Recent progress in the development of biofuel 2,5-dimethylfuran

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ABSTRACT

2,5-Dimethylfuran (DMF), which is considered as a promising new generation of alternative fuel, has the potential to relieve the global fossil fuel shortage and air pollution problems. In the last 5 years, the preparation methods, applications, and the oxidation and combustion characteristics of DMF have been studied extensively. Findings have shown that DMF could be produced from renewable biomass in large scale through converting cellulose. DMF has many desirable characteristics that overcome the drawbacks of low-carbon alcohols such as ethanol and n-butyl alcohol. It can be directly used in spark ignition (SI) engine or used after mixing with gasoline. When mixing with diesel, it can be used in compression ignition (CI) engine and the emission of soot can be cut dramatically. Although significant achievements have been achieved so far, some remaining problems need to be researched. Those problems include but are not limited to technologies for large-scale commercial applications of DMF, methods for increasing loads of the oil supply system, ways to reduce the NO_x emission from using DMF, and the detailed combustion mechanism of DMF. Especially, how to reduce the emission of small particles when fueling SI engines with DFM should be given the priority.

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Contents

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1. Introduction

Energy shortages and environmental pollutions remain the two major global problems in recent years. Known as the "blood of industries", oil functions as a pillar of human civilization, yet, large quantities of oil consumption and harmful emissions are detected from automobiles. To break through the dilemma, a series of new concepts and strategies, for emission reduction and combustion efficiency improvement of automobile engine, are proposed by worldwide researchers working for companies, governments, and research institutes. Furthermore, a clean fuel alternation is also a promising way to relieve environment pollution and solve the energy shortage.

The new carbon-based fuel must meet minimum three requirements as below [1]. Firstly, the carbon must be obtained from the atmosphere and the fuel derived from photosynthesis products. In this situation, carbon circulation between air and fuel can be balanced, and problems such as greenhouse gases and energy shortage can be solved simultaneously. Secondly, the fuel must be suitable for effective combustion in internal combustion engines with or without minor modifications. That is to say, the fuel must have physicochemical properties similar to gasoline or diesel fuels which allow it to be used in internal combustion engines and obtain high combustion efficiency, and achieve low emissions. The third, the fuel must be produced effectively and economically.

Since the 1970s, the first oil crisis has impelled many countries to seek alternative energy sources. In the past 40 years, with the development of alternative fuels, bio-ethanol and bio-butanol were researched extensively and deeply [1–6]. Although ethanol, a renewable fuel used in internal combustion engines, is currently produced in large quantities, it is facing many limitations such as low energy density, absorption of water from the atmosphere and high volatility. For every 10 g ethanol produced, 9.6 g biomass is expelled as carbon dioxide and released to the environment during the fermentation process [1]. The stable mixing of ethanol and diesel alone is unachievable, yet with the help of additives, this process can be done. However, ethanol has not been used in diesel engines on a larger scale. For reasons above, ethanol is seen as the first generation biofuel.

In this background, researchers have been trying to find a new generation of renewable fuel for the last 10 years [7–11]. In recent years, butanol fermented from sugar, starch, or crops-converted lignin has drawn much attention. Butanol can be used as fuel in internal combustion engines thanks to its ideal characteristics: (1) butanol has a longer carbon chain than methanol or ethanol, with approximately 21.6% of it consisting of oxygen. The latent heat of butanol is far lower than that of methanol and ethanol. (2) Without the assistance of any additive, butanol can be mixed with diesel or gasoline in any proportion which can be applied to gasoline or diesel engine directly, and phase separation will not occur. (3) The octane number of butanol is close to that of gasoline, and the heat value of butanol is only approximately 9% lower than that of gasoline and diesel. Theories and results from a large number of tests have unveiled the superiority of butanol for fuel as an internal combustion engine fuel but it failed to be used in a large scale due to its high cost of preparation.

Recently, it has been discovered that 2,5-dimethylfuran may be a potential alternative fuel for internal-combustion engines [12]. This is due to the fact that DMF has the potential for mass production. Joseph B. Binder and Ronald T. Raines reported a method of converting lignocellulosic biomass, which is an abundant raw material, to DMF [13]. Tong et al. summarized the methods of DMF production, and concluded that recent progress has achieved high efficiency in the conversion of DMF from biomass [14]. In fact, DMF has long been used as solvent in the perfume and pharmaceutical industries.

In addition, DMF has appropriate physicochemical properties to become a more optimal alternation. The physicochemical properties of DMF, ethanol, n-butanol, gasoline and diesel are listed in Table 1. The properties indicate that DMF is believed to overcome the drawbacks of ethanol and n-butanol.

From Table 1, conclusions can be reached that DMF has higher low heating value which leads to a less fuel consumption in comparison with ethanol and n-butanol. The higher boiling point of DMF than ethanol can help to restrain the vapor lock in the inlet. On the other hand, the lower boiling point of DMF than n-butanol will benefit the cold starting performance when the ambient temperature is low. Compared to ethanol and n-butanol, it is much harder for DMF to absorb water from the air which causes quality deficiency. This is advantageous to the DMF stored in the tank. DMF and gasoline have similar viscosity, which is conducive to the establishment of the injection pressure of DMF in the fuel system, and has a protective effect on the movements of engine fuel system components. The research octane number (RON) of DMF is about 119 [15] which is higher than gasoline.

Compared to ethanol and n-butanol, DMF has a lot of superiorities. However, potential issues for the direct usage of DMF in engine still exist which are listed as follows:

(1) DMF has higher energy density than ethanol and butanol, but lower than gasoline and diesel. To reach the same engine performance, the utilization of DMF as fuel for gasoline or diesel engine requires fuel-rate increases which lead to the load-increase of the oil supply system.

Table 1
Comparison of physicochemical properties of DMF, alcohols and fossil fuels.

Properties	DMF	Ethanol	1-Butanol	Gasoline	Diesel
Molecular formula	C_6H_8O	C_2H_6O	$C_4H_{10}O$		
Molecular mass (g/mol)	96.13	46.07	74.12	100–105	
Oxygen content (%)	16.67	34.78	21.6	0	–
Hydrogen content (%)	8.32	13.02	13.49		
Carbon content (%)	75.01	52.2	64.91		
Stoichiometric air–fuel ratio	10.72	8.95	11.2	14.7	14.3
Liquid density (kg/m³, 20 °C)	889.7	790.9	810	744.6	820
Latent heat vaporization (kJ/kg from 25 °C)	389.1	919.6	707.9	351	270–301
Lower heat value (MJ/kg)	33.7	26.9	33.2	42.9	42.5
Boiling point (°C)	93	77.3	117.25	27–225	180–370
Water solubility (wt%, 20 °C)	0.26	Miscible	7.7	Negligible	
Research octane number	119	110	98	90–100	–
Cetane number	9	8	25	10–15	40–45
Surface tension (mN/m)	25.9	22.3	24.6	20.0 m	
Kinematic viscosity (cSt, 20 °C)	0.57	1.5	3.6	0.37–0.44	
Auto-ignition temperature (°C)	286	434	385	420	246

(2) The molecular structure of DMF, including C=C double bond and ring enol ether, has great potential to generate the soot precursor during combustion.

(3) DMF's toxicity and impact on the environment and its combustion products need to be further studied [16].

In consideration of issues above, based on a series of published theoretical and experimental works concerning DMF's production, the combustion mechanism and application in internal combustion engines, the authors, in this paper, try to summarize the achievements on the potential use of DMF as internal combustion engine fuel and give some suggestion for future analysis.

2. Progress in the preparation of DMF

Global energy shortages and environment pollutions have urged scientists to develop a new generation of technologies that can cheaply synthesize biofuels from renewable biomass [7–9]. 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 [10].
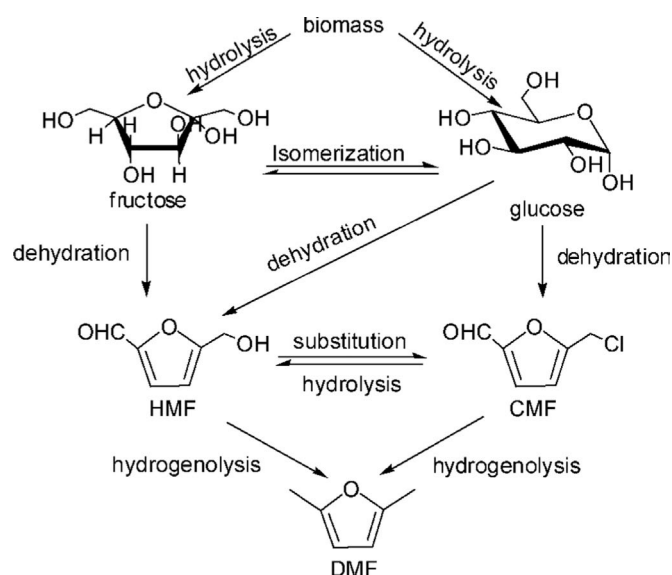

Fig. 1. Pathways of DMF preparation from biomass [12].

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 thousands 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 five to 15 carbon atoms. Thus, the main challenges in transforming biomass to biofuel are molecular miniaturization and the removal of oxygen atoms [11]. Up to now, the main approaches of using biomass to prepare DMF included two ways, as shown in Fig. 1 [12]. 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 [14]. 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.

2.1. Conversion of biomass to DMF with HMF as an intermediate

As a key intermediate in the process of biomass conversion to DMF, HMF has been studied widely in terms of its conversion efficiency. The recent achievements of diversified studies are listed in Table 2.

2.1.1. Conversion of glucose and fructose to DMF

In 2007, Yuriy et al. [15] firstly proposed a promising chemical reaction path for producing 2,5-dimethylfuran from fructose. The schematic is shown in Fig. 2. HCl was used as the catalyzer, and the fructose was converted to HMF with HCl 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. [17] tested the efficiencies of a series of

Table 2
HMF preparation methods by different authors.

| Diluents	Feedstock	Catalyst, amount	T [°C]	t	Yield [%]	Ref
DMA–10 wt% NaBr	Fructose	H_2SO_4, 6 mol%	100	2 h	93	[13]
[EMIM][Cl]	Fructose	$CrCl_2$, 6 mol%	100	3 h	68	[17]
DMSO	Fructose	$FePW_{12}O_{40}$, 0.02 g	120	2 h	97	[18]
DMSO	Fructose	H-BEA zeolite, 0.02 g	120	2 h	97	[18]
DMSO	Fructose	Amberlyst-15-P, 0.02 g	120	2 h	100	[18]
[BMIM][Cl]	Glucose and fructose	$NHC–CrCl_2$, 9 mol%	100	6 h	81	[19]
[BMIM][BF_4]	Glucose	$SnCl_4$, 10 mol%	100	3 h	60	[20]
[BMIM][Cl]	Glucose and Di-/polysaccharides	$CrCl_3$, 10 mol%	100	1 h	67	[21]
			120	5 min	67	
CPL–LiCl	Glucose	$CrCl_2$, 6 mol%	100	3 h	58.7	[22]
[BMIM][Cl]	Glucose and cellulose	$CrCl_3$, 9 mol%	–	1 min	91	[23]
[BMIM][Cl]	Cellulose	$CuCl_2$ and $CrCl_2$, 6 mol%	80–120	1 h	55.4	[24]
[OMIM][Cl]–HCl	Starch	$CrCl_2$	120	2 h	73	[25]
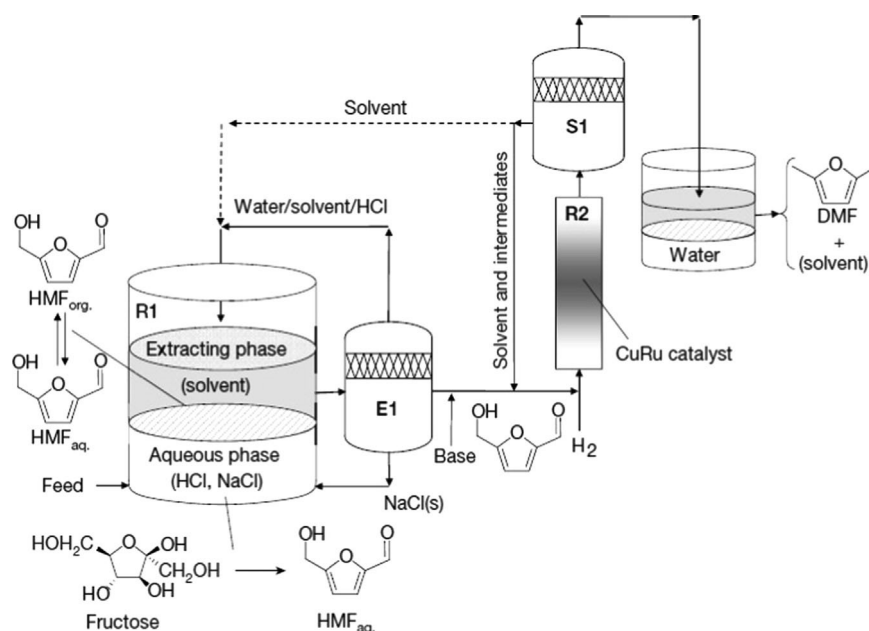
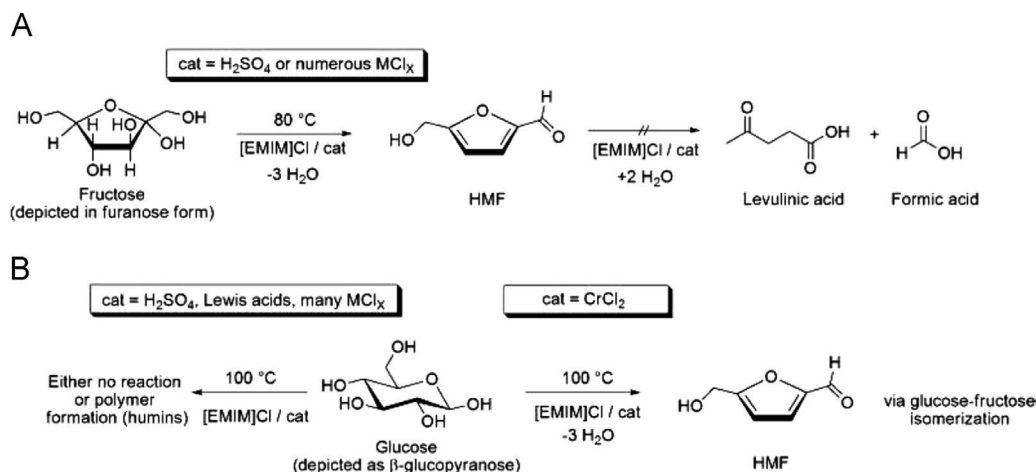**Fig. 2.** Schematic of the process for fructose conversion to DMF [15].

Fig. 3. Fructose and glucose conversion to HMF [17].

catalysts to convert sugars to 5-hydroxymethylfurfural (HMF) and found a low energy cost way (shown in Fig. 3). 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 3 h which may lead to low productivity. Chidambaram et al. [26] 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. [18] 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. [19] summarized the way to convert sugars selectively to HMF in an NHC-Cr/ionic liquid system, as shown in Fig. 3. The conversion efficiency from fructose to HMF can reach at least 96% and glucose 81%. Hu et al. [20] confirmed that the common Lewis acid $SnCl_4$ and [EMim]BF_4 system is the best group as a catalyzer to convert glucose to HMF. Even when the concentration 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.

Moreover, to simplify the conversion process, Thananatthana-chon et al. [27] used a one-step method to convert fructose to DMF in the presence of HCOOH, H_2SO_4, Pd/C and THF in a solution. In a sequence of conversions, fructose was firstly converted to HMF, followed by FMF, HMMF, FMMF and finally to DMF. The DMF was extracted by diethyl ether with total efficiency of approximately 51%. Considering the long reaction time of the above methods, Qi et al. [21] proposed an efficient method to convert glucose to
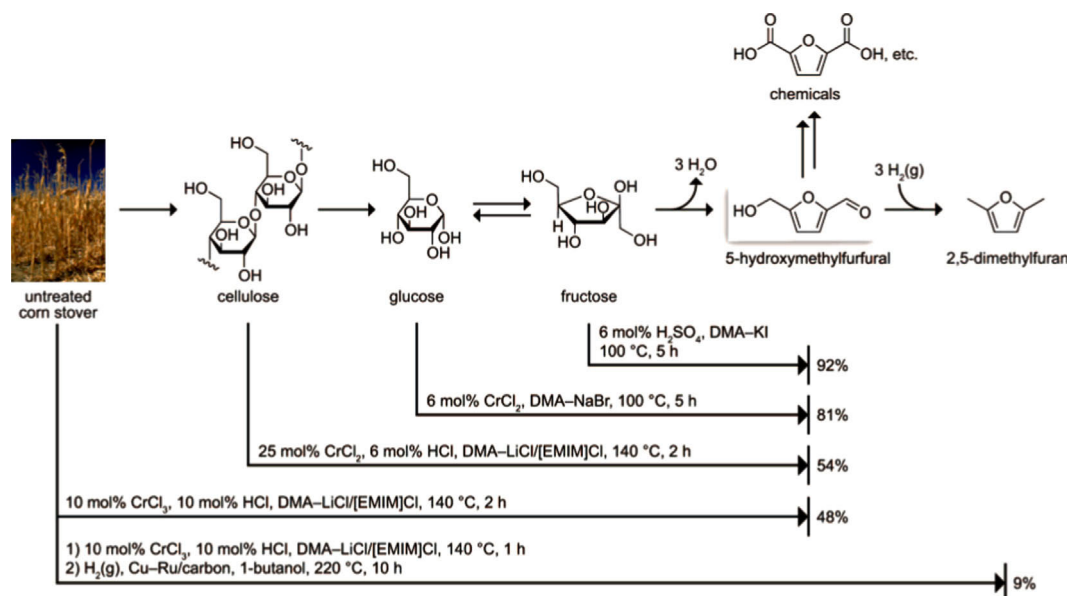
Fig. 4. Comparison of DMF yield through different pathways [13].

5-HMF in the presence of $CrCl_3$ as the catalyst using the ionic liquid 1-butyl-3-methyl imidazolium chloride as the solvent and with microwave heating. A 5-HMF yield of 71% was achieved in 30 s with 96% glucose conversion and microwave heating to 140 °C. Fructose, sucrose, cellobiose, and cellulose were tested, and a 5-HMF yield of 54% were obtained in a 10-min reaction time when the cellulose was used as the feedstock at 150 °C. Chen et al. [22] reported that caprolactam (CPL) containing lithium chloride (LiCl) was a privileged solvent that enabled the synthesis of the renewable platform chemical HMF from purified glucose. Metal halides in CPL–LiCl were used as catalysts, among which $CrCl_3$, $CrCl_2$, $SnCl_4$ and $SnCl_2$ were found to be distinctively effective, leading to a yield of 55–67% from glucose to HMF.

2.1.2. Conversion of cellulose to DMF

In 2009, Binder et al. [13] researched the conversions from lignocellulosic biomass (corn straw, cellulose), glucose and fructose to HMF with different catalyzers in different ion liquids. The efficiencies of each under different circumstances could reach approximately 48%, 54%, 81%, and 92% (shown in Fig. 4). Then, the chlorine ions were removed from the raw material–HMF mixtures by ion exclusion chromatography. Finally, the low purity HMF was converted to DMF by a hydrogenation reaction in 1-butanol solvent with Cu:Ru/C as catalyst. The total yield was 49%. In addition, untreated corn straw as feedstock was used by the authors to convert to DMF in only one step, reaching a yield of 9%. Regardless of the low conversion efficiency, the significance of Binder's work lies in expanding the raw material for the preparation of DMF. Corn straw as the raw material will reduce the dependence of biofuel on food.

In order to improve the conversion efficiency from cellulose to DMF, Li et al. [23] proposed a way to convert cellulose to HMF without separation of sugars. This method provided a new opportunity to transform abundant and inexpensive cellulosic biomass through a non-fermentative process into biofuels and bio-based products. HMF was obtained in 91% and 61% isolated yields in ionic liquids under microwave irradiation in the presence of a catalytic amount of $CrCl_3$. To further simplify the process, Su et al. [24] reported a single-step catalytic process in which the cellulose used as the feed was rapidly depolymerized and the resulting glucose was converted to HMF under mild conditions.

Fig. 5. Cellulose conversion to HMF.

A pair of metal chlorides ($CuCl_2$ and $CrCl_2$) dissolved in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl), at temperatures of 80–120 °C, collectively catalyzed the single-step process of converting cellulose to HMF with an unrefined 96% purity among recoverable products (at a 51–59% HMF yield). Zhang et al. [28] discovered that under relatively mild conditions (140 °C, 1 atm) and in the absence of added acids typically employed as the catalysts in biomass conversion, cellulose dissolved in certain ionic liquids (ILs) had been converted into water-soluble reducing sugars in high total, reducing the sugar yield (up to 97%), or had been converted directly into the biomass platform chemical HMF with high conversion (up to 89%) when $CrCl_2$ was added.

2.1.3. Conversion of starch to DMF

Starch, as an abundant resource, can be utilized in the sustainable production of diverse chemical intermediates such as 5-hydroxymethylfurfural (HMF). Chun et al. [25] presented a simple process of producing HMF from starches in an ionic liquid by using 1-octyl-3-methylimidazolium chloride ([OMIM]Cl) as the

solution and CrCl$_2$ as the catalyst. The addition of HCl and CrCl$_2$ significantly affected the yields of HMF. Eight kinds of starch sources (corn, wheat, rice, potato tuber, sweet potato, tapioca, acorn, and kudzu starch) were tested for the synthesis of HMF. When dissolving the tapioca starch in 0.5 M HCl, the highest yields of HMF (73.0 ± 3.8 wt%) were obtained.

Bredihhin et al. [29] studied the influence of different parameters on the conversion of carbohydrates and biomass into the potential biofuel intermediate 5-bromomethylfurfural (BMF). The optimized conditions avoided the use of lithium salt additives, making this method more economical and environmental friendly compared to previously reported methods. Different wood species and their potential as a raw material in BMF and furfural production had also been evaluated. In addition, a very simple and efficient procedure for the conversion of 5-hydroxymethylfurfural (HMF) into BMF or 5-chloromethylfurfural (CMF) was reported by the authors.

2.2. Conversion of cellulose and starch to DMF with CMF as an intermediate

In 2008, Mascal et al. [26] dissolved cellulose and glucose in concentrated HCl before using 1,2-two ethyl chloride to extract CMF. Afterwards, CMF was converted to DMF with Pd/C as the catalyst, as shown in Fig. 5. Recently, Mascal et al. [30,31] reported a new but possibly very valuable biomass-derived platform, 5-chloromethylfurfural (CMF). They stated that not only glucose, sucrose, and cellulose but also raw biomass (such as cotton, wood, corn, straw and stover) could be converted into CMF in high yields. It was predicted by the authors that CMF may emerge as the central intermediate in the conversion of carbohydrate-based material into useful organic commodities. Mascal et al. not only demonstrated the conversion from CMF to the biofuels 5-ethoxymethylfurfural (EMF) or ethyllevulinate (EL) in alcohol, but also studied the conversion technologies applied to convert CMF into HMF or LA in water.

Compared to ethanol, DMF is a better renewable fuel to replace gasoline in the near future. Various chemical pathways for biomass including glucose, fructose, starch, cellulose converted to DMF with high efficiencies have been put forward. The preparations of two key intermediates HMF and CMF are discussed in details. However some obvious shortcomings of technologies mentioned above remain. One example is the method put up by Atsushi et al. [18]. Although the yield of HMF can be even higher than 90% at 120 °C within 10 min, the preparation of solid acid catalysts is complex. And the pathway proposed by Gen Yong et al.

[19] which can convert fructose to HMF with yields even higher than 95% and 80% with glucose, yet requires the reaction mixture being kept at 100 °C for 6 h. And HMF needs be extracted three times. Further study is needed to explore a method with reasonable energy input and considerable output efficiency. It is worth noting that the usage of non-food biomass for the DMF production can avoid the conflicts over food supply and land. The progress put forward by Mascal et al. that converts cellulose to DMF can be appealing. Concerning the long reaction time and the concentrated HCL use, the development of a more effective catalyst and new solvent is necessary. By the way, to make the mass production possible, the effective separation and purification technology are urgently needed.

3. Application of DMF in internal combustion engines

As mentioned above, DMF has the appropriate physicochemical properties to be used as a new type of biofuel in internal combustion (IC) engines. In addition, many new achievements described in Section 2 have made it possible to produce DMF in huge quantities. The application of DMF in internal combustion engines has been deeply researched by many researchers in recent years. DMF can be mixed with gasoline and diesel steadily at any ratio without the help of additives, and the spray characteristics of DMF [32] and 2-MF [33] are similar to those of gasoline. Therefore, many researchers have studied the combustion and emission characteristics of pure DMF, DMF/gasoline mixtures, DMF/diesel blends in gasoline and diesel engines, respectively.

3.1. The application of pure DMF in gasoline engines

As described, DMF has a slightly lower yet comparable energy density (31.5 MJ/L) than gasoline and a higher research octane number (approximately 119), which means it can offer better anti-knock qualities. Hu and his co-workers analyzed the lubricity of DMF and found that DMF had better anti-wear effects than gasoline [34]. All of the characteristics listed above show that pure DMF can be ignited by a spark and directly used as fuel in direct injection spark ignition (DISI) engines.

Daniel et al. [35] compared the different effects of DMF, ethanol and gasoline on the optimum ignition timing (MBT/KL-MBT timing) with a four valve four stroke DISI engine. Because DMF and ethanol have higher RON and stoichiometric heat of vaporization than gasoline (better effect of cooling the inlet air), engines fueled with DMF or ethanol were less likely to exhibit engine knock than fueled with gasoline. The MBT/KL-MBT spark timings of DMF and ethanol were earlier than the spark timings with
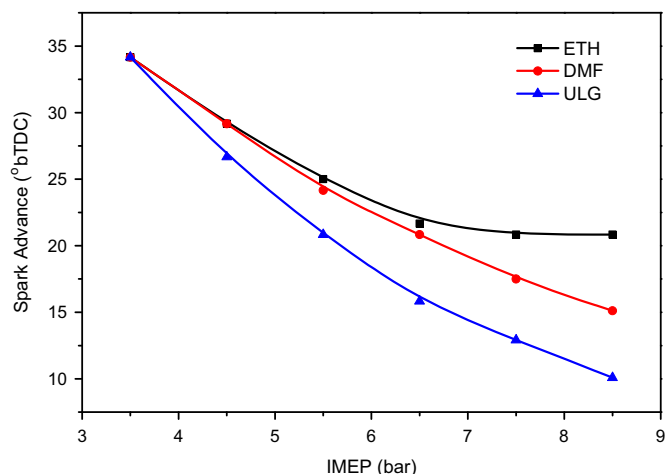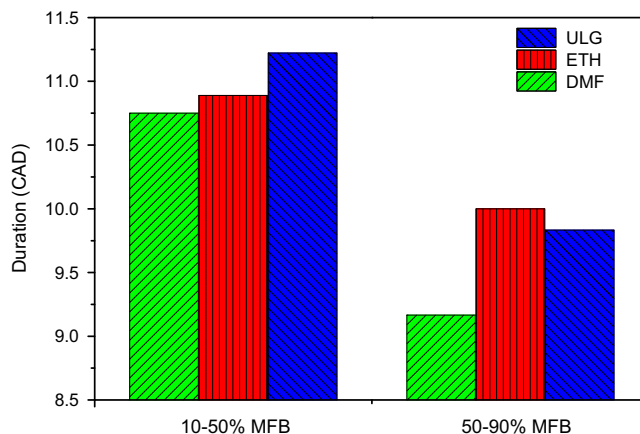

Fig. 6. Ignition timing of different fuels [35].

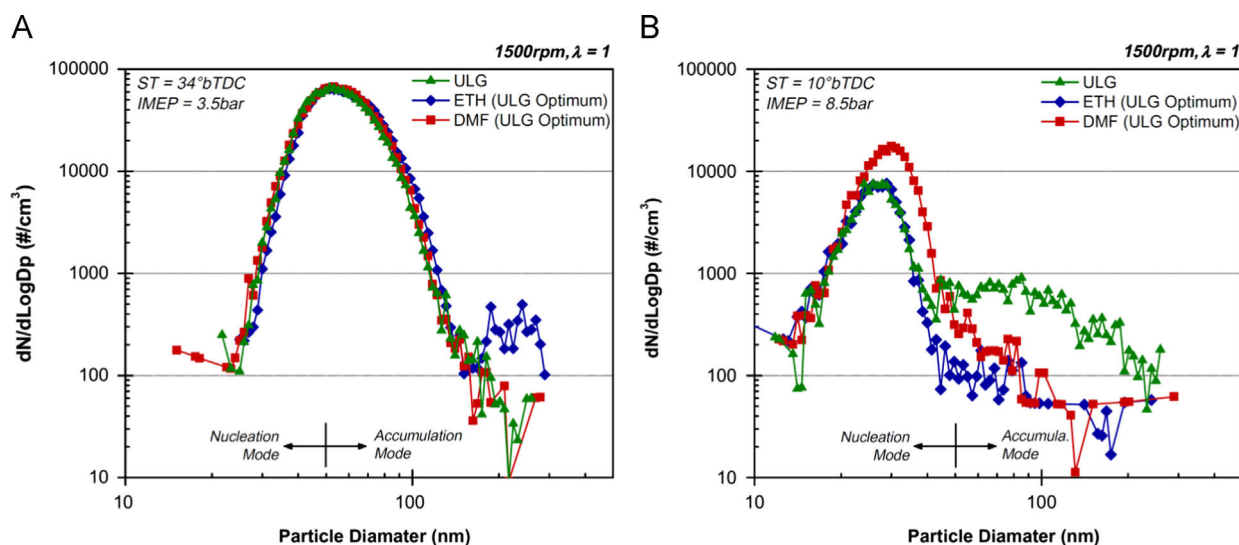**Fig. 7.** Combustion rate of DMF ethanol and gasoline [35].

Fig. 8. Characteristics of the particles of DMF ethanol and gasoline [35].

gasoline, as shown in Fig. 6. However, when fueled with DMF and IMEP was very high, the early spark timing would lead to engine knock. When adopting MBT/KL-MBT spark timings, the fuel consumptions of DMF and ethanol are larger than gasoline due to their lower energy density. With regard to the indicated thermal efficiency, when MBT/KL-MBT spark timings are adopted under a low load, the indication thermal efficiency of DMF is lower than that of gasoline and ethanol. With an increase in the loads, there is a trend suggesting that the indication efficiency of DMF will be higher than that of gasoline. From the view of combustion efficiency, the combustion efficiency of ethanol is higher than DMF which is higher than gasoline. This was partly due to the molecular oxygen content in ethanol and DMF. Under the condition of stoichiometric equivalence, the combustions of ethanol and DMF were more desirable. This phenomenon also leads to higher maximum cylinder pressure and higher maximum combustion temperature, with DMF possessing the highest one. The higher maximum combustion temperature would lead to a higher heat transfer loss. Combining these findings with DMF's higher bump loss leads to the indicated thermal efficiency being 1–2 percentage points lower than that of gasoline. However, under the same IMEP, with DMF or ethanol as the fuel, the engine will obtain more torque output than with gasoline due to the higher maximum cylinder pressure DMF and ethanol have. Under the condition of optimum ignition timing, the combustion durations (CA10–CA90) of DMF and ethanol were much shorter than with gasoline. This result shows that under the condition of optimum ignition timing, the flame propagation speed of DMF and ethanol are accelerated. A detailed comparison of the different fuels CA10–CA50 and CA50–CA90 is presented in Fig. 7. The conclusion can be reached that the differences of the combustion reaction rate among DMF, ethanol and gasoline will expand in the second half reaction.

Because the DMF–air mixture burns fast, the maximum pressure and maximum temperature in the cylinder are higher than they are with gasoline. The fast burning speed brings more concentrated heat release, which results in a higher temperature and finally leading to higher NO_x emissions in combustion products than gasoline or ethanol. The HC emissions in the combustion products of DMF are a little lower than gasoline but higher than ethanol which is mainly due to DMF's higher combustion temperature and molecular oxygen content. By comparing the HC emissions of ethanol and DMF, the conclusion that an increase in the proportion of molecular oxygen content brings lower HC

emissions can be reached. However, the CO emissions of DMF are higher than ethanol and gasoline.

Fig. 8 compares the concentration distribution curves of various diameter particles in the exhaust gas [35,36]. At low load (IMEP 3.5 bar), the particle distributions in the different fuels' exhaust gases are basically the same. There are some small differences in the size regions below 20 nm and above 150 nm. The combustion products of ethanol and gasoline contain almost no particles sized below 20 nm. In contrast, the DMF combustion products contain particles below 20 nm in diameter in a concentration of approximately 100–200 particles/cm³. In the region above 150 nm in diameter, the concentration of particles in ethanol exhaust gas is higher than in gasoline or DMF exhaust products. In comparison with the low load, under high load (IMEP 8.5 bar), more particles below 50 nm in diameter are generated by the nucleation mode from the main part of the exhaust products. There is an obvious difference among the concentration distribution curves of ethanol, DMF and gasoline in the number of particles with sizes above 50 nm. DMF produced smaller mean diameter sized particles than gasoline which is partly due to the higher droplet surface tension and viscosity of gasoline than those of DMF and alcohol.

2-Methylfuran (MF) is another main product from the dehydration and hydrogenolysis process of fructose. Wang et al. [37] analyzed the combustion and emission characteristics of MF, DMF, ethanol and gasoline with a spray guide DISI engine under IMEP conditions, ranging from 3.5 to 8.5 bar and adapting to the MBT/KL-MBT spark timings of the different fuels. They found that MF and DMF had similar anti-knock effects, but the combustion characteristics of MF were obviously different from those of DMF. Under the experimental conditions, the indicated thermal efficiency of MF was approximately 3% higher than DMF and gasoline. MF had significant reductions in the engine emissions of formaldehyde and acetaldehyde. Compared to gasoline, the emission of formaldehyde can be cut down to approximately 20% and acetaldehyde cut down to 40%.

Ritchaite et al. [38] researched the ignition timing sensitivities of pure DMF compared to gasoline and ethanol. The conclusion was that DMF's ignition timing sensitivity was less than gasoline but more than that of ethanol. Moreover, they also found that DMF could reach high exhaust gas temperature and could be a type of good cool-start fuel which means a smaller reduction in IMEP compared to gasoline when retarding the fuel injection timing at the same crank angle. Furthermore, the authors researched the
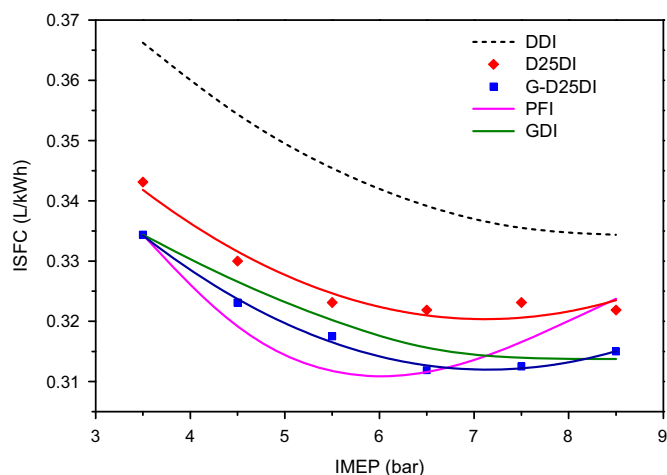
Fig. 9. Fuel consumption rate for different fuel supplying strategies [42].

hydrocarbon and carbonyl emissions of DMF [39]. Approximately 12 carbonyls yet less than that with gasoline were detected in the exhaust of DMF, including formaldehyde, acetaldehyde, benzaldehyde and so on. The HC emission of DMF was governed by unburned DMF.

3.2. The application of DMF/gasoline blends in gasoline engines

Given that the physicochemical properties of DMF are different from those of gasoline in some respects (e.g., vapor pressure, distillation and so on), blending DMF with gasoline will change the total physicochemical properties of the mixtures. Earl Christensen et al. [40] researched the physicochemical properties of the mixture. Blending DMF would decrease the vapor pressure and density of the blends but increase the viscosity. DMF can also improve the blends' octane number, but, its influence on the distillation temperatures and the extraction of water from air can be neglected.

David et al. [41] deeply researched the anti-knock properties of DMF–gasoline blends and ethanol–gasoline blends. The study included DMF/gasoline blends of 5%, 10%, and 15% DMF by volume, an ethanol/gasoline blends with 10% ethanol by volume and an ethanol/DMF blend with 10% ethanol and 10% DMF by volume. The amounts of different fuels injected into the cylinder were calculated to roughly ensure the same total energy release in the cylinder. This leaded to the indicated mean effective pressures of the different mixtures to be basically stabilized at a constant value when fueled with different blends. The authors found that when the spark time was −20 °CA ATDC and fueled with gasoline, obvious knocking occurred. However, no knocking was observed when fueled with DMF/gasoline blends or ethanol/gasoline blends. When the spark time was −25 °CA and fueled with gasoline, the knocking became extremely severe for the engine. Slight knocking occurred when fueled with DMF5. There was no distinctive difference between the knock suppression properties of DMF10 and DMF15. E10 had a better anti-knock property than DMF10 and DMF15. This result is mainly due to the latent heat of ethanol which is higher than that of DMF.

Based on the improved engine performance when fueled with DMF/gasoline blends, Ritchie Daniel et al. [42] researched the combustion performance of DMF blends using dual-injection compared to direct-injection in a SI engine. The differences in performance were examined using D25 (25% DMF in gasoline, by volume) in a single cylinder SI engine operating at 1500 rpm with varying load (3.5–8.5 bar IMEP). All tests were carried out at stoichiometry. To reach the highest volumetric efficiency and

homogeneity, an early start of the injection (SOI) timing (280 BTDC) was adopted. The comparison of the indicated specific fuel consumption with varying loads between D25 in DI (D25DI) and dual-injection (G-D25DI), neat DMF in DI (DDI) and gasoline in PFI and GDI is shown in Fig. 9. From Fig. 9, and conclusion can be reached the ISFC of G-D$_{25}$DI is lower than that of GDI when the load is less than 7.5 bar. When the load is higher than 7.5 bar, there is a trend that the ISFC of G-D$_{25}$DI would be higher than that of GDI. Wu et al. [43] also proved that the dual-injection strategy is advantageous at lower PFI fractions and higher MAPI.

3.3. The application of DMF/diesel blends in diesel engines

Zhang et al. [44] studied the DMF/diesel blends combustion properties with a diesel engine. The ignition delay of the fuel can be adjusted by mixing high octane number fuel and high cetane number fuel at a certain ratio. The ignition delay increase can drive the mixing of oil and gas, which significantly reduces the amount of soot generated by the diffusion combustion. DMF is a type of high octane fuel and has a very high potential in this area. The authors compared the ignition delay of different proportions of DMF–diesel blends and gasoline–diesel blends under different EGR rates. The start of injection (SOI) timing was 6 °CA BTDC. The authors found that DMF–diesel blends and gasoline–diesel blends affected to extend the ignition delay. Additionally, the ignition delay of DMF–diesel blends was longer than that of gasoline–diesel blends (shown in Fig. 10). When fueled with DMF20 and with an EGR rate of 0, the ignition delay was 1 °CA longer than pure diesel. This trend was further strengthened with an increasing EGR. When the ratio of EGR reached 40%, the ignition delay was extended by approximately 5 CAD. When the DMF percentage reached 40% by volume, the ignition was further delayed. For 0 EGR, the ignition was delayed for 3 °CA. When the EGR rate was up to 25%, the ignition delay increased rapidly. For EGR rates of 35% and above, the ignition delays were too long, and there was a risk of misfire.

Chen et al. [45] studied the combustion and emission characteristics for a diesel engine fueled with DMF/diesel, n-butanol/diesel and gasoline/diesel blends. Zhang et al. [46] blended the 2-ethylhexyl nitrate (EHN) into D40 as an additive. The mixture of EHN and D40 can shorten the ignition delay and reduce soot emission, but the combustion noise was lower than D40 and the NO$_x$ emissions increased slightly.

Based on aforementioned reviews, it is found that these researches cover various types of fuel supply strategies, from port injection to direct injection, from pure DMF to DMF/fossil-fuel
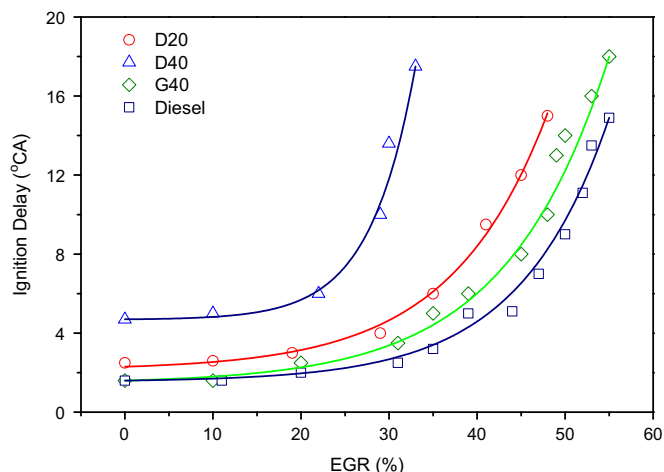

Fig. 10. The ignition delay of the blends at different EGR rates [44].

blends. In addition, dual-injection is also investigated. All these studies reveal some common characteristics:

(1) The application of DMF in SI engines. Due to the high octane number of DMF and the comparable energy density to gasoline, DMF can be directly used in SI engine. DMF has better knock suppression ability and burns faster than gasoline. When using MBT/KL-MBT timings of different fuels, DMF has lower initial and final combustion duration than gasoline which leads to higher max pressure rise of DMF than gasoline. DMF combustion efficiency is higher than gasoline, but lower indicated thermal efficiency. This is partly due to the higher combustion temperature of DMF and more thermal energy losses during the cylinder wall heat transfer. The HC emissions of DMF are dominated by unburned fuel. And the total carbonyl emissions of DMF are lower than gasoline. DMF produces lower emissions of the more harmful formaldehyde and acetaldehyde than gasoline. The NO_x, CO emissions of DMF are similar to those with gasoline. DMF produced smaller mean diameter sized particles than gasoline. The total mass of PM for DMF is lower than gasoline.

(2) The application of DMF in CI engines. For CI engine, it is very difficult to ignite by using pure DMF due to its higher octane number. The current studies focus on the combustions and emissions of DMF/diesel blends. Compared with neat diesel, DMF/diesel blends have longer ignition delay thanks to the lower CN, which leads to a faster burning rate and higher max pressure rise rate. With diesel as additive, DMF has small effects on NO_x, THC and CO emissions and BSFC, but greatly reduce soot emissions. When the fraction of DMF is up to 40% by volume, soot emissions are close to zero. With the increase of DMF fraction, the indicated thermal efficiency goes up slightly.

(3) Future directions. Due to the similar physicochemical properties of DMF and gasoline, DMF can be used in SI engine as fuel directly with few optimizations. And when fueled with DMF, the ignition timing can be advanced so as to obtain higher max cylinder pressure and higher thermal efficiency. Due to the lower energy density of DMF than gasoline and diesel, the fuel supply system load needs to increase so as to match the engine performance when fueled with DMF. When blended with diesel and injected directly into cylinder, the ignition delay of mixture would be enlarged due to DMF's molecular oxygen and high octane quality, thus, the soot emissions would be significantly inhibited. With EGR and mixed DMF conditions, it is expected to realize NO_x and soot emissions reduction at the same time. The present researches on DMF focus on pure DMF or DMF/gasoline blends combustion with the traditional gasoline combustion mode and DMF/diesel blends combustion with the traditional CI mode. In the follow-up study, in order to further highlight the physicochemical properties of DMF, pure DMF or DMF/gasoline-like-fuel blends or DMF/diesel-like-fuel blends can be researched in HCCI or LTC engines.

4. The oxidation and combustion kinetics of DMF

A thorough understanding of DMF's combustion mechanism is very important for the utilization of this type of biofuel in internal combustion engines. Many groups have researched the combustion mechanism of DMF in different ways. The main method is to apply ab initio to calculate the characteristic parameters of DMF, such as enthalpy; detecting the intermediates of the thermal decomposition of DMF; analyzing the laminar burning velocities; measuring the ignition delay of DMF ignited in a shock tube; and detecting the intermediates of the premixed laminar flame using tunable synchrotron photoionization.

4.1. Studies of the thermal chemical parameters of DMF

The DMF oxidation and combustion process generates many intermediates and final products. To accurately obtain the chemical kinetics parameters, data about the standard enthalpy of formation of DMF and different intermediates and the C–H, C–O, and C–C bond energies of different materials are needed. Ab initio quantum chemistry methods are based on quantum chemistry and can accurately calculate above-mentioned parameters by computers. John and his co-workers studied the decomposition of DMF using ab initio methods [47]. They calculated the reaction enthalpies of different types of reactions, including bond scission, formation of carbenes, methyl radical addition to O=CXY, H abstraction by OH, H-abstraction and addition reactions. They noted that it was most likely wrong to assume the formation of 2-ethenylfuran as a C_6H_6O intermediate in rich DMF flames. C_6H_6O can be isomeric 2,5-dimethylene-2,5-dihydrofuran. David et al. [48] used high-level ab initio methods to calculate the total atomization energies and enthalpies of formation of 2,5-dimethylfuran, 2-methylfuran, and furan. The final $\Delta fH°$ (298.15 K) values, with the available experimental values in parentheses, are furan -34.8 ± 3 (-34.7 ± 0.8), 2-methylfuran -80.3 ± 5 (-76.4 ± 1.2), and 2,5-dimethylfuran -124.6 ± 6 (-128.1 ± 1.1) kJ mol^{-1}.

4.2. DMF laminar flame velocities

The laminar burning characteristics are the important physicochemical properties of a combustible mixture. The properties are highly related to diffusivity, heat release, and the kinetic mechanism of DMF. The key parameters of the laminar burning flame are the laminar burning velocity Sn, stretch rate α, Markstein length L_b and the unstretched laminar burning velocity u_1. The Markstein length L_b is highly related to the flame stability. A positive L_b means that the flame is stable, and the diffusional–thermal effect on the flame front is neglected. In contrast, a negative L_b indicates that the flame is unstable due to the diffusional–thermal effect. The unstretched laminar burning velocity u_1 has a strong connection with the spark ignition stability of the flame when the fuel is used in an engine.

Wu et al. [49] researched the laminar burning velocities and Markstein lengths of 2,5-dimethylfuran (DMF)–air–N_2/CO_2 premixed mixtures at atmospheric pressure and at an initial temperature of 393 K. Three different dilution ratios were obtained by using an outwardly propagating spherical flame and a high-speed schlieren photograph system. It was found that the unstretched flame propagation was highly affected by the diluent percentage and diluent gas types. Larger diluent percentages led to lower laminar burning velocity and higher flame stability. In comparison with N_2, CO_2 had greater influences on the laminar burning velocity and Markstein length. In addition, the air–fuel ratio affected the flame deeply. A fuel-lean mixture has a better flame stability than a fuel-rich mixture. It is interesting that there is a linear correlation between the diluent ratio Φ_r and the laminar burning velocity. Moreover, the author further evaluated the effects of the initial temperature, pressure on the laminar burning velocities and Markstein lengths [50,51]. With the initial pressure held constant at 0.1 MPa and the initial temperature increased from 393 K to 473 K, the unstretched flame propagation speed and laminar burning velocity were increased. The unstretched flame propagation speed and the laminar burning velocity both peak near the equivalence ratio of 1.2. With an increase in the initial temperature, the unstretched flame propagation speed and the laminar burning velocity were increased. The Markstein length of

DMF–air mixtures increased with decreasing equivalence ratio and initial temperature. In contrast, when increasing the initial pressure from 0.1 MPa to 0.75 MPa while maintaining a constant initial temperature at 393 K, the unstretched flame propagation speed and laminar burning velocity were decreased.

In addition, given that DMF is usually partly substituted for gasoline and diesel, the flame propagation speeds of the DMF–gasoline blend and DMF–diesel blend at different proportions are very important. Therefore, Tian et al. [52] firstly compared the laminar burning velocities of DMF, ethanol and gasoline under different initial temperatures and pressures. Ethanol had the fastest burning velocity, and the burning velocity of DMF was closer to that of gasoline. The laminar burning velocity of gasoline was a little faster than that of DMF (within 10%). Soon afterward, Wu et al. [53] researched the laminar burning velocities of DMF–isooctane blends. They used 20% DMF and 80% isooctane in volume as fuel. When the equivalence ratio was greater than 1.2, 20% DMF had a positive effect on the laminar burning velocities. However, when the equivalence ratio was less than 1.2, the laminar burning velocity of D20 was lower than it was with pure isooctane. Li et al. [54] took different ratio blends of DMF and isooctane as fuels, including D00, D10, D20, and D30. Additionally, with an increase in the DMF ratio, the flame stability was increased. This result means DMF can be a good alternative fuel or additive to gasoline to improve the flame stability.

4.3. Studies of the pyrolysis mechanism of DMF

The pyrolysis of rich fuel at high temperatures plays a very important role in the formation of soot during the actual fuel combustion. There are two main ways to analyze the thermal decomposition characteristics of DMF. One way is by detecting the intermediates created during the reaction. Based on the qualitative or quantitative detection of intermediates, the mechanism can be inferred. The other method is based on software such as Gaussian-09. The energy changes of reactions can be computed by a computer. Through analyzing the energy changes, the mechanism can be inferred.

Grela et al. [55] used a heatable molecular flow reactor to research the very low pressure pyrolysis of DMF. The unimolecular decomposition of DMF occurred at a temperature between 1050 K and 1150 K in a pressure of 1 mTorr. The authors detected two different types of C_6H_6O as intermediates. They proposed an isomerizing reaction to explain this condition. Through ab initio quantum chemistry methods, Simmie et al. [47] discovered the DMF pyrolysis first in the broken C–H methyl side, resulting in the formation of β- and R-carbenes via 3,2-Hand 2,3-methyl shifts, respectively. Once the furan ring opens, demethylation leading to the production of highly unsaturated species, such as allenylketenes, appears to be a feature of this chemistry. H-atom addition to 2,5-dimethylfuran followed by methyl elimination was shown to be the most important route to the formation of the less reactive 2-methylfuran.

Lifshitz et al. [56] studied the thermal decomposition of 2,5-dimethylfuran with reflected shock waves over the temperature range of 1070–1370 K and at overall densities of $\sim 3 \times 10^{-5}$ mol cm^{-3}, corresponding to pressures from 2 to 3.7 bar. A large number of products resulting from unimolecular cleavage of the ring and consecutive free radical reactions were obtained under shock heating, including CO, acetylene (C_2H_2), methane (CH_4), vinylacetylene (C_4H_4), ethylene (C_2H_4), and ethane (C_2H_6), among others. The authors assembled a reaction scheme consisting of 50 species and some 180 elementary reactions, with the majority of the kinetic and thermochemical parameters being estimated. Unlike the isomerizing reaction proposed by Grela et al. [55], Lifshitz et al. [56] proposed the migration of the methyl

group from C(2) to C(3). Moreover, the H-abstraction from methyl was very important before a type of primary product 5-methyl-2-furanylmethyl radical was formed.
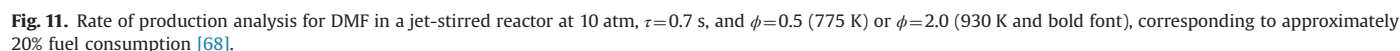
Marko Djokic et al. [57] studied the thermal decomposition of 2,5-dimethylfuran in a bench-scale pyrolysis setup equipped with a dedicated online analysis section including a GC × GC-FID/(TOF-MS). The reactor temperature varied from 873 K to 1098 K at a fixed pressure of 1.7 bar with a residence time of 300–400 ms. The main products at low conversions were hydrogen, CO, methane, phenol, 2-methylfuran, 1,3-cyclopentadiene and a $C_7H_{10}O$ isomer. At higher conversions, increasing amounts of mono- and poly-aromatics, such as benzene, toluene, indene and naphthalene, were formed. At the highest temperatures, more than 10 mol% of 2,5-dimethylfuran was converted into mono-, di-, tri- and tetra-aromatic products, which were known as soot precursors.

Baptiste Sirjean and his co-workers studied the thermal decomposition of the 5-methyl-2-furanylmethyl radical, which is considered to be the most important primary product formed by hydrogen abstraction from DMF [58]. By comparing the barriers of different reactions, the main pathway of DMF decomposition was obtained. First, the ring rupture reaction of R1 leads to the formation of R2 which then is converted to R3 by H-atom shift reaction. Because of the ring strain energy in the structure of R3, the most favorable pathway for R3 to form R4 was via ring enlargement. There were three different main decomposition pathways for R4. The first channel was the breaking of the C–H bond to form R5. The second channel was an H-atom shift in R4 to form R6. The third channel was the reaction that formed R9. The whole decomposition pathway led to the formation of annular hydrocarbon oxidations. These annular hydrocarbon oxidations may lead to the formation of soot. Recently, Baptiste Sirjean et al. [59] analyzed the unimolecular decomposition of DMF at the CBS-QB3 level of theory. A large number of pathways were explored: initial C–H bond fission, biradical ring opening, and H-atom and CH(3)-group transfers involving carbene intermediates. It was shown that the unimolecular decomposition of DMF was dominated by two product channels. For typical combustion conditions, the major product channel ($\sim$70% at 1500 K and 1 bar) was reached by a 3,2-hydrogen transfer in DMF, leading to a carbene intermediate that rearranges to hexa-3,4-dien-2-one, which in turn decomposes into CH(3)CO and C(4)H(5) by initial C–C bond fission. In contrast with previous studies, the initial C–H bond fission in DMF had not been found to be the major decomposition channel ($\sim$30% at 1500 K and 1 bar). Below atmospheric pressure, initial C–H bond cleavage yields increased, while CH(3)CO+C(4)H (5) branching ratios decreased.

4.4. Studies of the oxidation mechanism of DMF

To assess the potential of DMF as a gasoline replacement or additive, a validated detailed kinetic model for the oxidation of DMF is required. Such a model, when incorporated into computational fluid dynamics (CFD) simulations, will enable the predictive assessment of DMF's influence on engine performance. Therefore, in recent years, the oxidation mechanisms of DMF, MF and F have been studied by many researchers under different flame conditions, pressures and temperatures [60].

Tian et al. [61] researched the premixed laminar flame of furan at the equivalence ratios of 1.4, 1.8 and 2.2 with the VUV ionization in combination with MBMS at low pressure (35 Torr). They measured the mole fraction profiles of approximately 40 types of major reactants, intermediates and end matters, including furan; O_2;Ar; H_2; H_2O; CO and CO_2; C1–C3 species, including methane (CH_4), acetylene (C_2H_2), the propargyl radical (C_3H_3), and the allene (aC_3H_4) ethylene (C_2H_4) propyne (pC_3H_4) allyl radical (C_3H_5); C4–C7 species, including 1,2,3-butatriene/vinylacetylene

Fig. 11. Rate of production analysis for DMF in a jet-stirred reactor at 10 atm, $\tau = 0.7$ s, and $\phi = 0.5$ (775 K) or $\phi = 2.0$ (930 K and bold font), corresponding to approximately 20% fuel consumption [68].

(C_4H_4), 1,3-butadiene (C_4H_6), 1,3-cyclopentadiene (C_5H_6), 1,3,5-hexatriyne (C_6H_2), and the benzene (C_6H_6) diacetylene (C_4H_2) cyclopentadienyl radical (C_5H_5); and toluene (C_7H_8). A dynamics mechanism consisting of 206 species and 1368 elementary reactions was constructed. Furan was consumed mainly by metatheses, resulting in furyl radicals; by OH addition to the double bond of furan, resulting in 2-propenal and CH=CH–CHO radicals by scission; and by isomerization, forming formylallene via 1,2-hydrogen migration. Benzene was formed mainly by isomerization of fulvene that came from the combination of the propargyl radicals. A sensitivity analysis indicated that the reaction furan $CH_2CCHCHO$ had a strong promoting effect, while the decomposition of $CH_2CCHCHO$ to CO and pC_3H_4 in flame with $\Phi = 1.4$ and of $CH_2CHCHCHO$ to CO and C_3H_5 radical in flame with $U = 2.2$ had strong inhibiting effects on furan decomposition. Under pyrolysis conditions, the major decomposition products of furan were $CO + pC_3H_4$ and $C_2H_2 + CH_2CO$. Moreover, the present rate constants of furan dissociation at high pressures based on ab initio calculations were in line with previous experimental measurements and calculations. In addition, Wei et al. [62] used the reflected shock tube to measure the ignition delay of furan at elevated pressures (1.2–10.4 atm) for the mixtures with equivalence ratios of 0.5, 1.0, and 2.0 and furan concentrations of 0.25%, 0.5% and 1% diluted in argon.

Since the DMF generation process also produces MF, the combustion mechanism analysis of MF would be helpful in gaining a deep understanding of the combustion progress of DMF. Therefore, Wei et al. [63] detected the combustion intermediates in low pressure premixed laminar 2-methylfuran (MF)/oxygen/argon flames with equivalence ratios of 0.8 and 1.5 using tunable synchrotron vacuum ultraviolet photoionization and molecular beam mass spectrometry. By H abstraction, MF can be consumed and mainly converted into 2-furylmethyl. Then, 2-furylmethyl can further be consumed by oxidation, H abstraction, and radical combination reactions. Furfural is generated from the oxidation of 2-furylmethyl. H abstraction of 2-furylmethyl leads to the formation of (Z)-1-oxo-1,3,4-pentatriene. By radical addition, MF can also be consumed. H addition leads to the formation of 1-oxo-1,3-butadiene. OH addition leads to the formation of 2-oxo-2,3-dihydrofuran, 2-oxo-2,3-dihydro-5-methylfuran, and

(1E,2Z,3Z)-4-oxo-2-pentenal. CH_3 addition leads to the formation of 2,5-dimethylfuran.

Somers et al. [64] researched the ignition delay time for the promising biofuel 2-methyl furan (2 MF) at equivalence ratios of 0.5, 1.0 and 2.0 for mixtures of 1% fuel in argon in the temperature range of 1200–1800 K at atmospheric pressure. Laminar burning velocities were determined using the heat-flux method for mixtures of 2 MF in air at equivalence ratios of 0.55–1.65, initial temperatures of 298–398 K and atmospheric pressure. A detailed chemical kinetic mechanism consisting of 2059 reactions and 391 species has been constructed to describe the oxidation of 2 MF and was used to simulate the experiment. The reactions of hydrogen atoms with the fuel are highlighted as important under all experimental conditions studied, with abstraction by the hydrogen atom promoting reactivity and addition of the hydrogen atom to the furan ring inhibiting reactivity.

Wu et al. [65] studied the intermediates formed during the oxidation of 2,5-dimethylfuran, in a low pressure premixed laminar flame, by tunable vacuum-ultraviolet photoionization and molecular beam mass spectrometry, and Wu provided isomer specific qualitative (and in some cases quantitative) analysis of both stable and transient species. In the case of fuel-rich 2,5-DMF flames, the authors detected a large number of compounds ranging from the methyl radical to 2-methylnaphthalene. Some of the intermediates were identified by comparing computed ionization energies, most likely from G3 calculations but with a 6-311++G(2d,p) basis set, with those measured experimentally. In addition, the authors also researched bond dissociation energies, computed in an unspecified manner, of 535 kJ mol^{-1} for the ring methyl group, 531 kJ mol^{-1} for the ring C–H bond and 370 kJ mol^{-1} for the same bond in the methyl side chain. Jiao et al. [66] utilized electron impact ionization combining with Fourier transfer mass spectrometry to research the five major product ions of DMF in the energy range of 10–200 eV: the parent ion C_6H_8O+, and four fragment ions C_6H_7O+, C_5H_5O+, C_2H_3O+, and C_4H_5+, with their neutral partners expected to be H, CH_3, $H + C_4H_4$, and $H + CO$, respectively. Sirjean et al. [67] reported a detailed kinetic model describing the oxidation of 2,5-dimethylfuran based on the ignition delay of DMF at temperatures between 1300 K and 1800 K at a pressure of 0.25 bar, measured by a

reflected shock tube, and on the DMF pyrolysis speciation measurements of Lifshitz et al. The most sensitive inhibitive reaction was H-abstraction by H atoms from DMF, leading to the formation of $R_1C_6H_7O+H_2$. The second most sensitive reaction was related to the unimolecular initiation of DMF. $M_4C_6H_8O$ subsequently decomposes to CH_3CO and buta-1,2-dien-1-yl(C_4H_5-1s). Sensitivity analysis also revealed that reactions involving important primary DMF fragments, such as cyclopentadiene and phenol, could have a substantial influence on the conversion of DMF.

Somers et al. [68] researched the oxidation and decomposition mechanism of DMF based on the research of 2 MF. Ignition delay times for mixtures of 0.75% DMF in argon have been measured at atmospheric pressure and temperatures of 1350–1800 K at equivalence ratios of 0.5, 1.0 and 2.0, along with auto-ignition measurements for stoichiometric fuel in air mixtures of DMF at 20 and 80 bar with temperatures ranging from 820 to 1210 K. Combining the scission reaction under the conditions of 1200–1350 K and 2–2.5 atm, the retention time of 2 ms, the JSR reaction and laminar flame speed under the conditions of 770–1220 K at 10.0 atm, the

residence time of 0.7 s and the equivalence ratios of 0.5, 1.0 and 2.0, the detailed mechanism was developed with the construction of 545 substances and 2768 step reactions. At high temperatures, a hydrogen atom transfer reaction is found to be the dominant unimolecular decomposition pathway of DMF. At intermediate temperatures, the resonantly stabilized 5-methyl-2-furanylmethyl radical is found to predominantly undergo bimolecular reactions, and as a result, sub-mechanisms form 5-methyl-2-formylfuran and 5-methyl-2-ethylfuran. Fig. 11 shows the comparison of the reaction paths of DMF in the lean and rich fuel flame.

As a part of the research, the research group of Université de Lorraine and Frédérique Battin-Leclerc worked together with the group of Katharina Kohse-Höinghaus from Bielefeld University, studying the laminar premixed flames of F, MF, and DMF at low pressure (20 and 40 mbar) flat argon-diluted (50%), and the equivalence ratios are 1.0 and 1.7 [69–71]. They utilized high resolution electron-ionization molecular beam mass spectrometry combined with gas chromatography to detect two laminar premixed low pressure (20 and 40 mbar) flat argon-diluted (50%)
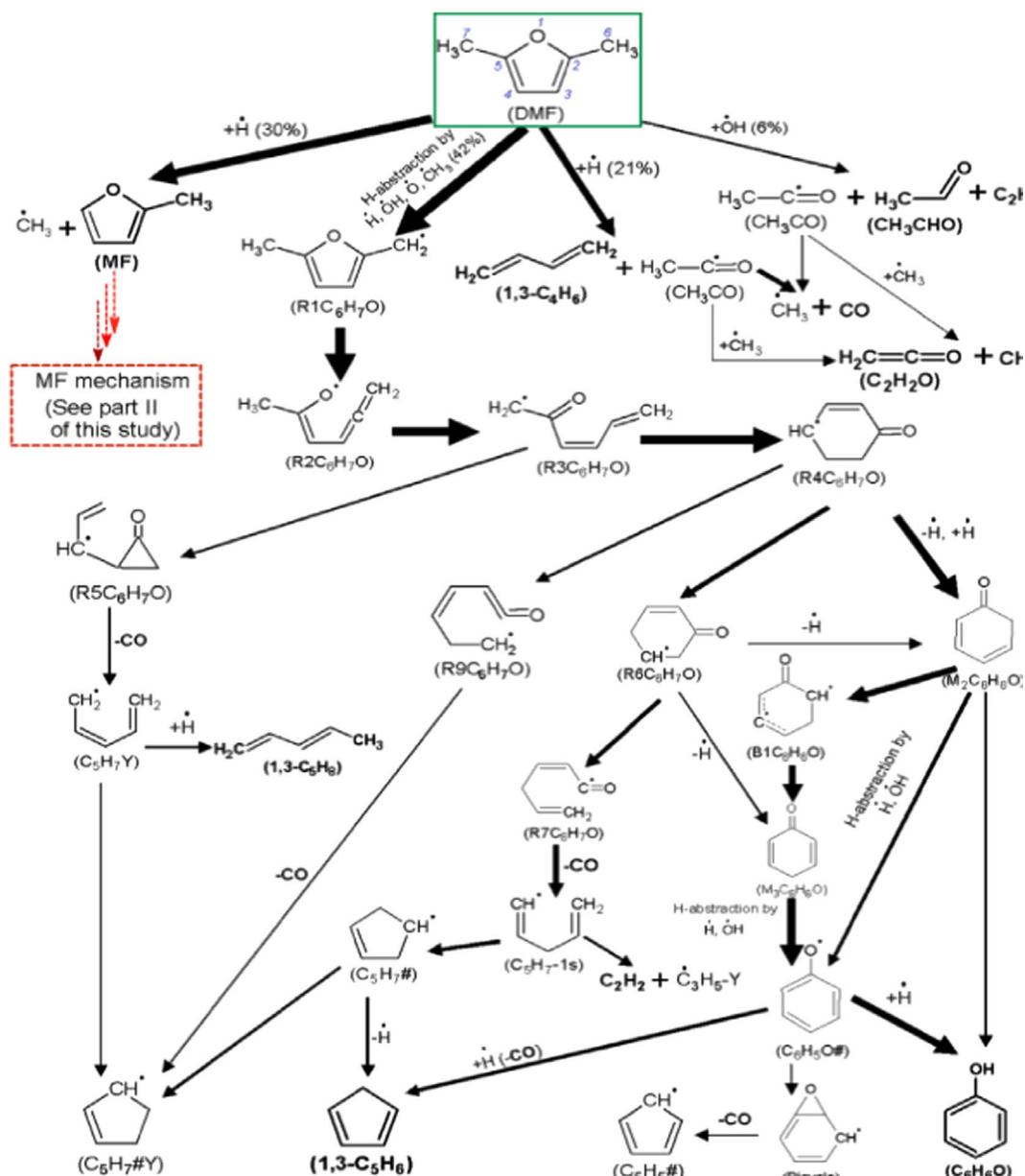
Fig. 12. Reaction flow analysis for the consumption of DMF in the fuel-rich flame ($\phi=1$, simulated temperature of 1101 K and a 73% conversion of DMF) [71].

flames. The mole fractions of the reactants, products, and stable radical intermediates of the different flames were measured as a function of the distance to the burner. Based on the work of Tian et al. [61], the dynamic mechanism of furan was included in the mechanism of MF and DMF as a sub-mechanism. The predominant furan consumption pathway is initiated by H-addition on the carbon atom neighboring the O-atom, with acetylene as one of the dominant products. Fig. 12 shows the main reaction path of DMF under the rich flame. Tong et al. [72] identified the main species in the lean flame of DMF with synchrotron radiation. They found that DMF was mainly consumed by an H-abstraction reaction and converted to 2-(5-methyl) furan methyl. 2-(5-Methyl) furan methyl can be consumed by oxidation or by a ring opening reaction and can react with other free radicals to generate more complicated furan derivatives before being further consumed. In addition, 2-methyl furan was also observed in the flame of DMF.

In this part, the DMF oxidation and combustion mechanism are summarized. Many researchers studied the combustion mechanism of DMF in the ways of ab initio quantum chemistry methods, laminar flame, RCM, shock tube and vacuum sampling photoionization diagnosis of intermediate product. Some detailed combustion mechanisms were established. And the following conclusions can be reached: When adopting pressure boost, the laminar burning velocities of DMF will decrease; The laminar burning velocities of DMF is faster than isooctane; Under higher temperature, DMF is more likely to pyrolysis to the forerunners of soot.

It is found that the current researches are limited to the study of mechanism of DMF single fuel combustion. In order to realize the application of DMF in the engine, the following aspects need further research. First, it is necessary to develop convincible and widely validated mechanism of DMF, in a detailed and/or simplified manner. Second, it is urgent to establish the mechanisms of blend fuels including DMF/gasoline-like-fuel and DMF/diesel-like-fuel.

5. Conclusions

DMF has the potential to be a new biological alternative fuel with many advantages, such as high energy density, oxygen content, high octane number, suitable boiling point, water insolubility, and miscibility with gasoline and diesel oil at any ratio. Moreover, DMF has the advantage of extensive sources. The preparation methods of DMF are usually one-step or two-step methods. Cellulose and starch raw materials are converted to a monosaccharide (fructose or glucose) in ionic liquid with a catalyst. Fructose and glucose are converted into HMF or CMF by a dehydration reaction. Finally, HMF or CMF will be converted into DMF by a dehydrogenation reaction. Usually, a yield of 70% HMF can be reached from the conversion of the monosaccharide. Therefore, future research directions should cover greatly in the efficiency improvement of monosaccharide's conversion to DMF through the optimization of the catalyst, technology usage applied to convert cellulose directly to DMF, cost cut of the conversion process and reduction of the conversion time.

When fueled with DMF instead of gasoline, the spark timing can be shorter due to its higher octane number. However, under high load, the too early spark timing may lead to engine knock. When adapting MBT/KL-MBT spark timing, the fuel consumption of DMF is larger than that of gasoline due to the lower energy density of DMF than gasoline. The fast burning speed of DMF leads to a high concentration of released heat, which results in high temperature. Finally, the higher temperature leads to higher NO_x emissions in the combustion products of DMF than in those of gasoline. DMF is enjoyed with slightly lower HC emissions but higher CO emissions than gasoline. When fueled with a mixture of

DMF and diesel oil, the oxygen content and the low boiling point can help to reduce soot emissions while decreasing the low temperature combustion relying on EGR rates at the same time. Although DMF is believed to be an alternative fuel, many issues still need to be researched, such as the wear and tear on the fuel system caused by DMF; the compatibility of fuel systems with DMF [35]; the toxicity of DMF [16,73]; the abnormal emissions of DMF; how the mechanism of DMF can influence engine emissions; and the regulation of DMF applied to gasoline or diesel engines based on its adaptability.

Given the demand of DMF's application in engines, in recent years, DMF ignition and combustion characteristics were studied. In particular, the laminar flame speed, scission reaction mechanism, low pressure premixed flame, and shock tube ignition delay have been examined in a series of studies. Many intermediates and final products were detected, and some detailed oxidation and pyrolysis mechanisms have been constructed. In the future, the accuracy and range of application of these mechanisms need to be further studied, including the DMF oxidation and pyrolysis products of thermodynamics, the construction and validation of the mechanism of DMF's application in engines under similar conditions, the construction of oxidation and pyrolysis mechanisms of mixed fuel containing DMF, the construction and validation of the simplified dynamic mechanism, as well as the research on the chemical kinetics of DMF's influence on engine emissions.

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