

Catalytic production of 2,5-dimethylfuran for liquid fuels from biomass-derived carbohydrates

SHI Gaofeng*, LI Feiyun

(School of Petrochemical Engineering, Lanzhou University of Technology, Lanzhou 730050, Gansu, China)

Abstract: Renewable fuels in substituting of fossil fuels have attracted much interest with diminishing fossil fuel reserves and growing concerns about global warming. 2,5-Dimethylfuran (DMF) from biomass has been considered as an attractive liquid transportation fuel. In this paper, the DMF production pathways and methods from biomass-derived carbohydrates are summarized, the advantages and disadvantages of methods are reviewed and proposals for the future work are prospected.

Keywords: liquid fuel; biomass; 2,5-dimethylfuran; 5-hydroxymethylfurfural

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生物质糖类催化制备液体燃料 2,5-二甲基呋喃

史高峰*, 李飞云

(兰州理工大学 石油化工学院, 甘肃 兰州 730050)

摘要:在化石燃料储量不断减少,温室效益趋势加重的情况下,寻求可以替代化石燃料的可再生燃料已经引起了人们的广泛关注.人们普遍认为源于生物质的2,5-二甲基呋喃(DMF)是很有前景的一种可再生液体交通燃料,为此本文作者对近年来生物质制备DMF的方法及途径进行了综述,同时对今后的研究作了展望.

关键词:液体燃料; 生物质; 2,5-二甲基呋喃; 5-羟甲基糠醛

Faced with increasing resource constraints, severe environmental pollution and a deteriorating ecosystem, recently renewable fuels in substituting of fossil fuels have attracted much interest^[1-3]. Ethanol, used as a liquid transportation fuel, is the only renewable liquid fuel currently produced in large quantities, but it suffers from several limitations, including limited raw materials, low energy density, high volatility and contamination by the absorption of water from the atmosphere^[4-6]. However, compared to ethanol, 2,5-dimethylfuran (DMF) from renewable biomass not only has a higher energy density, higher boiling point and research octane number, but has such benefits as im-

miscibility with water and ideal evaporation separation process. So DMF has been considered as a kind of promising liquid fuel^[7] (Table 1). Recently studies, considering the implications of DMF used in burners, show that the fuel consumption rate is slightly higher than that of gasoline in the low load, lower than that in the high load^[8]. At the same time, the spray characteristics of DMF is superior to ethanol, and the power performance and fuel economy of gasoline-DMF fuel are better than those of gasoline-ethanol^[9]; Then DMF produces the lowest total carbonyl emissions and more significantly, the lowest emissions of the more harmful formaldehyde among the four oxygenated fuels and gasoline^[10]; Besides, when the EGR rate is more than 50%, the soot and NO_x emissions of the mixing ratio of diesel fuel-DMF are even zero^[11]. All in all, DMF is one emerging biofuel candidate.

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Biography: SHI Gaofeng (1963-), male, professor, majoring in the extraction of nature products. *Corresponding author, E-mail: gaofengshi_lzh@163.com.

In this paper, the DMF production methods and pathways from biomass-derived carbohydrates are summarized, and the future research trends are prospected.

Table 1 Comparison of the properties of DMF, gasoline, ethanol and DME

property	unit	DMF	gasoline	ethanol	DME
molecular formula		C ₆ H ₈ O	C ₄ —C ₁₂	C ₂ H ₆ O	CH ₃ OCH ₃
molecular mass		92.1	98	46.1	46.069
oxygen content	%	16.0	0	34.8	34.8
sulfur content	%	0	—	0	0
liquid density	kg /L	0.9	0.73	0.789	0.668
boiling point	°C	93	30—90	78.4	—25
flash point	°C	7.2	—40	14	
water solubility		insoluble	insoluble	highly soluble	insoluble
Infuriating pressure	MPa		0.044—0.078	0.021	0.53
Stoichiometric air	kg/kg		14.8	9.00	
latent heat of vaporization	kJ/mol	31.91	38.51	43.25	
enthalpy of formation of vapor	kJ/mol	124.6			
energy density	MJ/L	31.5	35	23	
research octane number	RON	120	91—98	111	
	MON		82—88	92	
research cetane number					55—60

1 Chemical pathways of production of DMF

The dehydration of 2,5-hexanedione to give DMF has been reported^[12], but the production path of 2,5-hexanedione is not economical. The issue to produce DMF including by an economically and environmentally acceptable route, from renewable sources, has been being pursued. It involves a multistep process (Fig. 1), namely, to begin with, pretreatment of biomass into sugar components

fructose or glucose, *via* cellulosic components; next, catalytic dehydration of sugars into intermediates of 5-hydroxymethylfurfural (HMF) or 5-chloromethylfurfural (CMF)^[13–14]; Finally, hydrogenolysis of HMF or CMF into DMF^[15–25]. Although the production of DMF by electrocatalytic hydrogenation of HMF has been claimed^[15], catalytic production of DMF from biomass-derived carbohydrates has been accepted by people just because biomass is renewable.

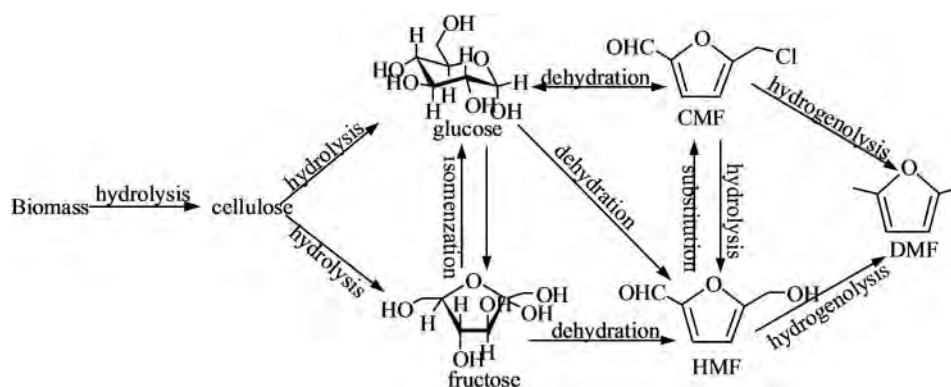


Fig. 1 Chemical pathways of production of DMF from biomass^[6]

2 Catalytic production of DMF from biomass

2.1 Catalytic production of DMF from fructose

ROMAN-LESHKOV et al^[4] reported a new path for the production of DMF as a liquid transportation fuel. The converting can be accomplished in two steps: the first step involves the dehydration of fructose to produce HMF in the presence of 1-butanol and water biphasic conditions (HMF is extracted by the organic phase), employing 0.25 mol/L HCl as the catalyst. The catalytic system produces a fructose conversion of 88%, high HMF selectivity of 82% with the addition of 35% NaCl to the aqueous phase at 180 °C for 3 min. The literature showed that HMF selectivity not only depends on the affinity of the solvent for HMF, but also on the ability of the salt to separate both phases. And the liquid-phase or the vapor-phase hydrogenation and hydrogenolysis process of HMF, employing carbon-supported copper-ruthenium (CuRu/C) as the catalyst, is subsequently conducted at 220 °C with 6.8 bar H₂ for 10 h, with a DMF yield of more than 71% (liquid-phase: 71%, vapor-phase: 76%–79%). The research also indicated that the CuRu/C catalyst is applied in order to alleviate sintering of copper. Compared to the liquid-phase experiments, the vapor-phase hydrogenolysis experiments have multiple benefits, for example, it can process both dilute and concentrated HMF solutions. However, it is inevitable that the CuRu/C catalyst is poisoned by chloride ions (introduced during the dehydration step and not

completely removed during the evaporation step). The strategy of converting biomass into DMF (yield of 50%) is created by ROMAN-LESHKOV et al^[4], then our reliance on petroleum may be diminished. And the biphasic system is helpful for the selectivity of HMF just because of the high solubility of fructose and the extracting of HMF. However, challenges of the corrosion of equipment and poisoning of the CuRu/C catalyst remain for commercial application.

THANANATTHANACHON et al^[16] presented a new catalytic strategy for one-pot synthesis of DMF from fructose. The paper also showed that the conversion of HMF into DMF is achieved with an ideal yield (> 95%) in the presence of tetrahydrofuran (THF), FA, H₂SO₄ and Pd/C. The hydrogenation and hydrogenolysis processes of HMF are conducted at mild conditions (75 °C). For the sake of that, NMR analysis of the reaction revealed that FA plays an essential role, a source of hydrogen (H₂) and a deoxygenating reagent of furanymethanols. Gratifyingly, FA is also an excellent acid catalyst for dehydration of fructose to HMF, so one-pot synthesis of DMF from fructose is experimented with a suspension of THF, FA, H₂SO₄ and Pd/C (0.2 g metal catalyst per 0.18 g fructose), with a better yield of the isolated DMF: 51%. The path is shown in Fig. 2, first, removing three oxygen atoms by dehydration to produce HMF; Second, removing two oxygen atoms by hydrogenolysis to produce DMF, *via* the intermediates of 5-[(formyloxy)methyl]furfural (FMMF), 2-hydroxymethyl-5-methylfuran(HMMF) and 2-

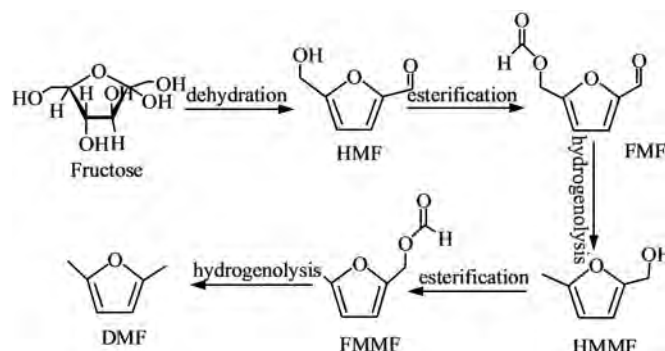


Fig. 2 One-pot process to generate DMF from fructose

(formyloxy)-methyl-5-methylfuran (FMMF). The converting strategy creates a route for transforming abundant renewable biomass resources into a liquid fuel at mild conditions, and may diminish our reliance on H_2 and implement safe production. But lots of participation of the expensive metal catalyst Pd/C is a long stop for large-scale production of DMF.

LUCAS et al^[17] produced a new catalyst, 2% (w) Ru-K-OMS-2, used as the catalyst of synthesis of DMF. First, the solid acid catalytic conversion of fructose to HMF is carried out in the aqueous phase at 165 °C for 1 h; In a consecutive step, the HMF, which is extracted by the methyl isobutyl ketone, is converted to DMF in 1-butanol by hydrogenation and hydrogenolysis reactions using the 2% (w) Ru-K-OMS-2 as the catalyst at 220 °C with 10 bar H_2 for 6 h. The research also tested catalytic activity and selectivity of various catalysts, such as microporous zeolites and aluminophosphates and mesoporous AISBA-15 for the dehydration of fructose to HMF. The result showed that high acidity and strong acid sites are good for the dehydration, but it does not favor selective formation of HMF. So the AISBA-15 is a good choice for the synthesis of HMF, with the conversion of fructose, 66% and selectivity to HMF, 61%. Significantly, this approach cannot necessitate difficult and energy intensive isolation procedures for the recycling of the solid acid catalyst. HANSEN et al^[18] also produced a new catalyst Cu-PMO for the converting HMF to DMF in supercritical methanol, with an yield of DMF: 48%; And NISHIMURA et al^[19] reported the DMF yield of 95%, employing Pd_xAu_y/C as the catalyst. But HUANG^[20] also produced a new catalyst 7Ni-30W₂C/AC for the converting HMF to DMF, with an excellent yield of DMF: 96% (7Ni-30W₂C/AC is prepared with nickel nitrate, ammonium metatungstate and activated carbon by co-impregnation methods). LUCAS et al^[17] reported that the DMF yield of 33% from HMF is less than the yield of 96%^[20], and Ru is no cheaper than Ni. So the non-noble bimetallic catalyst will attract much attention.

Biphasic system for preparation of HMF, a source of H_2 for the converting HMF into DMF, such as FA, supercritical methanol, and non-noble bimetallic catalyst were reported since ROMAN-LESHKOV et al^[4] claimed the new path for the production of DMF from biomass. However, problems, such as the lower yield of DMF (< 51%), expensive prices of fructose and metal catalyst, corrosion of equipment, recycling of catalyst for the dehydration of fructose, the separation and purification of HMF and so on, still need to be solved for the commercial application of DMF.

2.2 Catalytic production of DMF from glucose

The catalytic production of DMF from glucose has also attracted much interest because the price of glucose is cheaper than that of fructose. A high-profile contribution in this area by MASCAL and coworkers^[21] showed that not only glucose, but cellulose itself, could be efficiently converted into CMF (yield: 71%), which is easily sequestered into 1,2-dichloroethane in a two-phase reaction medium containing solution of lithium chloride ($w = 5%$) in concentrated hydrochloric acid. The result also demonstrated that the dehydration of glucose or the extraction of CMF is the rate-limiting component of the process. Given that our interest in this area had less to do with the problem of CMF hydrolysis than that of HMF hydrolysis. BINDER et al^[22] reported the synthesis of HMF from glucose in DMA-halide system, and indicated that chromium, which catalyzes the isomerization of glucose into fructose, is the key to synthesis of HMF. CHIDAMBARAM et al^[23] also reported that 100% yield of HMF from glucose could be achieved using 12-molybdophosphoric acid (12-MPA) in a solution of 1-ethyl-3-methylimidazolium chloride (EMIMCl) and acetonitrile. Liquid acid and heteropoly acids catalysts were screened for the dehydration of glucose in ionic liquid. The analytical result of reaction systems suggested that the high HMF selectivity achievable with heteropoly acid catalysts is attributed to the stability of 1,2-enediol and other intermediates in the dehydration of glucose (which does not involve the isomerization of glucose to fructose as the first step of the

reaction) (Fig. 3). Carbon-supported Pd, Pt, Ru and Rh are investigated for the hydrogenation of HMF, neat HMF, extracted HMF or HMF in EMIMCl-CH₃CN, with DMF selectivity of more than 28% employing Pd/C. The research also indicated that a combination of the lower temperature, shorter time of reaction and the low solubility of H₂ contributes to the lower yield (< 15%). At last, the pathway for the conversion of glucose to DMF is composed of two steps: i) dehydration to

produce to HMF; ii) HMF hydrogenation to DMF, *via* intermediates of 5-methylfurfural (MF), 5-methylfurfuryl alcohol (MFA). In a word, CHIDAMBARAM et al.^[23] produced the highest yield of HMF, but the catalytic conversion of glucose to DMF in ionic liquids is dective just because of inexpensive ionic liquids except the lower yield of DMF. So the isomerization of glucose to fructose is still the key to give DMF from glucose.

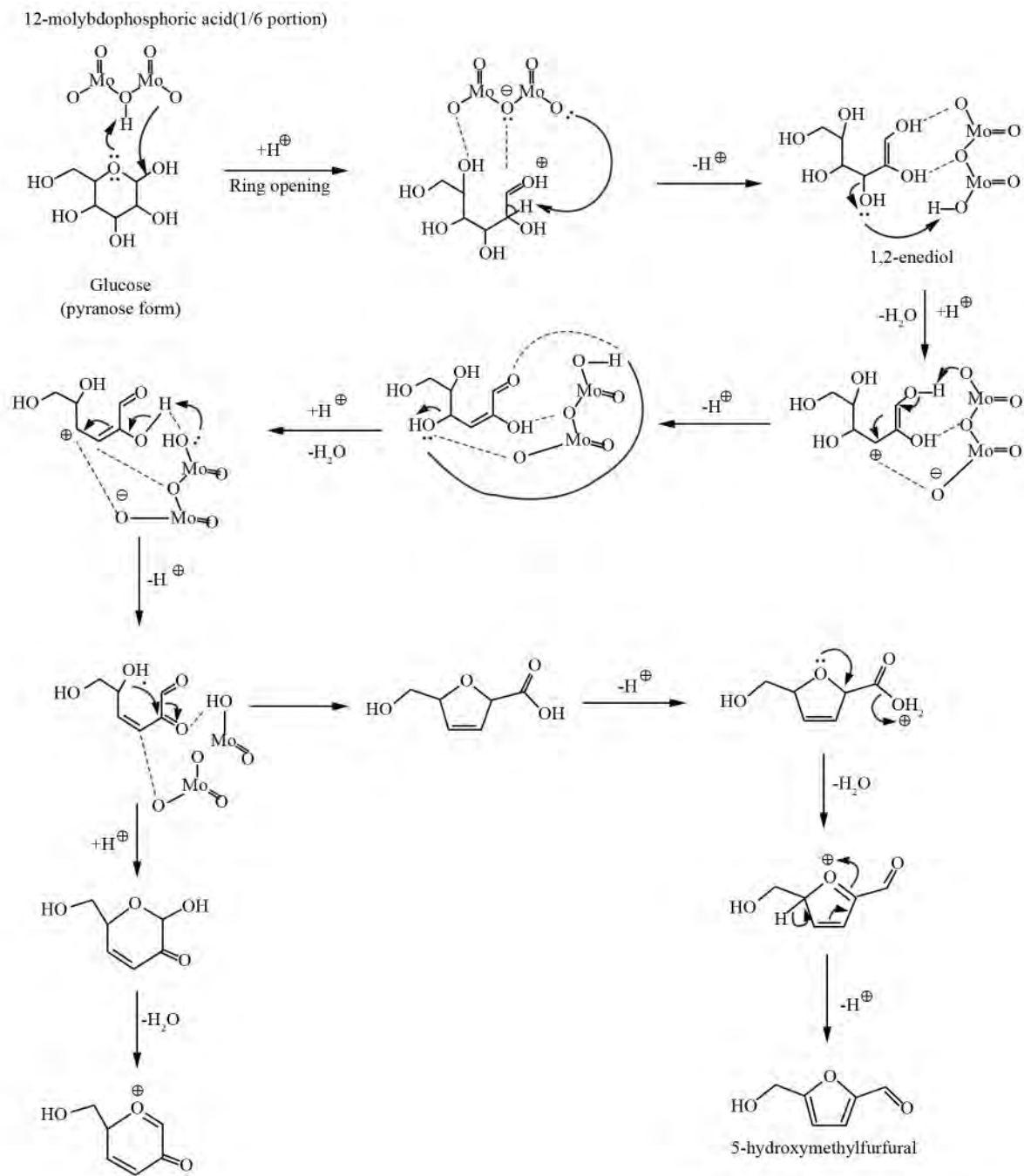


Fig. 3 12-MPA catalytic dehydration of glucose to HMF^[23]

2.3 Catalytic production of DMF from cellulose

MASCAL et al^[21] mentioned hydrogenation of CMF from cellulose, using a Pd/C catalyst to give DMF in high yield, and provided a solution to the long-standing glucose to HMF conversion problem, given that CMF can be easily hydrolyzed to HMF. And DEETAL et al^[24] found that the Ru/C catalyst is quite effective for the production of DMF from fructose, giving a maximum yield of 32% DMF, then respectively achieved one-pot conversion of cellulose into DMF (yield: 14%) under oil-bath heating or microwave-assisted heating. The dehydration of cellulose to give DMF is catalyzed by $[\text{DMA}]^+ [\text{CH}_3\text{SO}_3]^-$ (DMA, N,N-dimethylacetamide) in DMA/LiCl system because of the robust crystalline structure of cellulose. In a consecutive step, HMF in FA was found to undergo hydrogenation and hydrogenolysis into DMF upon addition of THF slurry of the Ru/C catalyst. They also suggested the reaction costs less time under microwave-assisted heating than under oil-bath heating. All in all, a combination of the lower solubility of cellulose, the lower selectivity of DMF of mental catalyst and problems of the production of DMF from fructose or glucose gives the lower yield of DMF. However, the conversion of cellulose to DMF is a skip for the production of DMF from biomass.

2.4 Catalytic production of DMF from biomass-derived cellulose

BINDER et al^[22] (Fig. 4) reported that, untreated lignocellulosic biomass, as well as purified cellulose, glucose, and fructose, are converted to HMF in a single step in the presence of DMA containing halide with unprecedented yields. The research also indicated that loosely ion-paired halide ions in DMA-LiCl are critical for the remarkable yield of this low-temperature, and the conversion of cellulose into HMF is unabated by the presence of other biomass components, such as lignin and protein. Based on these results, the conversion of untreated corn straw into DMF is achieved with the 9% yield of DMF, which is less than that obtained by DEETAL et al^[24] using agar (27%). The process to synthesize DMF is accomplished in two

chemical reactions from corn straw. In the first step of our process, HMF is synthesized by the dehydration of that in DMA-LiCl containing CrCl_2 , HCl and $[\text{EMIM}]\text{Cl}$; Next, the HMF removed chloride ions by ion-exclusion chromatography in water, is converted to DMF by hydrogenolysis in 1-butanol with CuRu/C. The reason of lower yield of DMF may be 3D network of hydrogen bonding interactions of corn straw, the lower solubility of cellulose and poisoned CuRu/C by chloride ions. After all, raw materials basis for the generation of DMF varied from fructose or glucose to nonfood raw materials, *i. e.* lignocellulosic biomass. Indeed, it is a leap to make DMF become a bulk-scale industrial product.

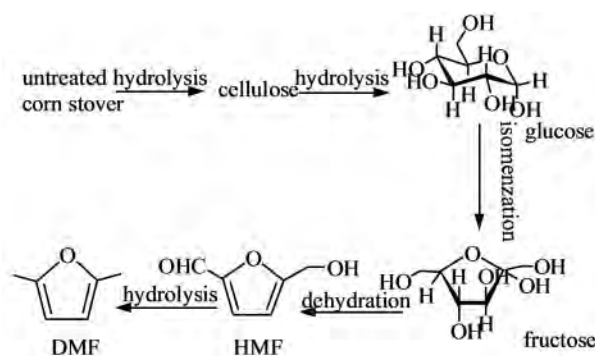


Fig. 4 DMF production from biomass

3 Perspective

Increasingly, DMF has been considered as a kind of promising liquid fuel with the rapid development in methods for transforming biomass into DMF. Unpleasantly, challenges^[25] remain for the implementing of economical and environmental route to produce commercial DMF. Any of the following proposals should be considered for the further work: i) Concentrating on the exploration of more efficient and repeatedly re-used non-noble metal catalysts for the conversion of biomass to DMF by a one-step reaction; ii) Exploring the conversion of nonfood biomass to DMF, *e. g.*, cellulosic biomass from agriculture and forestry waste or switch grass and the like; iii) Exploring more efficient green and multifunctional reaction reagent, *i. e.*, an acid catalyst for dehydration of biomass to HMF, a hydrogen source for hydrogenation of HMF and a re-

used reaction solvent; iv) Anticipating further mechanistic studies of conversion of biomass to DMF; v) Anticipating further studies of industrial enlarge and commercial application.

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