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2-Methylfuran: A bio-derived octane booster for spark-ignition engines

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ABSTRACT

The efficiency of spark-ignition engines is limited by the phenomenon of knock, which is caused by auto-ignition of the fuel-air mixture ahead of the spark-initiated flame front. The resistance of a fuel to knock is quantified by its octane index; therefore, increasing the octane index of a spark-ignition engine fuel increases the efficiency of the respective engine. However, raising the octane index of gasoline increases the refining costs, as well as the energy consumption during production. The use of alternative fuels with synergistic blending effects presents an attractive option for improving octane index. In this work, the octane enhancing potential of 2-methylfuran (2-MF), a next-generation biofuel, has been examined and compared to other high-octane components (i.e., ethanol and toluene). A primary reference fuel with an octane index of 60 (PRF60) was chosen as the base fuel since it closely represents refinery naphtha streams, which are used as gasoline blend stocks. Initial screening of the fuels was done in an ignition quality tester (IQT). The PRF60/2-MF (80/20 v/v%) blend exhibited longer ignition delay times compared to PRF60/ethanol (80/20 v/v%) blend and PRF60/toluene (80/20 v/v%) blend, even though pure 2-MF is more reactive than both ethanol and toluene. The mixtures were also tested in a cooperative fuels research (CFR) engine under research octane number and motor octane number like conditions. The PRF60/2-MF blend again possesses a higher octane index than other blending components. A detailed chemical kinetic analysis was performed to understand the synergetic blending effect of 2-MF, using a well-validated PRF/2-MF kinetic model. Kinetic analysis revealed superior suppression of low-temperature chemistry with the addition of 2-MF. The results from simulations were further confirmed by homogeneous charge compression ignition engine experiments, which established its superior low-temperature heat release (LTHR) suppression compared to ethanol, resulting in better blending octane numbers. This work explores and provides a chemically sound explanation for the potential of 2-MF as an octane enhancer.

1. Introduction

Engine knock has always been a significant bottleneck in improving the efficiency of spark-ignition (SI) engines [1]. The resistance of a fuel to auto-ignition, and therefore knock, is quantified by two octane numbers, viz., research octane number (RON) and motor octane number (MON). The octane numbers are measured according to ASTM 2699 (RON) [2] and ASTM 2700 (MON) [3] standards. These tests measure the anti-knocking tendency of a fuel using a scale with *n*-heptane as the lower boundary (ON = 0, highly prone to knocking) and *iso*-octane as the upper boundary (ON = 100, less prone to knocking) [4].

Fuel specifications in many countries have established minimum octane ratings for regular and premium gasoline fuels. Isomerization and reformation processes synthesize the hydrocarbon species in the fuel that increase its octane index to meet the specifications. The incorporation of these processes results in additional capital and operational expenses making gasoline more expensive to the end user. The mandate to blend renewable fuels in gasoline, especially ethanol, has reduced the burden on some large refiners. The synergistic blending effect of ethanol especially at low volume ratios dramatically increases the octane rating of gasoline [8] and aids in the reduction of cost of production of refinery gasoline streams. Ethanol's resistance to auto-ignition is, at least for direct-injected engines, due to its charge cooling effect, driven by the high latent heat of vaporization, and its radical scavenging nature, which suppresses the OH formation responsible for chain branching reactions leading to auto-ignition [5,6].

The use of ethanol as a biofuel has garnered much criticism. Ethanol production from food crops has been estimated to have a thermodynamically net negative energy flow [7]. Several studies [8,9] have

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shown that increased production of crops for biofuel production has a detrimental effect on land use. Biofuels from biomass, cultivated on lands unsuited for agriculture or agricultural waste, are an attractive proposition. This biomass feedstock would be primarily lignocellulosic, and a variety of chemical compounds could be extracted from it for use as fuel. Furans are one of the classes of compounds that could be produced from lignocellulosic biomass [10]. They have generated research interest due to their higher heating value being comparable to commercial gasoline on a volumetric basis and superior anti-knock properties. Improved production methods of furanic compounds have also been realized in 2009 [11–17]. Researchers at the University of Wisconsin-Madison accomplished the conversion of hexose and other sugars to 2-MF through hydroxymethylfurfural (HMF), formed by the elimination of three oxygen atoms, which further undergoes hydrogenolysis to produce 2-MF [16]. Zhao et al. improved the method, thereby dramatically reducing production costs [17]. 2,5-Dimethylfuran and 2-Methylfuran have both been tested for their benefits in spark ignited engines [11–14,18].

The potential of 2-MF as a biofuel derives from the possibility of its production from lignocellulosic biomass [19]. A select number of physical properties and octane numbers of 2-MF are compared with that of ethanol, toluene, and 2,5-DMF in Table 1. Although the furanic molecules (2,5-DMF and 2-MF) show similar behavior, 2-MF has some advantages, such as a lower boiling point than 2,5-DMF and ethanol, hence better cold-start performance. The lower flash point of 2-MF also means safer handling, storage, and transport. The greater enthalpy of vaporization of 2-MF compared to 2,5-DMF would result in a better charge cooling effect increasing charge density and power output [14]. The significantly larger viscosity and density of 2-MF compared to ethanol would impede the fuel flow from the injector nozzle, resulting in lower droplet velocity and poor spray break-up. However, lower boiling point, accompanied with lower latent heat of vaporization, results in improved evaporation [20,21]. Higher viscosity and poorer spray break-up would also cause higher particulate emissions [22]. The faster flame speed of 2-MF compared to 2,5-DMF provides high knock resistance and peak pressure rise rates [23]. Combustion duration is considerably faster than ethanol, 2,5-DMF, and gasoline [14]. The use of 2-MF resulted in high oxygen content and combustion temperature, as well as lower hydrocarbon emissions and increased NO_x emissions, compared to 2,5-DMF and gasoline [14,20]. The indicated thermal efficiency was found to be higher than gasoline and 2,5-DMF over the entire load range [14,20]. 2-MF also exhibited more robust combustion under stoichiometric as well as lean operation making it a strong candidate for homogenous lean operation engines, another future engine technology. The cycle-to-cycle variations were also the lowest for 2-MF when compared to ethanol and 2,5-DMF. Combustion and indicated thermal efficiency were lower than ethanol, and higher than DMF, over the load range. Indicated specific emissions of NOx were observed to be higher than either ethanol or DMF. Indicated specific HC emissions were higher than ethanol, and lower than DMF. Indicated specific CO emissions were the highest, compared to DMF and ethanol, at lower loads, while they were lower than DMF at higher load operation [14]. Engine studies in port fuel injected (PFI) SI engines yielded higher thermodynamic efficiencies and 30% lower indicated specific fuel consumption than ethanol. Although they have similar molecular structure, 2-MF and 2,5-DMF have disparate combustion characteristics, marked by higher burn rate and superior knock resistance of 2-MF.

Table 1
Properties of 2-MF, ethanol, toluene, and 2,5-DMF.

Properties	2-MF	Ethanol	Toluene	2,5-DMF	Ref.
Density (kg/m^3)	913.2	790.9	867	889.7	[23]
Viscosity (mPa*s)	4.00	1.08	0.59	0.65	[20]
Boiling Point (°C)	64	78	111	92	[20]
Enthalpy of Vaporization (kJ/kg)	358	912	413	332	[20]
Flash Point (°C)	–22	16.6	6	16	[14]
Stoichiometric	10.08	8.98	13.43	10.72	
Lower Heating Value (MJ/l)	27.63	21.09	35.19	32.89	[20]
RON	~103	~108	~120	~101	[14]
MON	86	89.7	~100	88.1	[14]
Sensitivity	17	18.3	20	12.9	[14,24]

Kalghatgi [25–27] proposed the use of octane index (OI), a better representation of anti-knock characteristic for modern engines. Equation (1) represents the OI as,

$$OI = RON - K*S \quad (1)$$

S refers to the octane sensitivity, and it is the difference between RON and MON of a fuel. K is an empirical constant depending on the engine and the operating condition, and independent of the fuel. The superior performance of OI in predicting fuel behavior compared to the RON-MON metric was demonstrated in Ref [28]. K values of modern turbocharged SI engines are exceedingly negative at high load points. The implication being that a fuel with high RON and S (lower MON) will have a greater OI at these operating points. The K of RON and MON tests are, by definition, 0 and 1, respectively. Modern engines tend to be turbocharged, direct injected, and operate at lower engine speeds, which leads to lower in-cylinder temperatures than RON and MON test conditions. The continuing trend of engine design towards even more negative K values is driving research into fuel sensitivity and understanding the chemical kinetics dictating it [29–34]. In this regard, 2-MF could be a very interesting future fuel, as it has a high S value (mostly attributed to chemical kinetic pathways), coupled with high RON.

Several compounds raise both the RON and S of a base fuel when blended. Blending octane number (BON) is a metric that quantifies the effect of blending on octane number. BON is the linearly-extrapolated octane number of a pure compound from the octane number of the blend [35]. A positive deviation of BON from the measured RON of a compound indicates a synergistic blending effect. Lovell [36] determined that 2-MF has a BON of 209 at RON-like condition and 180 at MON-like condition when blended in 20% volume with the primary reference fuel having octane number of 60 (PRF60). The RON and MON of pure 2-MF were found to be close to 100 and 86, respectively. In contrast, the BON of toluene was 124 (at RON-like conditions) and 112 (at MON-like conditions), even though its measured RON and MON were 120 and 100, respectively. Recent results by Tiunov et al. showed maximum blending octane number of 2-MF and 2,5-DMF blended with toluene primary reference fuel TPRF80 at 10% v/v blends. An increase in the S value with a higher furanic component in the fuel was also reported [37].

This work experimentally reaffirms the exceptional synergistic blending effect of 2-MF by measuring and comparing its blending octane number (BON) with ethanol and toluene. The chemical kinetics leading to the observed results is also explored using a well-validated ignition kinetic model for PRF60/2-MF [38].

2. Methodology

2.1. Experimental (IQT tests)

The baseline fuel used was PRF60, which is a mixture of 40% *n*-heptane and 60% *iso*-octane (v/v). PRF60 is representative of blendstock into which high octane components are blended. PRF60 has also been used as a base stock for finding blending octane number (BON) in ASTM D-908 [36]. The purity of the chemicals was greater than 99%. 2-MF was mixed in 5%, 10%, and 20% (v/v) in PRF60. All three 2-MF mixtures were compared to respective mixtures of ethanol or toluene in PRF60. The proceeding nomenclature uses PRF60, followed by MF for 2-MF, E for ethanol and T, indicating toluene, followed by their volume concentration in the mixture. Initial screening of the mixtures was performed in an ignition quality tester (IQT). The details of the