Oxidation of Alkane Rich Gasoline Fuels and their Surrogates in a Motored Engine

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Abstract
The validation of surrogates formulated using a computational framework by Ahmed et al.[1] for two purely paraffinic gasoline fuels labelled FACE A and FACE C was undertaken in this study. The ability of these surrogate mixtures to be used in modelling LTC engines was accessed by comparison of their low temperature oxidation chemistry with that of the respective parent fuel as well as a PRF based on RON. This was done by testing the surrogate mixtures in a modified Cooperative Fuels Research (CFR) engine running in Controlled Autoignition Mode (CAI) mode. The engine was run at a constant speed of 600 rpm at an equivalence ratio of 0.5 with the intake temperature at 150 ℃ and a pressure of 98 kPa. The low temperature reactivity of the fuels were studied by varying the compression ratio of the engine from the point were very only small low temperature heat release was observed to a point beyond which auto-ignition of the fuel/air mixture occurred. The apparent heat release rates of different fuels was calculated from the pressure histories using first law analysis and the CA 50 times of the low temperature heat release (LTHR) were compared. The surrogates reproduced the cool flame behavior of the parent fuels better than the PRF across all compression ratios.

Introduction

Primary reference fuels (PRF) which are binary mixtures of n-heptane and 2, 2, 4-trimethyl pentane which exhibit the knocking behavior of the fuel in an ASTM D-2699 test have been long used as a surrogate for gasoline fuels to represent their chemical behavior in engine simulations. The octane or anti-knocking quality of the fuel is given by the Research Octane Number (RON) which is the volume percentage of 2, 2, 4-trimethyl pentane in the mixture. Knocking is the result of the rapid chemical reactivity of the fuel/air mixture that releases enough heat to self-sustain and propagate a flame before the flame emanated from the spark reaches that region of the cylinder. Therefore, knocking is fundamentally a chemical process driven by the physical conditions in the combustion chamber. The pitfall of using PRF mixtures based on the RON arrives from the limited number of chemical groups represented by them, namely paraffin and iso-paraffin which reproduce the ignition quality of the fuel at one engine operating point while actual gasolines contain a variety other chemical groups such as olefins, naphthenes and aromatics. These groups exhibit significantly different oxidation and pyrolysis chemistries to that of paraffin due to the negative temperature coefficient found in the latter[2].

The octane quality of fuels with non-paraffinic components depends on the test conditions. This dependence is called sensitivity[3]. This is clear from the ASTM-D 2700 testing as most gasoline fuels have different MON numbers. The MON conditions are more aggressive than that of RON. The RON and MON tests were formulated to bracket the engine operating conditions present at the time they were developed[4]. The test conditions of these methods however do not represent the present engine operating conditions as investigated and elucidated by Kalghatgi[3][5]. The combustion chamber geometry has changed, along with the temperature and pressure of the intake charge. The CFR has a flat-roof with the spark plug at the side while most present engines have pent-roof heads with a central park plug. This has an effect on the burn rates of the fuel as the length of the flame travel is halved in the second case[4].

Even if the fuel is purely paraffinic and the sensitivity is zero, the PRF based on RON failed to replicate the low temperature ignition of the gasoline fuels tested by Sarathy et al [6] as both Rapid Compression Machine (RCM) and shock tube experiments showed differences in the low temperature reactivity of real alkane-rich gasoline and the PRF surrogate based on RON. However, high temperature reactivity remained the same between the surrogates and the real fuels[7].

The paraffinic fuels compared in the aforementioned experiments are designated as FACE A and FACE C where FACE stands for Fuels for Advanced Combustion Engines. These fuels have been blended and supplied by the Conoco Philips Chemical Company and are used for studying the effect of fuel composition on Advanced Combustion Engine concepts such as Homogeneous Charge Compression Ignition (HCCI), Reactivity Controlled Compression Ignition (RCCI), and Premixed Charge Compression Ignition (PCCI) which are being developed to reduce emissions without compromise on efficiency. The chemical kinetics of the fuel controls the ignition event and combustion phasing in these engines.

The RON and MON of both fuels is 84 and both are bound to exhibit two-stage ignition and hence Low Temperature Heat Release (LTHR), as most fuels in this octane range[8]. The cool flame behavior of these fuels is very important in these engines as it helps to phase

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combustion[9]. The advantages of using such fuels for operation of HCCI engines is summarized in Sjöberg and Dec[8].

The surrogates used for simulating the chemical behavior of these fuels in such engines then have to accurately reproduce low temperature chemistry as well as the high temperature chemistries of the real fuel.

Background on Surrogates

A computational methodology was developed by Ahmed et al. [1] drawing from the previous works of Dooley et al.[10][11], Mehl et al.[12], Puduppakkam et al. [13], Pera [14] and Sarathy et al.[6] to arrive at multi-component surrogates that would closely match target properties of the real gasoline fuels across all engine operation conditions. The methodology was based on the need to match wider number properties of the surrogate to the target fuel unlike RON based PRF or TRF mixtures which looked only into the auto-ignition quality in a limited number of engine operating conditions.

The properties identified that were relevant to gasoline fuels were hydrogen to carbon ratio, density, compositional characteristics, distillation curve, research octane number (RON). Each property was weighted in an objective function which is a regression model that represents the difference between the surrogate and the parent fuel. The minimum value of the function gives the surrogate mixture that has the least deviation from the real fuel. The composition (mol. %) of the proposed surrogate mixtures is presented in Table 1. FGA-2 and FGC-2 are the surrogate mixtures of FACE A and FACE C, respectively.

Palette Component	FGA-2	FGC-2	PRF	RON[15] [16]
n-butane	7.7	18.4	0	93.6
n-heptane	10.0	12.5	17.6	0
2-methylbutane	12.0	5.0	0	92.3
2-methylhexane	10.3	4.7	0	42.4
2,2,4-trimethylpentane	60.0	54.6	82.4	100
Toluene	0	4.8	0	116

Table 1. Composition of Surrogates (mol. %)

Experimental Methodology

Validation of Surrogates

The validation of surrogates based on gas phase kinetics have been usually done through measurement of a global combustion property such as ignition delay times in shock tubes [9], [10], [16], [17] or laminar burning velocities [19], [20],[21]. They provide an experimental method to accurately determine and compare gas phase kinetics of different fuels under various pressures and temperatures with high accuracy without any physical effects such as atomization, mixing and thermal diffusivity. The other reason for their use comes from the ease of modelling these reactors compared to a complicated internal combustion engine. These methods

are however restricted to high temperature conditions and are not well suited for cool flame regime.

The alternative is the use of an engine which operates at these temperature regions in which oxidation and autoignition events are purely controlled by the kinetics of fuel/oxidizer thus eliminating the effects of physical processes. Knop et al. [22] had earlier conducted such a validation of toluene reference fuels (TRF) in engine relevant conditions under Controlled Auto-Ignition (CAI) mode in its entire operating range. This mode allows for the study and comparison of the surrogates against the real fuels purely from a chemical kinetics perspective. The engine operating in this mode can be treated as a reactor to explore the chemical kinetics of the fuel oxidation by analyzing the heat release rate and exhaust at different conditions by changing the physical parameters such as intake air temperature, pressure or compression ratio. The fuel injection is done into a heated manifold or on the valve to fully vaporize and premix the fuel. The experiments by Leppard[23], Sahetchian[24], Yang et al.[25],[26],[27], and Szybist et al.[28] used a similar methodology to study low and intermediate temperature oxidation of various compounds in which they used a modified Cooperative Fuels Research (CFR) engine which was originally devised to measure the octane rating of the fuel at fixed engine speed, intake air temperature and pressure. The GC-MS analysis of the exhaust reveled the chemistry behind the oxidation of the fuel.

Engine Setup

In this study the experimental validation was done here in a modified motoring Cooperative Fuels Research (CFR) engine whose specification are given in Table 2 and the schematic of the engine is presented in Fig. 1. The intake air flows through a mass flow meter into the heater wherein the desired air temperature is achieved. The gas phase component of the surrogate mixtures, n-butane, was added into the intake line through a port. The quantity of n-butane was computed from the intake air flow rate for the desired equivalence ratio and supplied though a mass flow controller. The liquid fuel was injected on the intake valve through a Port Fuelled Injector (PFI). The fuel was supplied to the injector from a tank in which the fuel is pressurized by helium. The fuel was completely vaporized as it comes in contact with the hot intake valve and was thoroughly premixed with the oxidizer (air) in the intake manifold before entering the combustion chamber. The equivalence ratio is first set by adjusting the compression ratio to achieve stable hot combustion. The air to fuel ratio value was then given by the oxygen sensor (λ sensor) in the exhaust. The compression ratio is then lowered to point where no reactivity was observed and then raised gradually till the point when autoignition occurred.

The in-cylinder pressure was recorded at each compression ration using a Kistler Pressure Transducer at every 0.05° degree of crank angle. The in-cylinder pressure recorded was averaged over 100 cycles and used

to compute the heat release rate according to first law analysis as given in Equation 1. The ratio of specific heats, γ was computed using Equation 2[29]. The ratio of specific heat is a function of temperature[29]. The temperature inside the cylinder is derived from the pressure data using ideal gas equation where the mass of the charge is kept constant.

$$\frac{dQ}{d\theta} = \frac{V\frac{dP}{d\theta} + \gamma P\frac{dV}{d\theta}}{\gamma - 1} \qquad (1)$$

$$\gamma = (1 - \frac{R_g}{C_p})^{-1} \qquad (2)$$

Results and Discussion

The ability of both surrogates to accurately replicate the different regimes of reactivity close to the real fuel was earlier presented in Ahmed et al.[1] by plotting carbon mono-oxide (CO) measured in the exhaust against the respective compression ratio. CO was chosen because it is good indicator of low and intermediate reactivity[30] while its consumption and conversion to carbon di-oxide points to the start of high temperature combustion. The transition of the fuel reactivity into different combustion regimes was well captured by the proposed surrogates.

The cool flame behavior of the surrogates accessed here by comparison of the apparent heat release rates calculated as described in the previous section. The heat release rate of FACE A at different compression ratios is presented in Fig. 2. The data was smoothed using a Gaussian fit. The different regimes of combustion can be observed in it. The Low Temperature Combustion (LTC) starts from a compression ratio of 5.7. There is a noticeable shift in the onset of reactivity and increase in the peak heat released as the compression ratio is raised. The shift happens because the temperature and pressure at which peak low temperature reactivity is achieved for the fuel is attained at an earlier crank angle with increase in compression ratio. At about 7.1 the oxidation process moves into the Negative Temperature Coefficient (NTC) region. The start of LTHR still shifts to an earlier crank angle but the rate gets slower and the increase in peak heat release rate is also very small. The transition into High Temperature Combustion (HTC) occurs at 9.7 where autoignition of the fuel takes place leading to a high temperature heat release (HTHR).

The cumulative heat released at each point was then divided by the total heat release to determine the normalized heat release. The start, middle and end of low temperature oxidation is indicated by CA10, CA50 and CA90 which represent 10%, 50% and 90% of the LTHR. They can be determined from the plotting the normalized heat release against crank angle as shown in Fig. 3. The duration of the combustion is the difference between CA90 and CA10. CA 50 is used as the metric for assessing combustion phasing. The difference between CA 50 of surrogate and parent fuel is the measure of deviation of their chemical kinetic behavior.

Engine Type	Single Cylinder
Injection System	Port Fuel Injection
Combustion Mode	Controlled Auto-Ignition
Bore	82.55mm
Stroke	114.3mm
Connection Rod Length	254 mm
Compression Ratio	Variable till 12:1
Engine Speed	600 rpm
Fuel/Air Eq. Ratio	0.5
Intake Pressure	98 kPa
Air Flow Rate	9.378 kg/h
Intake Temperature	150 $\pm$ 2 ℃

Table 2. Specification and Operation Conditions of Modified CFR Engine

The CA 50 of LTHR at different compression ratios for FACE A, C and PRF is presented in shown in Fig. 4. The PRF demonstrates a significantly higher reactivity compared to FACE A and C across compression ratios and FACE A is more reactive than FACE C. The variation between the fuels can be explained if LTHR is considered mainly as a characteristic of the concentration as well as octane rating of only the most reactive species in the fuel. The octane number of the species (only alkanes here) depend on the chain length and branching[16]. This is because the initiation of oxidation of paraffin at low temperatures is mainly through H-atom abstraction by molecular oxygen or radicals[22][23]. The rate of H-atom abstraction is highest for the hydrogen atoms attached to the tertiary carbon atom followed by secondary and primary carbon[24]. The longer the chain the greater the ratio of secondary to primary hydrogen atoms which increases the reactivity. Branching has the opposite effect on the ratio since there will be more terminal carbon atoms and hence primary H-atoms which reduces reactivity of the compound.

The high reactivity component is solely n-heptane (RON – 0) for the PRF. The components with lowest octane rating but with significant concentrations in FACE A are n-heptane, 2-methylhexane (42.4) and 3-methylhexane (52) while it is n-pentane (61.7) and n-hexane (24.8) in FACE C. The combined mol. % of these species are 17.6, 17.86 and 24.69 for PRF, FACE A and C respectively. Even though FACE C has a higher mole fraction of the high reactivity component and FACE A has a similar mole fraction to that of PRF the combined RON determined by linear-by-mole blending[15] of these species are 0 (PRF), 5.44 (FACE A)and 11.23 (FACE C).
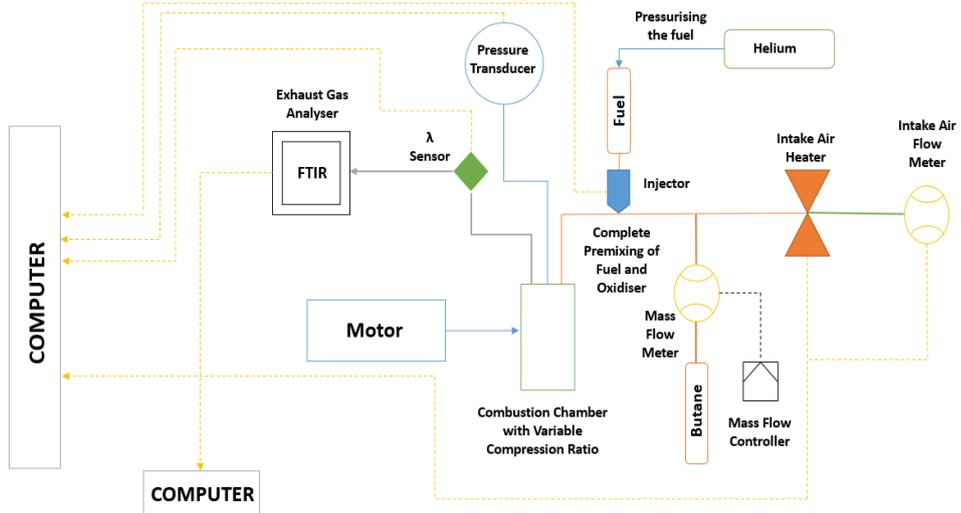
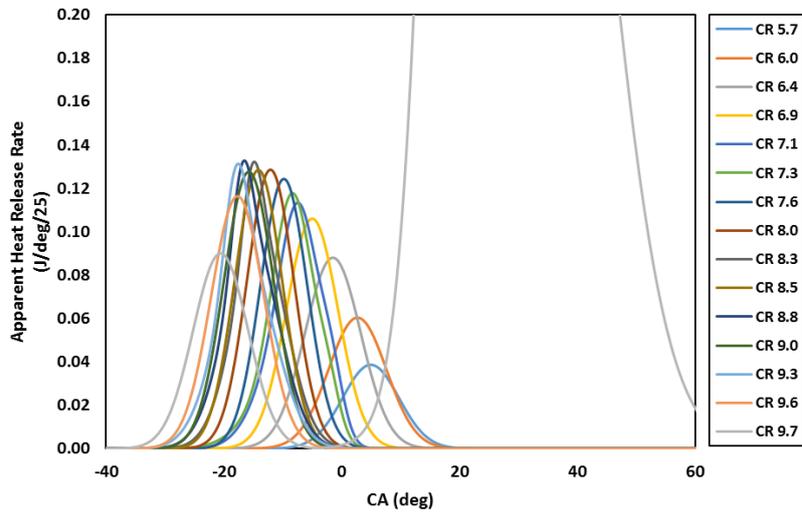**Figure 1. Schematic of the Modified CFR Engine**
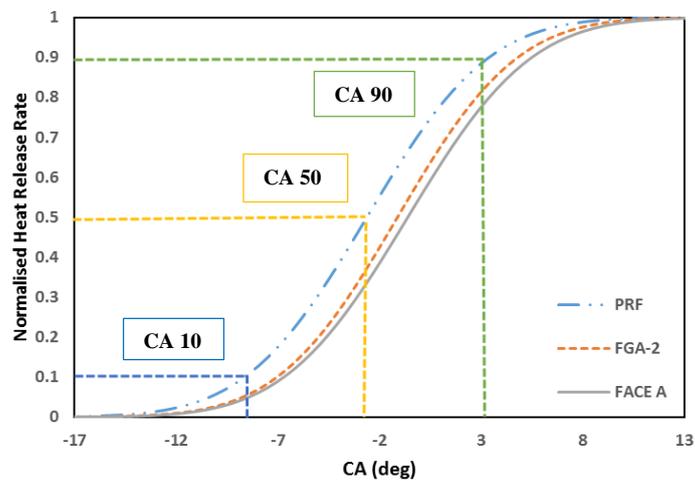

Figure 2. Apparent Heat Release Rates of FACE A

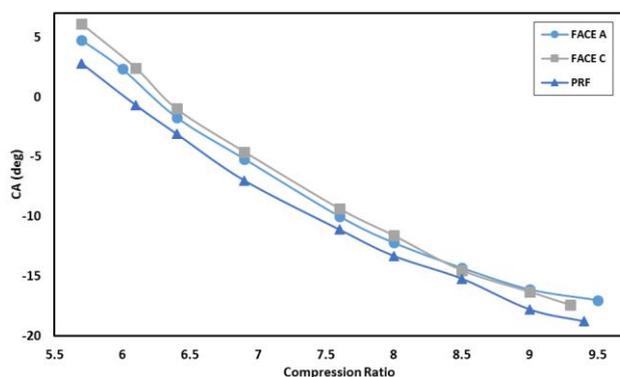**Figure 3. Normalised Heat Release at Compression Ratio 6.5**

Figure 4. Comparison of Low Temperature Reactivity in Terms of CA 50 of LTHR
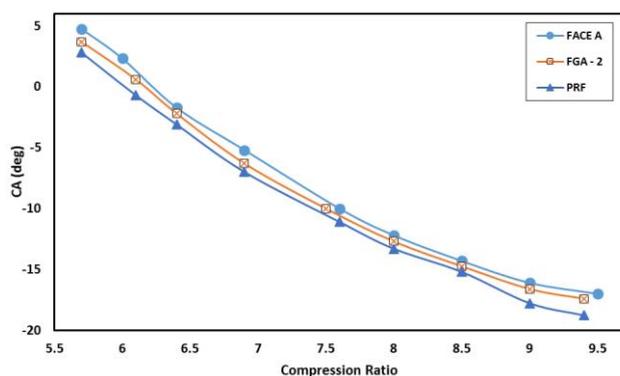

Figure 5. Performance of FGA-2 in Reproducing LTHR (CA 50) of FACE A

FGA-2 performs better than PRF in replicating the FACE A's cool flame behavior at all compression ratios as seen in Fig. 5 and the main components in it promoting LTHR are n-heptane and 2-methylhexane with a combined mole fraction percentage of 20.3 and RON of 4.36. The octane number is very close to that of FACE A but the higher mole fraction increases reactivity of FGA-2.

The palette species that are likely to contribute the most to the low temperature oxidation in FGC-2 are the same of that FGA-2. The combined mole fraction of n-heptane and 2-methylhexane is 17.2 whose combined RON is 2. The difference in the octane rating of these species to that of FACE C is quite large compared to that of FACE A and FGA-2. However, the lower concentrations compensates for the decrease in octane rating. FGC-2 performs again performs better than PRF in reproducing the cool flame behavior of FACE C and at higher compression ratios almost converges with the it as presented in Fig. 6.

Conclusions

The ability of FGA-2 and FGC-2 to replicate the low temperature reactivity of their respective parent gasolines was tested in a modified CFR engine across LTC and NTC combustion regimes by the comparison of heat release rates (LTHR). These surrogate mixtures performed better than a PRF mixture based on RON. The reactivity of the fuels in these conditions is mainly driven by the low RON components. The matching of concentration and combined octane number arrived at by linear blending (molar) of these components are the most important metrics to might need to be matched to formulate surrogate mixtures for gasoline fuels to be used in LTC engine simulations.
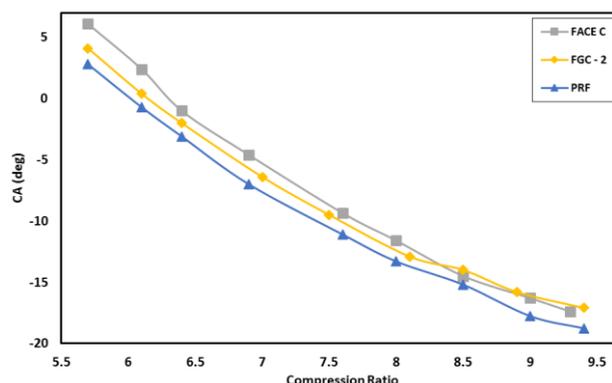

Figure 6. Performance FGC-2 in Reproducing LTHR (CA 50) of FACE C

Acknowledgements

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