1 **2-Methylfuran: A Bio-Derived Octane Booster for Spark-Ignition Engines**

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8 **Abstract**

9 The efficiency of spark-ignition engines is limited by the phenomenon of knock, which is caused
10 by auto-ignition of the fuel-air mixture ahead of the spark-initiated flame front. The resistance of
11 a fuel to knock is quantified by its octane index; therefore, increasing the octane index of a
12 spark-ignition engine fuel increases the efficiency of the respective engine. However, raising the
13 octane index of gasoline increases the refining costs, as well as the energy consumption during
14 production. The use of alternative fuels with synergistic blending effects presents an attractive
15 option for improving octane index. In this work, the octane enhancing potential of 2-methylfuran
16 (2-MF), a next-generation biofuel, has been examined and compared to other high-octane
17 components (i.e., ethanol and toluene). A primary reference fuel with an octane index of 60
18 (PRF60) was chosen as the base fuel since it closely represents refinery naphtha streams, which
19 are used as gasoline blend stocks. Initial screening of the fuels was done in an ignition quality
20 tester (IQT). The PRF60/2-MF (80/20 v/v%) blend exhibited longer ignition delay times
21 compared to PRF60/ethanol (80/20 v/v%) blend and PRF60/toluene (80/20 v/v%) blend, even
22 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.

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 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 NO_x 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].

Methodology:

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 >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 experimental apparatus are provided in Ref [39]. The experiments were performed according to standard ASTM D6890 [40]. The pressure inside of the constant volume chamber was maintained around 25 bar and the fuel was injected with a pressure of 150 bar. The temperature of the air was maintained so that ignition delay of *n*-heptane was at the specified value of 3.78 ($\pm$ 0.03) milliseconds. A gradient method was used to determine the start of ignition. The point of interaction of two tangential lines, one at the pressure recovery point, the point where chamber

pressure reaches back to initial pressure after evaporative cooling and the second at the maximum slope of the pressure-time curve, is considered to be the start of ignition. The time between the start of injection, marked by needle lift, and start of ignition is the ignition delay time (IDT). Other methods used for determining the IDT, and their implications on the final IDT value, have been discussed in Ref [39]. The ASTM standard also provides for the conversion of IDT to derived cetane number (DCN), according to the equations

$$DCN = 4.46 + \left(\frac{186.6}{IDT (ms)} \right) \quad (2)$$

$$DCN = 83.99[(IDT(ms) - 1.512^{-0.658})] + 3.547 \quad (3)$$

Equation (2) is applied for IDT between 3.1 ms to 6.5 ms. Equation (3) is for IDT greater than 6.6 ms. An empirical relation between the IDT and RON was proposed in Ref [41] as elucidated in equation (4),

$$RON = -293 \left(\frac{DCN}{100} \right)^2 - 52 \left(\frac{DCN}{100} \right) + 114.1 \quad (4)$$

The IQT used in the study has been modified to accommodate fuels with longer IDT. The modifications have resulted in greater standard deviations of the measured results compared to Ref [41].

Experimental (KLSA tests)

The knock-limited spark advance (KLSA) of the mixtures were determined in RON-like and MON-like conditions. The geometrical and operating specifications of the cooperative fuels research (CFR) engine used in the experiments are listed in Table 2. The CFR was modified by replacing the carburetor with a port fuel injector. The air temperature was measured and

controlled in these tests, as opposed fuel-air charge temperature in MON tests. Therefore, in subsequent discussions, the tests are referred to as RON-like and MON-like.

Table 2: Configuration of CFR engine used for KLSA tests and HCCI experiments

	RON-like	MON-like
Engine Type	Modified CFR F-1/F-2	
Number of Cylinders	1	
Bore (mm)	82.5	
Stroke (mm)	114	
Connecting rod Length (mm)	254	
Fuel Injection	Port fuel injection	
Equivalence Ratio	1.0	
Compression Ratio	5.5	5
Speed	600	900
Intake Temperature (°C)	52	149

The RON-like tests were performed with an intake air temperature of 52 °C and an engine speed of 600 rpm. The compression ratio of 5.5 was utilised as negligible knock intensity was recorded for the base fuel with the spark timing at +4°CA after top dead centre (aTDC). The spark timing was advanced and knock intensity (in the form of knock peak value), was recorded for 180 cycles. The average values of knock peak with standard deviations are reported. For KLSA tests at MON-like conditions, the intake air temperature and the engine speed were increased to 149°C and 900 rpm, respectively. The compression ratio was lowered to 5 for the reason stated above.

Computational

The chemical kinetic mechanism used for simulating the ignition of the fuel mixture studied in this work is a combination of two validated models for primary reference fuel (PRF) [42] and 2-MF [38]. The details of the PRF mechanism is fully detailed in Atef *et al.* [42] and has been utilized here without modification. The mechanism contains a well-validated C₀-C₆ base chemistry along with detailed oxidation pathways of *n*-heptane and iso-octane [42]. A detailed model of 2-MF covering both low and high temperature reaction pathways was adopted from the work of Tripathi *et al.* [38] and added together with the PRF mechanism. The high-temperature specific 2-MF chemistry in their model [38] was adopted from Somers *et al.* [43], and extensively revised, based on more recent kinetic studies [44, 45]. The 2-MF mechanism considered, incorporates several updates to older 2-MF mechanisms in the literature. The most significant alterations include the addition of O₂ to 2-MF fuel radical, the alkene specific low-temperature pathways of 2-MF, and co-oxidation reactions between 2-MF and *n*-heptane. The incorporated 2-MF mechanism was extensively validated against ignition delay times, laminar flame speeds, and species profiles in various experimental setups [38]. The results of compilation have been added to the supplementary material.

Zero-dimensional chemical kinetics simulations were performed using the homogenous batch reactor model in Chemkin Pro [46]. The program solves energy equations at constant volume to determine energy released, pressure, temperature, and species fractions as a function of time. Ignition is defined as the point of maximum slope of the temperature-time curve. If there are multiple local maxima, as in the case of two-stage ignition process, the latest value was considered as the time of ignition. The ignition delay times for mixtures of equivalence ratio 1, from 650 K to 950 K at intervals of 25 K at a pressure of 20 bar were simulated for PRF 60,

PRF60MF20, PRF90, and PRF60T20. The conditions of the simulations have been demonstrated to cover the in-cylinder conditions during the octane rating tests [21, 47]. IDT is mostly insensitive to temperatures beyond 950 K [48-52]. The temperature range covers the negative temperature coefficient (NTC) region. Fuels with a higher S value tend to show low-to-no NTC region and have monotonically increasing IDT with temperatures [53-55]. The time histories of heat release, temperature, and evolution of OH, HO₂ at 750 K and 25 bar were investigated to quantify the suppression of low temperature chemistry (LTC) due to different high octane components. The IDT at this condition correlates well with RON.

Experimental (HCCI tests)

The trends observed were then validated against the homogeneous charge compression ignition (HCCI) experiments, also conducted in the CFR engine. The methodology followed for conducting the experiments was based on HCCI number methodology first proposed in Ref [56], and later used by Waqas *et al.* to ascertain fuel reactivity at lean homogenous conditions [57]. The HCCI experiments were conducted with an intake temperature of 52°C, engine speed of 900 rpm and equivalence ratio of 0.3. The compression ratio was adjusted to phase the CA 50 of the combustion at 3 deg aTDC. The compression ratio required to maintain this combustion phasing provides the HCCI number of the fuel as proposed in Ref [57]. The HCCI number calibration for this experimental apparatus was performed and reported by Waqas *et al.* The engine was run with base fuel PRF60, and the compression ratio was varied to achieve CA50 of 3 CAD after TDC at $\lambda = 3$ (λ = ratio of actual air-fuel ratio to stoichiometric air-fuel ratio). Thereafter, mixtures of PRF60 with ethanol and 2-MF in blend ratios of 5%, 10%, 15%, and 20% (v/v) were tested. With the addition of octane boosting additives, the compression ratio had to be increased to maintain CA50 to be 3 CAD after TDC. The compression ratio can be used to give a rating

(HCCI #3) to the fuels; this is based on the volumetric blend of *iso*-octane in a mixture of *iso*-octane and *n*-heptane, required to match the compression ratio of the tested fuel. The correlation developed by Waqas *et al.* [57] has been updated to include a wider range of PRFs, and therefore, HCCI number. The blending HCCI number can also be ascertained from this, based on linear rating correlation given by:

$$HCCI_{base}C_{base} + BON.C_{booster} = HCCI_{mix} \quad . \quad (5)$$

A comprehensive heat release analysis was performed on the pressure data obtained from the HCCI experiments. The first law of thermodynamics, in conjunction with heat losses from heat transfer to the wall, crevices and blow-by losses, was considered. The analysis was performed separately on each of the 190 cycles at operating conditions mentioned above. **The standard deviation of the pressure data was 0.04 bar.** The average value of the heat release is reported here. More details on heat release calculations are provided in the Appendix of Ref [5].

Results and Discussion

Ignition Delay Time from IQT:

The results from the IQT are tabulated in Table 3. It can be seen that PRF60MF10 is nearly as reactive/unreactive as PRF60T20 and PRF60E20. The surprisingly high BON of 2-MF reported by Lovell [36] is reaffirmed. DCN was obtained from the ignition delay period according to ASTM 6890. Previous researchers have correlated this DCN value with RON, accurate to few points [41]. **Relatively simpler IQT tests provide a RON bracket for the blend fuel, not an accurate RON value, as pointed out in [41].** These calculated RON values are plotted in Fig. 1. It can be observed that 2-MF is highly effective at suppressing reactivity of PRF60, even at very low concentrations. It is already known that ethanol (a radical scavenger) has a high BON value,

as it displays synergistic non-linear octane behavior with gasoline [58]. RON values of ethanol blends, however, plateau at 20% v/v concentration, while 2-MF blends shows a much higher RON value at 20% v/v, after closely following RON of ethanol blends at 5% and 10% v/v. Pure 2-MF shows inferior resistance to auto-ignition tendency compared to both ethanol and toluene, as measured in IQT (and shown by previous researchers); but in small quantities, it improves the octane quality of PRF60 dramatically.

Table 3: Measured IDT and Calculated DCN.

Blend	IDT	Std. Dev	DCN	Std. Dev
	(ms)	IDT	(#)	DCN
PRF60E5	6.66	0.14	32.13	0.58
PRF60E10	7.64	0.16	29.02	0.42
PRF60E20	7.09	0.11	30.67	0.36
Ethanol	93.09	14.27	7.95	0.87
PRF60T5	6.30	0.12	34.08	0.70
PRF60T10	6.52	0.16	32.66	0.83
PRF60T20	7.09	0.11	29.03	0.31
Toluene	213.17	9.86	6.03	0.16
PRF60MF5	6.64	0.09	32.21	0.34
PRF60MF10	7.64	0.11	29.03	0.31
PRF60MF20	10.37	0.40	23.54	0.69
2-MF	72.39	-	6.84	0.96

After comparing ignition delay times in IQT, the same mixtures were run on a CFR engine in knock-limited spark timing (KLSA) tests at RON-like and MON-like conditions.

Figure 1: Calculated RON values from IQT ignition delay times.

Knock limited Spark Advance Tests in CFR:

The results of KLSA tests near RON-like conditions are presented in Fig 2. The observations qualitatively compare well with IDT measured in the IQT discussed previously. Knock intensity decreased in the following order: PRF60, PRF60MF5, PRF60E20, PRF60T20, PRF60MF10, and PRF60MF20. The knock suppression characteristics of 10% 2-MF in PRF60 is better than 20% of toluene and ethanol in PRF60. Figure 3 shows KLSA test observations for MON-like conditions. 2-MF performs even better in MON-like conditions. The trend was same as in the RON condition, however, the engine was not knock-limited at any spark timing when using 20% (v/v) 2-MF (considering threshold knock intensity value to be 0.5 bar).

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261 Figure 2: KLSA tests performed in RON-like conditions.

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263 Figure 3: KLSA tests performed in MON-like conditions.

264 ***Ignition delay calculations:***

265 The chemical kinetics supporting the highly effective knock suppression of 2-MF blends was
 266 explored using chemical kinetic simulations. Several authors have related the S-value of a fuel
 267 with the NTC region observed when plotting IDT versus $1000/T$. The simulated IDT for

different mixtures are presented Fig. 4. The two vertical lines refer to temperature corresponding to end gas temperature in RON and MON testing [32]. A highly disparate ignition behavior of PRF60MF20 blend can be observed. 2-MF is found to be very effective in increasing ignition delay time at intermediate and low temperatures, which explains its extremely effective behavior in the KLSA tests above. The addition of 2-MF completely suppressed the LTC reactivity, leading to higher ignition delay times in both RON and MON conditions. This is a result of the high S-value of the fuel, which was captured well in the simulations. In contrast, PRF60 showed pronounced NTC regions. PRF60T20 increased the S-value and the IDT at low- and intermediate temperatures was higher. PRF60MF20 mixture show a higher ignition delay time compared to ethanol and toluene mixtures. The difference is higher at low temperatures because of absence of the LTC chemistry. PRF60MF20, for example, increases monotonically, while the other mixtures show reduced ignition delay times due to the dip in NTC regime.

Previous research has shown that IDT at fixed temperature-pressure conditions for a homogenous batch reactor case can replicate the fuel behavior at RON and MON conditions [54, 59, 60]. RON is well represented at 750 K and 25 bar [32]. These conditions are indicative of end-gas conditions on the verge of auto-ignition (or knock). The evolution of reactivity at these conditions in a batch reactor simulations would represent the chemistry of fuel-air mixture in octane tests. The mixtures analyzed earlier were then simulated in a homogenous batch reactor with constant volume. The temporal history of temperature, heat release and the evolution of OH and HO₂ was studied. OH and HO₂ are primary markers of the radical pool, therefore the reactivity was chosen for this analysis. The results of PRF60 and 2-MF (5%, 10%, and 20%) are compared with respective blends of ethanol, and toluene blended with PRF60 are presented in Figs. 5-10. Two-stage ignition behavior is observed in all cases. The first-stage is the low-

temperature heat release (LTHR), which marginally increases the temperature. Next, there was a second-stage delay period before high-temperature reactions (HTHR) began, leading to faster heat release. OH and HO₂ mole fraction followed the heat release closely with local peaks occurring in the LTC region. *n*-Heptane in the given plots exhibited substantial low-temperature chemistry. Essentially, alkyl radicals undergo O₂ addition at low temperatures, and peroxy radical intramolecular isomerization and subsequent O₂ addition leads to the formation of ketohydroperoxides and other chain branching intermediates [61]. These highly oxygenated molecules can dissociate to yield reactive OH radical leading to heat release. However, with an increase in temperature, the pathway leading to low-temperature branching is no longer essential. The HO₂ radical abstracts H atom from the fuel, forming meta-stable H₂O₂, eventually decomposing to OH radicals and leading to HTHR.

As expected, the total IDT increased from 0.02 sec for PRF60 to 0.14 sec for PRF60MF20, and close to 0.03 sec for both PRF60E20 and PRF60T20. The simulations, apart from capturing the trend well, show that the increase in IDT is due to LTHR suppression by 2-MF addition, as shown in Fig. 6. LTC suppression was confirmed by tracking OH and the HO₂ radical pool. Because of the reduced LTHR, the temperature increase at the end of LTHR was less than in the case of PRF60. This delays the onset of high-temperature chemistry, and therefore, increases ignition delay time.

Assuming that high-temperature reactions take place roughly at the same temperature, the delta T between the temperature at the end of LTHR and onset of HTHR is directly proportional to a mixture's resistance to its auto-ignition. Another noteworthy observation from Figs. 5-8 is that, with increasing 2-MF fraction in the 2-MF/PRF60 blend, the second-stage ignition delay is reduced. Previous research work focusing on fuel sensitivity reports a similar trend of shorter

second-stage ignition delay and subsequent lower intermediate-temperature heat release with increasing S value [32]. Relative to the total IDT, the second-stage IDT falls linearly with the addition of 2-MF.

The similar magnitude of LTHR suppression, as well as second-stage IDT (more or less), is also seen when toluene is the additive. The qualitative agreement with the observations made in IQT and thereafter in KLSA tests, can also be observed. Fig. 9 summarises the observations in terms of maximum peaks of heat release rate (HRR), OH, and HO₂ with several mixtures. For comparison, as a low-temperature chemistry-neutral molecule, *iso*-octane, was used. *iso*-Octane addition to PRF60 would merely yield a higher PRF blend (PRF62 (5%), PRF64 (10%), PRF66 (15%) and PRF68 (20%) mixtures). As expected, LTHR decreases linearly with *iso*-octane addition. Ethanol, which acts as a radical scavenger, suppressed the LTHR non-linearly and reduced the reactivity more than with *iso*-octane addition, which can be seen by the reduction in the radical pool of OH and HO₂. With the addition of 2-MF, it was seen that LTHR suppression was much stronger than either *iso*-octane or ethanol. This is achieved by suppressed reactivity, as evident from the radical pool in Figs. 9 (b) and 9 (c).

330 Figure 4: Simulated IDT in a batch reactor using CHEMKIN PRO for stoichiometric fuel/air
 331 mixtures.

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333 Figure 5: Time history of HRR, temperature, OH, HO₂ for PRF60 at 750K 25bar.

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337 Figure 6: Time history of HRR, temperature, OH, HO₂ for (a) PRF60MF5, (b) PRF60E5 and (c)
 338 PRF60T5 at 750 K 25 bar.

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342 Figure 7: Time history of HRR, temperature, OH, HO₂ for (a) PRF60MF10, (b) PRF60E10 and
 343 (c) PRF60T10 at 750 K 25 bar.

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347 Figure 8: Time history of HRR, temperature, OH, HO₂ for (a) PRF60MF20, (b) PRF60E20 and
 348 (c) PRF60T20 at 750 K 25 bar.

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Figure 9: Maximum HRR (a), OH (b) and HO₂ (c) in low-temperature region. Black (square symbol) corresponds to 2-MF addition. Red (circle) corresponds to ethanol addition and pink (triangle) corresponds to *iso*-octane addition in PRF60.

HCCI experiments in CFR:

To experimentally establish the efficacy of 2-MF addition on LTHR suppression (subsequently leading to improved knock behavior), a set of fuel blends were run in a CFR engine in HCCI mode. HCCI experiments often correlate well with the knocking tendency of the fuel, since knock is also an end-gas auto-ignition phenomenon, and HCCI is a combustion technology based on auto-ignition of complete charge. There are always greater disparities between the two phenomena, as auto-ignition ahead of the spark-ignited flame front also depends on the flame front propagation speed. However, in the past, the two have been correlated with good confidence. Correlations by Waqas *et al.* [57] have been improved herein, with the inclusion of PRF60 into the dataset, which changes the constant coefficients for obtaining the HCCI #3. Details of the methodology are elaborated in [57]. The HCCI # is related to the compression ratio, at which CA50 ~ 3 CAD after TDC is maintained for $\lambda = 3$. By including PRF60 in the previous model, a second-order polynomial was found to be the best fit with $R^2 = 0.9954$.

$$HCCI \#3 = -0.1325(CR)^2 + 10.688(CR) - 37.335 \quad (6)$$

where CR is the compression ratio at which CA50 of 3 CAD after TDC is achieved for $\lambda = 3$.

Figure 10 shows experimental results. The compression ratios reached using 2-MF were much higher than in the case of ethanol; this is directly translated to a higher HCCI #3, as shown in Fig. 10(b). PRF60MF20 shows HCCI #3 close to 90, which corresponds to the behavior of PRF90. In comparison to ethanol, 2-MF was superior in every volumetric blend. The BON, as

described in the methodology section, is also shown. 2-MF shows blending octane behavior close to 208, as opposed to 146 shown for ethanol at 20% blend (v/v). In contrast to ethanol, the BON of 2-MF continues to increase with the increasing blend ratio, a testament to the better utilization of the fuel as a blending agent (rather than pure fuel, as previously suggested by several authors).

Figure 10: (a) CR for achieving CA50 ~ 3CAD aTDC (b) HCCI #3 and BON for mixtures of 2-MF (square) and ethanol (triangle) in PRF60. Left (black) axis is for HCCI #3, shown in solid black shapes. Right (red) axis for HCCI #3, shown in hollow red shapes.

Heat release analysis of the HCCI experiments was performed on the basis of the methodology described earlier and is shown in Fig. 11. By concentrating on the area of low temperature chemistry, it becomes clear how heat release is suppressed with the addition of boosting agents. The tests were also conducted using ethanol blended in PRF60, for comparison. These observations experimentally confirmed that LTHR suppression by 2-MF is superior to ethanol. At 20% volumetric blend, ethanol addition still shows some heat release, while the 2-MF addition completely suppressed LTHR. At each point (5%, 10%, and 15%), the LTHR

magnitude with a 2-MF addition was lower than with the addition of ethanol. Being a lighter molecule, ethanol has a higher number of moles for similar volumetric blend compared to 2-MF. The mole fraction corresponding to the volume fractions appears in parenthesis in the legend. This validates an even greater effectiveness of 2-MF on a mole basis. Furthermore, complete suppression of LTHR at 20% (v/v) blend reinforces the fact that PRF60MF20 is the blend with higher blending octane improvement behavior, established by the fact that 2-MF alone shows no LTC in its pure state. If a low octane non-LTC blend (PRF60MF20 in this case) is combined with a high-octane non-LTC fuel (pure 2-MF), the octane boosting tendency is close to linear and the blending octane number goes down. This has been shown previously by the authors in an example with ethanol [5]. Hence, the non-linear trend of octane boosting, by both ethanol and 2-MF can be explained as follows: low temperature reactions lead to an increase in temperature, subsequently accelerating the progress to high temperature reactions. When a radical scavenging fuel is blended, it takes up the HO_2 radicals formed in low temperature chemistry, thereby, suppressing the reactivity and not allowing the temperature to increase. This further extends the high temperature reactions too. Once the LTC is fully suppressed, the effect of octane booster addition is merely replacing the low octane fuel with a high octane molecule, and hence linear. A molecule showing stronger radical scavenging, and hence higher LTC suppression, should show enhanced non-linearity in octane boosting tendency, up to the point of complete LTC suppression. Additionally, it follows that full suppression of LTC can also be regarded as the point of maximum gain from the octane boosting additive, which is shown to be lower for 2-MF (20% v/v in our study) compared to ethanol.

Figure 11: (a) Heat release rate (HRR) of various blends based on HCCI methodology (b) close up of LTHR for the same case. (Mole fraction in brackets)

Conclusion

2-MF is a bio-derived compound that can be extracted from lignocellulosic biomass; it has several advantages over other octane boosters. The physical properties and the energy density are closer to gasoline, as opposed to ethanol. The intent of this work is to test the efficacy of the compound as a knock suppressant.

Initial IQT tests provided promising results, showing very high blending octane numbers. Tests on a modified CFR engine showed that 10% (v/v) of 2-MF was more effective in mitigating knock than even 20% (v/v) mixtures of toluene or ethanol in PRF60. Simulated ignition delay times using a well-validated chemical kinetic mechanism in CHEMKIN PRO agreed with the experimental observations. Further analysis investigated reactions leading to the suppression of reactivity after adding octane boosting molecules. It was found that LTC suppression is responsible for the highly effective nature of 2-MF as an octane booster. Engine experiments in

HCCI mode showed very high BON of 208 with 20% 2-MF addition to PRF60. Heat release analysis of the experiments revealed that LTHR suppression using 2-MF is much higher at every blend ratio than for the known radical scavenger, ethanol. On a mole basis, the effectiveness of 2-MF only increases further.

This paper successfully demonstrates the use of 2-MF as a prospective octane booster. Factors such as material compatibility and toxicity must be considered before it can be a viable option for replacement or augmentation of ethanol, used ubiquitously as an octane booster. Moreover, unlike previous work which focuses on the pure component, support is made for better utilization of the fuel in lower volumetric blends. As the efficacy of 2-MF plateaus after 20% (v/v) ratio; this method also provides an opportunity for a more economic utilization for production of 2-MF, as well as for refiners. In conclusion, the benefits of 2-MF can be better realized as an octane booster than as a pure fuel.

Acknowledgements

The authors gratefully acknowledge the support of this work from the Clean Combustion Research Center (CCRC) at King Abdullah University of Science and Technology (KAUST). The work at RWTH Aachen University was performed within the Cluster of Excellence “Tailor-Made fuels from Biomass”, which is funded by the Excellence Initiative by the German federal and state governments to promote science and research at German universities.

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