time of 60 min to obtain 62.45 per cent yield of HMF and 18.22 per cent yield of levulinic acid.

2.2 Synthesis of HMF using Ionic Liquid

The ionic liquids are water-soluble, polar salts that melt below 100 °C, with negligible vapour pressure[10]. The ionic liquids dissolve polysaccharides such as cellulosic material[11]. The ionic liquids have ability to disrupt the network of hydrogen bonds by using their charged constituents form electron donor–electron acceptor complexes with the hydroxyl groups of cellulose, by which polymer strands get de-aggregated and allow dissolution to occur[6]. Mora[12], *et al.* reported that dialkylimidazolium chlorides are especially known for their capacity to dissolve high concentrations of cellulose. The ionic liquid 1-ethyl-3-methylimidazolium chloride ([EMIM] Cl) and 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) are efficiently used for the conversion of carbohydrate to HMF. Ionic liquids have also been reported as catalysts for the transformation of hexose sugars into HMF[13]. Similarly, Nasirudeen[14], *et al.* also reported the conversion of HMF from glucose and fructose in [BMIM] Cl ionic liquid with solid catalyst under reactive vacuum distillation. The yield of HMF from fructose and glucose were 82 per cent and 65 per cent respectively at 180°C for 2h.

Qi[15], *et al.* described a two step method for production of 5-HMF from cellulose. The first step comprise of the cellulose hydrolysis by a strong acidic cation exchange resin in 1-ethyl-3-methyl imidazolium chloride ([EMIM][Cl]) with gradual addition of water and obtained glucose yields above 80 per cent. In the second step, $CrCl_3$ was used as catalyst for conversion of glucose to 5-HMF with 73 per cent yield. Additionaly, Jiang[16], *et al.* reported Bronsted Lewis-Acid ionic liquid ([Hmim][HSO$_4$]-0.5FeCl$_2$) as catalyst for conversion of chitosan to 5-HMF with 44.11 per cent yield. Recently, Yu[17], *et al.* reported ionic liquid and solid acid catalyst in one pot process for conversion of sucrose to 5-HMF in DMSO/water mixed solvent under hydrothermal conditions. Two type of solid catalyst such as cesium salt of dodecatungstophosphoric acid ($Cs_{2.3}H_{0.7}PW_{12}O_{40}$) and ionic liquid such as N-methylimidazolium hydrogen sulfate ([Hmim][HSO$_4$]) were studied and achieved 82.0 per cent and 91.8 per cent HMF with respective catalyst from fructose at 180°C for 3 h.

2.3 Synthesis of HMF using Heterogeneous Catalysts

Heterogeneous catalysts are also used to convert carbohydrates to HMF due to the advantages namely, facile product separation, catalyst recyclability, high temperature tolerance and modulation of surface properties (acidity, basicity, and pore size) so as to achieve maximal HMF selectivity and yields. Therefore, the further discussion is limited only to heterogeneous catalyst and green solvent medium for synthesis HMF from plant cellulose.

2.3.1 Metallic Chlorides Catalysts

A variety of metal chlorides are used as catalyst to convert glucose to HMF as metal ions enhance the rate of HMF production in comparison to the acid catalyst. Aluminum salts and oxygenated solvents were used to convert glucose to HMF with high yield and selectivity[18]. The studies had been carried out using alternative sugar sources such as maltose, cellobiose, starch and cellulose. Beckerele and Okuda[18] compared the catalytic activities of lanthanum chloride ($LaCl_3$) to the rare earth salts yttrium chloride (YCl_3) and scandium chloride ($ScCl_3$) for the conversion of glucose and cellobiose to HMF in the organic solvent *N, N*-dimethylacetamide.

It has been reported by Hu[19], *et al.* the catalytic system of metallic chlorides in ionic liquids i.e. $SnCl_4$/ [EMIM]BF_4 to convert glucose in 5-HMF in high yield of 62–69 per cent. Mittal[20], *et al.* studied others chlorides, $NbCl_5$, $TaCl_5$, VCl_3 in ionic liquids to dehydrate fructose to 5-HMF. The highest yield of 5-HMF was reported over $NbCl_5$. The high selectivity of HMF was obtained with weak Lewis acidity while strong Lewis acid favoured side reactions.

Jia[21], *et al.* studied alternative sources such as sugar (mannose) derived from hemicellulose for the conversion of HMF with 60 per cent yield by using $AlCl_3.6H_2O$ as catalyst in DMSO / water mixed solvent at 130 °C for 45 min. These catalysts were also used for conversion of di/trisaccharides such as cellobiose and melezitose into 5-HMF.

2.3.2 Metal Oxides as Catalyst

The HMF formation from glucose and fructose in hot compressed water with heterogeneous catalyst TiO_2 and ZrO_2 has been reported by Watanabe[22], *et al.* The study illustrates that the acidity of titania (TiO_2) promotes the dehydration of fructose to HMF, on the other hand zirconia (ZrO_2) promotes the isomerisation of glucose. In addition, the effect of crystallinity (i.e. amorphous, tetragonal and monoclinic phases) of the mesoporous titania nanoparticles material on the conversion yields of glucose and HMF was studied. Because of the existence of relatively strong acidity, crystalline mesoporous zirconia nanoparticle materials (i.e. either tetragonal or monoclinic phase) exhibited higher HMF yields than amorphous mesoporous zirconia nanoparticles. The tetragonal mesoporous zirconia nanoparticles catalyst presented better performance than monoclinic and amorphous mesoporous zirconia nanoparticles catalysts because its acidity at higher temperature (i.e., over 450 °C) was higher than that of the other two, which reflects great potential in one-pot synthesis of HMF from cellulose.

The α and γ structures of zirconium and titanium hydrogenphosphates as catalysts for fructose and inulin dehydration to HMF has been studied by Benvenuti[23], *et al.* These reactions were carried out in aqueous media and subsequent rehydration to levulinic and formic acids. In terms of activity and selectivity, cubic zirconium pyrophosphate and γ-titanium phosphate showed the best performances. Qi[24], *et al.* reported that zirconia based catalysts facilitate dehydration of carbohydrates to HMF. The sulfated zirconia was reported as catalyst in [BMIM]Cl for conversion of fructose to HMF with 88 per cent yield in a short reaction time i.e. 30 min at 100 °C. Further Qi[25], *et al.* reported the sulfated zirconia with microwave heating in an acetone–DMSO mixture to dehydrate fructose to HMF with 73 per cent yield in 20 min at 180 °C.

The mesoporous AlSiO catalyst in $THF/H_2O/NaCl$ biphasic system for direct conversion of carbohydrates to HMF with 63 per cent yield has been reported by Li[26], *et al.* The WO_3/reduced graphene oxide catalyst has been reported by Han[27], *et al.* for conversion of fructose into 5-HMF with 84.2 per cent yield. Moreover, the sulfonic acid functionalised mesoporous carbon/supported on silica has been documented as efficient catalyst for dehydration of fructose to 5-HMF with higher yields[28].

2.3.3 Heteropolyacids

Heteropolyacids or polyoxometalates are acids consisting of transition metal-oxygen anion clusters. The heteropolyacid salt, $Ag_3PW_{12}O_{40}$ has been reported in the literature for the conversion of fructose and glucose to HMF in biphasic system of water and methyl isobutyl ketone with yields of 78 per cent and 76 per cent respectively[29]. The catalyst was recycled easily and demonstrated no loss of activity over multiple reactions. It was also observed to be tolerant to high feedstock concentrations. Similar study in biphasic system was reported by Zhang[30], *et al.* using heteropolyacid ($CH_xH_{3x}PW_{12}O_{40}$ where x=1, 2 and 3) for conversion of cellulose to HMF with 75 per cent yield. The Bronsted–Lewis–surfactant-combined heteropolyacid $Cr[(OSO_3C_{12}H_{25})H_2PW_{12}O_{40}]_3$ to achieve both cellulose depolymerisation and conversion to HMF with 53 per cent yield in 2 h at 150°C[31]. In addition, Gomes[32], *et al.* studied two type of heteropolyacid catalyst such as phosphotungstic acid (HPW) supported on MCM-41 and Cs-exchanged phosphotungstic acid (HCsPW) for HMF synthesis. The reaction was carried out by using HPW catalyst with the mass ratio of catalyst and fructose 1:10 at 120 °C for 30 min. The resultant conversion of fructose and HMF was 100 per cent and 92 per cent with respective catalyst. The HPW/MCM-41 showed the best catalytic activity.

2.3.4 Zeolites

Zeolites are composed of Bronsted and Lewis acid sites derived from the Al atom. A particular class of aluminosilicates has excited huge interest in zeolites because of different ways of arrangements of their atoms. Their three dimensional structures reveals large vacant spaces for cations such as sodium, calcium and molecules such as water. The impregnation of ethylene dichloride solution of chloro-sulfonic acid $Zr(OH)_4$ and $Zr(OH)_4–Al(OH)_3$ has been reported to have catalytic activity

for conversion of fructose and glucose to HMF with yields of 68 per cent and 48 per cent respectively[33]. Similary, Morales[34], *et al.* studied that the dehydration of glucose to HMF with zirconium containing mesoporous MCM-41 silica catalyst. The dehydration of glucose with zirconium containing MCM-41 silica catalysts activated at 550 °C and 750 °C temperature (Zr-MCM-550, Zr-MCM-750). Zr-MCM-550 is most active, exhibiting high glucose conversion 82 per cent with exclusive formation of 13.2 per cent selectivity and yield of 23 per cent of HMF at 175 °C for 2.5 h. Moreno[35], *et al.* studied HZSM-5 (Si/Al ratio of 18.9) in a biphasic system of 20 per cent NaCl in water-methyl isobutyl ketone (MIBK) as organic solvent for conversion of glucose to HMF. The conversion of glucose was 80 per cent with yield of 42 per cent HMF in reaction time of 30 min at 195 °C. The effect of different lewis acids with zelolite were studied for selective conversion of glucose to HMF. Three zelolites catalysts such as Cu-ZSM-5, HZSM-5 and Fe-ZSM-5 were reported with HMF yield of 26 per cent, 8.5 per cent and 30 per cent respectively. Sn-β- zelolite has also been reported[36] for conversion of hexose sugar to HMF. These zeolites are efficient catalyst for isomerisation of glucose to fructose in aqueous media under acidic conditions. The yield of HMF from glucose was only 8 per cent which was further improved to 53 per cent under acidic conditions.

2.3.5 Resins
Polymer based resins are cost effective and reusable from the liquid mixture after the reaction causes less corrosion. Amberlyst 15 and Amberlyst 36 are strong acidic and sulfonic acid resin, based on cross-linked styrene-divinyl benzene copolymer beads. The ion exchange resins i.e. macroporous strong-acid, macroporous weak-acid and gel strong acid may also be used for carbohydrates conversion to HMF. However, macroporous strong acid has improved activity compared to other resins. Qi[37], *et al.* reported Amberlyst 36 as strong acidic resins followed by DOWEX-50wx8-100 as gel strong-acidic resin for synthesis

of HMF. The activity of macroporous strong acid resins was found to be better than gel strong acid resins. Moreover, Researchers[38] from Noguchi Institute patented the use of ion-exchange resins such as Amberlite® IR-116 or Diaion® PK-228 cross-linked with divinylbenzene for synthesis of HMF.

3. 2,5-DIMETHYLFURAN
Dimethylfuran (DMF), as an alternative biofuel is derived from catalytic hydrogenation of HMF ia alternative to gasoline[39]. Other salient properties of DMF are the energy density compared to ethanol (31.5 MJ/L vs. 23 MJ/L), lower volatility (b.p. 92–94 °C vs. 78 °C), and is immiscible with water. The properties of gasoline, ethanol and dimethylfuran are compared in Table 1.

3.1 DMF as Alternative to Gasoline
The DMF has the advantages over gasoline since it is a renewable fuel and carbon neutral to the environment. The combustion performance of DMF in a gasoline direct-injection (GDI) engine was compared with that of gasoline and ethanol and its fuel characteristic of DMF was found to be comparable to both of gasoline and ethanol. Zhong[40], *et al.* observed that using pure DMF did not adversely affect the performance of the research engine. Wang[41], *et al.* studied with different loads of DMF for different initial combustion performance and engine knock was induced at 7.1 bar indicating mean effective pressure. Emissions of CO, hydrocarbons, NOx, and particulate matter of DMF were found to be similar to gasoline exhaust but were lower than emission from ethanol. Similar findings were also achieved using dual-injection of DMF or ethanol with gasoline in a spark-ignition engine. The effect of spark timing and load of DMF was further analysed on a direct-
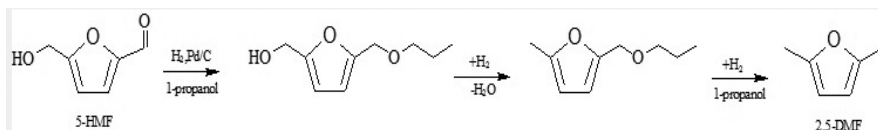

Figure 3. Catalytic hydrogenolysis of HMF to DMF.

injection spark-ignition engine[42]. As compared to gasoline, DMF have more resistant to engine knock, have lower initial and total combustion. Thus, Co-blending of DMF and ethanol in gasoline could give a greater benefit than biofuel blended with gasoline alone.

3.2 Technology for the Conversion of DMF from Biomass or HMF
The potential advantages of DMF as a biofuel, derived from various lignocellulosic biomass have been discussed in the literature. Electrocatalytic hydrogenation of HMF to DMF was studied by Nilges and Schroder[43] to have high selectivity, which may be a tool for storage of electrical energy into liquid organic fuel.

Luijkx[44], *et al.* reported palladium (Pd/C) based catalyst in 1-propanol to derive DMF from HMF. The alcohol bond was first reduced to ether bond and subsequently to DMF as depicted in Fig. 3. The one pot process of fructose to DMF by Pd/C catalyst in formic acid has been reported[45]. The synthesis

Table 1. Comparison of fuel quality of gasoline, ethanol and dimethylfuran

Property	Gasoline	Ethanol	Dimethylfuran (DMF)
Motored octane number	88.5	89.7	88
Heat of combustion (volumetric, MJ/L)	31.82	21.22	29.55
Density (kg/L)	0.742	0.789	0.888
Boiling point (°C)	31 (initial) 203 (final)	78	93
Heat of vaporization (289 K, kJ/kg)	~349	931.1	380.7
Water solubility (g/L)	0	> 1000 (miscible)	1.47

of DMF from glucose is a two step process: In first step using Pd/C catalyst in an ionic liquid/acetonitrile mixture with 98 per cent yield glucose. In second step, Glucose was converted to HMF using 12-molybdophosphoric acid, after which the catalyst could be replaced with the Pd/C without isolation of HMF to derive DMF with 16 per cent yield[46]. Leshkov[47], *et al.* reported a two-step process for the conversion of fructose to DMF. The first step acid-catalysed dehydration is used to convert fructose to HMF, which is extracted into 1-butanol. The HMF undergoes hydrogenation in the second step with 3:1 atomic ratio of copper–ruthenium (Cu:Ru/C) catalyst to derive DMF with 71 per cent yield. The techno-economics for the production of DMF using copper–ruthenium catalyst has been reported by Kazi[48], *et al.* where the cost of DMF is reported to be \$ 2.02/litre, which is 1.8 times the cost of gasoline presently.

4. CONCLUSIONS

HMF has the potential to serve as a renewable alternative for fuels and chemicals. Primarily the isomerisation of glucose to fructose is important than fructose dehydration to HMF. Considerable work has already been reported to derive HMF from carbohydrate resources but there is still scope for further research to make the process of lignocellulose to HMF, much simpler and economically viable. The conversion of fructose from other carbohydrates such as glucose and cellulose still remain difficult. Transition metals, lanthanide metals, and heterogeneous catalysts are some of the most studied catalysts for glucose isomerisation to fructose but these types of catalysts are toxic and require extreme reaction conditions. Ionic liquids are typically costly. It is essential that processes become more eco-friendly and economically viable by using high amount of carbohydrate loadings and also facilitating their continued use. The homogeneous catalytic method is preferred for lignocellulosic biomass conversion to cellulose, its hydrolysis further dehydration to HMF.

2,5-Dimethylfuran derived from HMF has a great promise to meet our fuel demands. The studies show that it can be used as a fuel or part of a fuel blends in our existing fuel infrastructure. Initial studies have been focused on converting fructose to HMF and further to DMF from the biomass resources. However, it requires specific reaction conditions for hydrogenation of HMF to DMF, some studies have been reported the use of robust catalysts for this transformation. The Cu-Ru/C and related catalysts are preferred for hydrogenation of HMD to 2, 5-dimethylfuran. DMF is better alternative to fossil fuels to develop a green, sustainable energy economy. The biomass based fuel is renewable and sustainable, although further research and developments are still required to transfer the process from laboratory to the industry.

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