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Production Resources for dimethyl furan and its application in internal combustion engine

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Abstract
Diminishing fossil fuel resources and growing concerns about global warming indicate that sustainable sources of energy are needed in the near future. Renewable biomass resources have the potential to serve as a sustainable supply of fuels and chemical intermediates. Hydroxymethylfural, HMF is an aldehyde and a furan compound formed during the thermal decomposition of sugars and carbohydrates. It can be produced from renewable biomass resources. HMF's derivative, 2,5-Dimethylfuran (DMF), has been identified as a biofuel with great potential. DMF is considered as an octane improver for gasoline. As an alternative biofuel, DMF exhibits a number of attractive properties such as higher boiling point, higher octane number, which will allow for the use of high engine compression ratios for improved fuel economy. Moreover, DMF is stable in storage and insoluble in water. Hence, it will not get contaminated through water absorption from the atmosphere. The paper presents the manufacturing methods from cellulose and review the using DMF as alternative fuel in internal combustion engine (ICE). The results will orientate to use DMF for ICE in order to reduce fuel consumption and emission.

Keywords: 2, 5-dimethylfuran (DMF), internal combustion engine, biofuel, biomass, alternative fuel

1. Introduction

Although the idea of fuelling internal combustion engines with biofuels is not new, its use is receiving increased worldwide attention, including that of novel alternatives. Liquid biomass offers a high energy density option and is compatible with existing combustion systems. In Europe, the promotion of biofuels has led to a legislative approach; by 2020, all EU member states must conform to a 10% minimum target on the use of alternative fuels (biofuels or other renewable fuels) in transportation. In the US, tax incentives have been used to promote the use of ethanol in gasoline. For large energy consuming nations, such as China and India, which have an increasing gap between energy demand and supply, the biofuel route offers improved energy security and reduced dependency on imported oil. Therefore, scientists are keen to convert the abundant biomass feedstock into liquid fuels or fuel additives from the perspective of sustainable chemistry [1]. 5-Hydroxymethylfurfural (HMF), a high boiling point furanic compound produced from the dehydration of biomass-derived carbohydrates, is viewed as a key intermediate [2]. Plentiful work has already been carried out on conversion of HMF into fuels and chemicals [3]. As HMF itself is oxygen-rich and non-volatile, it is necessary to lower the polarity and the boiling point to obtain liquid fuels or fuel additives derived from HMF. Several potential fuel products such as 2, 5-dimethyl-furan (DMF), 2, 5-dimethyl-tetrahydrofuran (DMTHF), methyl levulinate (LM) and γ-valerolactone (GVL) have been obtained from HMF [4]. Recently, another group of HMF derivatives, 2, 5-bis-alkoxymethylfurans (BAMF), has attracted attention and they are regarded as potential bio-diesel candidates [5]. Despite that, PtSn/Al2O3hydrogenation catalyst can only achieve about 80%selectivity in converting HMF into BHMF with over 10% by-products produced. Whether Amberlyst-15 is the best choice among the solid acid catalysts for the etherification of BHMF with methanol still remains to be further investigated. Moreover, the physical properties especially the cetane number that makes BAMF suitable to be used as a diesel additive have not been investigated yet [6].

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DMF is used as an octane improver for gasoline. As an alternative biofuel, DMF exhibits a number of attractive features. DMF has a 20 K higher boiling point. DMF has a high research octane number (101), which will allow for the use of high engine compression ratios for improved fuel economy. DMF is stable in storage and insoluble in water. Thus, it will not get contaminated through water absorption from the atmosphere (in comparison to the very high miscibility of ethanol). DMF consumes only one-third of the energy in the evaporation stage of its production, in comparison to that required by fermentation for ethanol. DMF is manufactured on a large scale and low cost using cellulose (fructose or glucose).

2. Properties of DMF

Some advantages of DMF such as high energy density, insoluble in water, high octane rating, physical properties very close to gasoline, low volatility and stable in storage and some disadvantages such as toxic, liberates Oxides of Nitrogen (NOx) & Carbon monoxide (CO) as a product of combustion, produces hazardous intermediates on combustion may be shown. The properties of DMF are given in Table 1.

Table 1: Properties of DMF in comparison with gasoline and ethanol

Properties	Gasoline	Ethanol	DMF
Molecular formula	C_2-C_{14}	C_2H_6O	C_6H_8O
Molecular mass (kg/mol)	100-105	46	96
Density at 20°C (kg/m^3)	745	791	890
Water solubility at 25°C	Insoluble	Highly soluble ≥100	Insoluble ≤ 1.47
H/C ratio	1.795	3	1.33
O/C ratio	0	0.5	0.1667
Oxygen content (%)	0	34.78	16.67
Stoichiometric air-fuel ratio	14.56	8.95	10.72
Calorific value (MJ/kg)	43	27	33
Octane number	96.8	107	101
Ignition temperature (°C)	257	423	286
Latent heat of vaporization at 20°C (kJ/mol)	38.51	43.25	31.91
Boiling point (°C)	32.8	78.4	92
Flash point (°C)	40	13	0-1

Table 1 shows that, DMF has a relatively high volumetric energy density (31.5 MJ/l), which is comparable to that of gasoline (32.2 MJ/l) and almost 40% higher than that of ethanol (23 MJ/l). To provide the equivalent energy output of 1m^3 of gasoline, 1.512 m^3 of ethanol and 1.073 m^3 of DMF were required. Of the three fuels, ethanol has the minimum volumetric calorific value. Hence, more ethanol is required to maintain the same engine load, which increases the fuel requirement and, thus, the fuel flow rate, compared to gasoline and DMF. Higher combustion temperature contributes to more complete combustion. Relative oxygen content in each fuel also is a vital factor which affects the level of combustion completeness. Higher the oxygen element in fuel molecule, more is the availability of oxygen during combustion that helps to increase combustion efficiency. Amongst these fuels, the oxygen content in DMF (O/C ratio = 0.1667) is lower than ethanol (O/C ratio = 0.5). Ethanol (97-97.5%) has the highest combustion efficiency followed by DMF (95.5-96%) & Gasoline (95%). Efficiency of DMF is similar to gasoline. Ethanol, on the other hand, has a consistently high indicated efficiency, which is probably due to its high combustion efficiency and oxygen content (35% oxygen content by mass, 18% higher than DMF). The efficiency does not drop off as suddenly as experienced with DMF and gasoline and remains above 37%.

3. Production resources and process

Global energy shortages and environment pollutions have urged scientists to develop a new generation of technologies that can cheaply synthesize biofuels from renewable biomass [7]. The second generation biofuels must be established in usage of sustainable chemical products and produced through modern and mature chemical technologies such as pyrolysis, Fischer Tropsch synthesis, or a catalytic process, all of which can produce complex molecules or transform materials into sustainable biofuels [8]. More than 75% biomass, such as corns (maize), trees and grass, consist of carbohydrates (such as starch and cellulose). These carbohydrates usually exist as polymer chains consisting of thou- sands of units (glucose or fructose). And each unit has six carbon atoms and one oxygen atom, meaning molecules of biomass contain more than 100 carbon atoms. Conversely, the common fuels for internal combustion engines usually have molecules consisting of 5 to 15 carbon atoms. Thus, the main challenges in transforming biomass to biofuels are molecular miniaturization and the removal of oxygen atoms [9]. Up to now, the main approaches of using biomass to prepare DMF included two ways [10]. The first method is to pretreat the biomass and degrade it to glucose or fructose before three oxygen atoms are removed from the glucose or fructose by selective dehydration to form 5-hydroxymethylfurfural (HMF). Finally, HMF can be converted to DMF by hydrogenolysis. The second pathway is to have biomass, including cellulose or glucose, transformed to 5-chloromethylfurfural (CMF) by dehydration first. Then, convert CMF to DMF by hydrogenolysis [11-13]. Because of the sufficient supply of biomass and its low cost as a raw material, the preparation progress and the yield of DMF will directly determine whether it can be used as an alternative fuel for vehicle engines extensively. Therefore, in recent years, many researchers have focused on biomass such as glucose, fructose, and starch as raw materials for conversion to HMF or CMF using these two respective paths and have tried to increase the conversion efficiency by different catalysts and solutions [13]. The schematic is shown in

Figure 1.

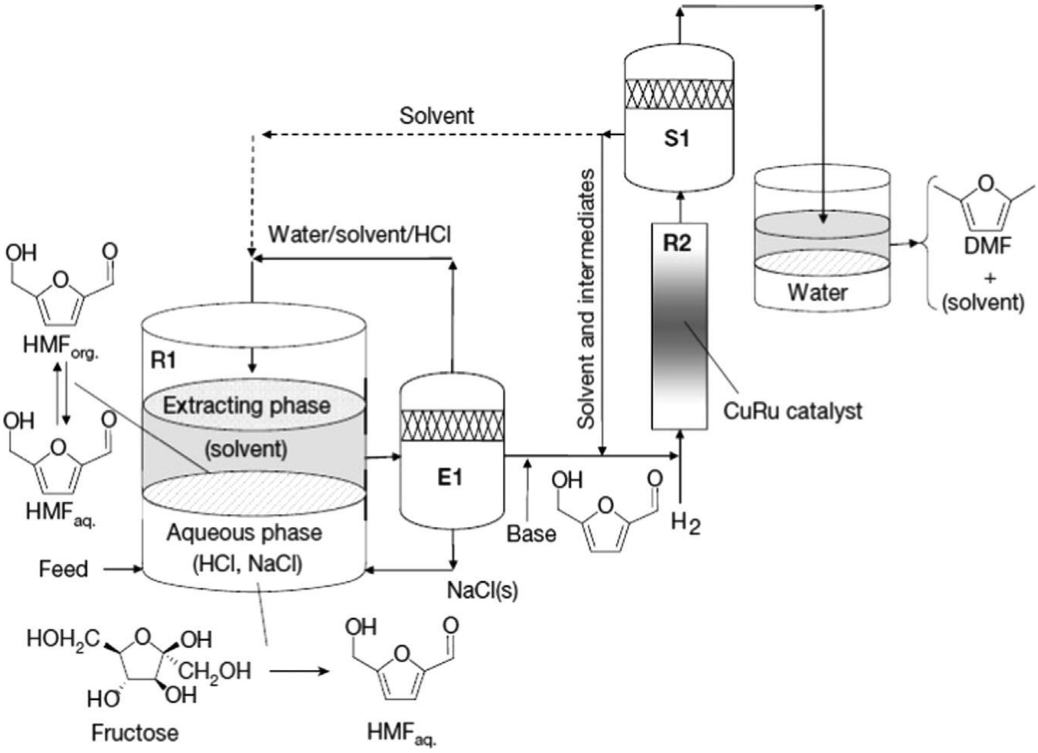

Fig 1: Schematic of the process for fructose conversion to DMF [13, 14]

HCl was used as the catalyzer, and the fructose was converted to HMF with HCI as catalyzer in a 35% NaCl solution. Then, HMF was extracted from the solution by 1-butanol. Finally the HMF was converted to DMF by the catalysis of a carbon-supported copper-ruthenium (CuRu/C) catalyst. This method has conversion efficiency (62–70%) with no byproducts. In addition, the catalyst is renewable. But butanol, is used as an extracting agent, still needs to be researched for large scale manufacture which one's manufacture on a large scale is still under research. Zhao et al. tested the efficiencies of a series of catalysts to convert sugars to 5-hydroxymethylfurfural (HMF) and found a low energy cost way (shown in Figure 2).

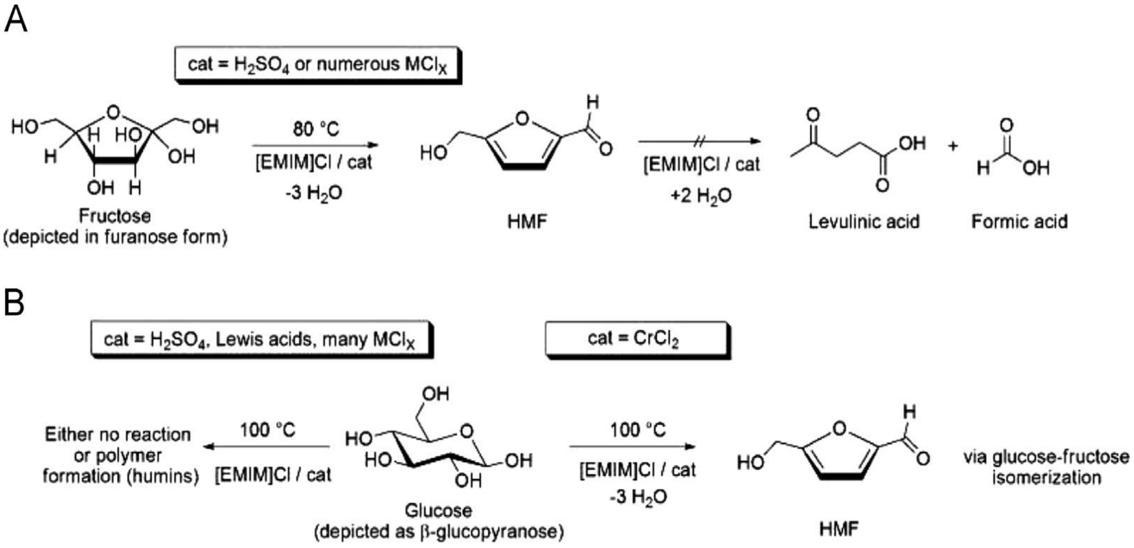

Fig 2: Fructose and glucose conversion to HMF [13, 15]

Among different types of metal halides in 1-alkyl-3-methylimidazolium chloride, chromium (II) chloride was found to possess uniquely high efficiency, with a yield of nearly 70% in terms of the conversion from of glucose to HMF having a yield near 70%. The whole process lasted 3h which may lead to low productivity. Chidambaram et al. discovered that phosphor–molybdic acid, a new kind of catalyst, can help to increase the conversion efficiency up to more than 99% from glucose conversion to HMF even higher than 99% in the ionic liquid with a two-step approach. After this step, 44–47% of the HMF was converted to DMF by a hydrogenation reaction in the presence of Pd/C as catalyst and acetonitrile as the additive. It is worth noting that during the hydrogenation reaction, HMF was firstly converted to MF before the conversion to MFA and finally to DMF via hydrogenation reaction. Shimizu et al. tried to change pressure inside the reactor vessel and presented two simple ways to increase the HMF yield through fructose dehydration in the presence of various solid acid catalysts. One method was by removing water from the reaction mixture with a mild evacuation at 0.97–105 Pa, and it increased the HMF yield with heteropoly acid, zeolite, and acidic resin acting as catalysts. The other method was to reduce the particle (bead) size of the resin (Amberlyst-15). Yong et al. summarized the way to convert sugars selectively to HMF in an NHC-Cr/ionic liquid system, as shown in Figure 3. The conversion efficiency from fructose to HMF can reach at least 96% and glucose 81%. Hu et al. confirmed that the common Lewis acid SnCl4 and [EMim]BF4 system is the best group as a catalyzer to convert glucose to HMF. Even when the concen- tration of glucose is higher than 26%, this method can still obtain high efficiency. Satisfactory results were also obtained when fructose, sucrose, cellobiose, inulin and starch were used as the feedstock. This high efficiency, lower cost, harmless and reusable catalytic system has great potential for application.

4. Conclusion

DMF has an energy density higher by 60 % in volume and by 40% in mass. It consumes only one-third of the energy in the evaporation stage of its production, compared with that required to evaporate a solution of ethanol produced by fermentation for biofuel applications. The most attractive advantage is that making DMF will not compete with land and food, and therefore it can be an ideal candidate for a new generation of sustainable biofuels. It has very similar properties to gasoline with regards to combustion, which means that it can be easily adopted with current spark-ignition engine technologies without the need for major modifications.

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