Optimization of the octane response of gasoline/ethanol blends

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HIGHLIGHTS

- New experimental data for five components with ethanol addition are collected.
- A new blending rule for PRF, TPRF and multi-components + ethanol octane numbers is proposed.
- The developed model is validated against real gasoline fuel data.
- Methods to optimize the octane response due to ethanol addition are proposed.

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ABSTRACT

The octane responses of gasoline/ethanol mixtures are not well understood because of the unidentified intermolecular interactions in such blends. In general, when ethanol is blended with gasoline, the Research Octane Number (RON) and the Motor Octane Number (MON) non-linearly increase or decrease, and the non-linearity is determined by the composition of the base gasoline and the amount of added ethanol. The complexity of commercial gasolines, comprising of hundreds of different components, makes it challenging to understand ethanol-gasoline synergistic/antagonistic blending effects. Understanding ethanol blending effects with simpler gasoline surrogates is critical to acquire knowledge about ethanol blending with complex multi-component gasoline fuels. In this study, the octane numbers (ON) of ethanol blends with five relevant gasoline surrogate molecules were measured. The molecules investigated in this study include: n-pentane, iso-pentane, 1,2,4-trimethylbenzene, cyclopentane and 1-hexene. These new measurements along with the available data of n-heptane, iso-octane, toluene, various primary reference fuels (PRF) and toluene primary reference fuels (TPRF) with ethanol are used to develop a blending rule for the octane response (RON and MON) of multi-component blends with ethanol. In addition, new ON data are collected for six Fuels for Advanced Combustion Engine (FACE) with ethanol. The relatively simple volume based model successfully predicts the octane numbers (ON) of the various ethanol/PRF and ethanol/TPRF blends with the majority of predictions being within the ASTM D2699 (RON) and D2700 (MON) reproducibility limits. The model is also successfully validated against the ON of the FACE gasolines blended with ethanol with the majority of predictions being within the reproducibility limits. Finally, insights into the possible causes of the synergistic and antagonistic effects of different molecules with ethanol are provided.

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1. Introduction

Ethanol is the most widely used biofuel and blending agent for commercial gasoline fuels [1,2]. A key benefit of ethanol blending is the ability to meet the demand for higher octane RON numbers in modern downsized spark ignition (SI) engines [3,4]. Higher

octane numbers allow engine operations at higher compression ratios and hence greater thermal efficiencies [5–8]. When ethanol is added to the fuel, it burns in a cleaner manner and releases fewer regulated emissions in comparison to pure gasoline [9–14]. The US Energy Independence and Security Act (EISA) of 2007 [15] endorsed a mandatory target to increase the transportation renewable fuel use from 9 billion gallons in 2008 to 36 billion gallons by 2022. Along the same lines, the European Council in March 2007 [16] mandated all EU member countries to have at least 10 vol% biofuels in the transportation fuel by 2020.

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Nomenclature

API	American Petroleum Institute	SI	spark ignition
CFR	Cooperative Fuel Research	TPRF	toluene primary reference fuel
EISA	Energy Independence and Security Act	US	United States
ETBE	ethyl <i>tert</i> -butyl ether		
EU	European Union		
FACE	Fuels for Advanced Combustion Engines	<i>Symbols</i>	
DHA	detailed hydrocarbon analysis	α	scaling factor
DISI	direct injection spark ignition	D	difference factor
HCCI	homogenous charge compression ignition	ϕ	volume fraction
GHG	greenhouse gas		
MON	motor octane number	<i>Subscripts</i>	
MTBE	methyl <i>tert</i> -butyl ether	eth	ethanol
ON	octane number	Mix	mixture
PRF	primary reference fuel	I,T	<i>iso</i> -octane and toluene
RON	research octane number	H,T	n-heptane and toluene

Because of the relevance of ethanol, many previous works have investigated the emissions offset by blending ethanol into gasoline and/or the effect of ethanol on engine performance [3,4,17–28]. Today, the ethanol fuel that is available in the market is mainly made from sugar cane or corn [29–33]. Its production as a first-generation biofuel, especially in North America, has been associated with publicly discussed drawbacks, such as reduction in the food supply, need for fertilization, extensive water usage, and other ecological concerns. More environmentally friendly processes are being considered to produce alcohols from inedible plants or plant parts on wasteland [34].

Ethanol has higher octane ratings compared to regular gasoline [35]. Engine knock is one of the limiting factors inhibiting spark ignition (SI) engines from achieving higher thermal efficiencies. Higher octane fuels, such as ethanol, can enable more efficient SI engine technologies. A chief motivation of the present work is to develop models that predict how ethanol blending increases the octane number of a gasoline blendstock. This information can be useful for designing fuel formulations which offer higher engine efficiency while potentially leading to a net lifecycle greenhouse gas (GHG) emissions reductions [24,36].

2. Background

This section summarizes the literature on ethanol's antiknock quality, knocking in engines, blending effects, and gasoline fuels.

Sarathy et al. [37] attributed ethanol's high antiknock quality to its lack of low-temperature ignition reactivity, wherein ethanol favors chain termination pathways leading to the formation of acetaldehyde and hydroperoxy radicals over conventional hydroxyl radical chain branching pathways. In addition, the high latent heat of vaporization of ethanol reduces the charge-gas temperature when directly injected, which in turn delays the autoignition [6,7]. This feature is commonly known as the charge cooling effect. However, ethanol has lower heating value than gasoline, resulting in a lower energy content per unit volume [10]. Another interesting application of alcohols (methanol and ethanol) is the newly studied octane-on-demand technology where the alcohols are used as the high octane fuels enabling the achievement of higher thermal efficiencies and lower GHG emissions [9–11]. In addition, butanol isomers might also be good octane booster candidates with higher energy density compared to methanol and ethanol. We recently investigated the ignition delay times of mixed butanols/TPRF surrogates [38].

Engine knock is known as the metallic ringing noise caused by the autoignition of the unburned air/fuel mixture ahead of the propagating flame front [39,40]. This autoignition phenomenon generates pressure waves, which can cause severe damage to the engine's hardware [41]. The fuel's tendency to autoignite is described by two parameters known as research octane number (RON) and motor octane number (MON), whose specifications are defined in ASTM D2699 [42] and ASTM D2700 [43], respectively. It is established that the RON of a regular gasoline increases with ethanol addition, but the extent of the increase is still not fully understood yet. Recently, AlRamadan et al. [44] and Yuan et al. [45] proposed molar based blending rules for predicting the octane response of toluene primary reference fuels (TPRF) mixtures with ethanol. Hunwartz et al. [46] reported a linear by volume increase of the RON with ethanol addition to gasoline, which has been contradicted by an American Petroleum Institute (API) study [47] and Anderson et al. [27]. Anderson et al. [27] reported that the ON (RON and MON) increase follows a linear by mole response for gasoline fuels with certain compositions when blended with ethanol and methanol. They have also investigated the ON response due to the addition of other alcohols (*iso*-butanol) and ethers (methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE)). Recently, Anderson et al. [48], Foong et al. [49] and Aronsson et al. [50] reported non-linear by volume and non-linear by mole increases of RON when ethanol is blended with gasoline, suggesting a synergistic effect (a further increase from the linear volume or molar model). The reported synergistic effect depends on the composition of the base fuel. For ethanol blending to gasoline at the MON condition, a linear by mole response was proposed by Anderson et al. [27], synergistic increases were reported by Foong et al. [49] and Anderson et al. [48] and antagonistic effects (a decrease from the linear volume or molar model) were reported by Hunwartz et al. [46] and Foong et al. [49]. The aforementioned discrepancies can likely be attributed to the specific distribution of paraffins, *iso*-paraffins, olefins, naphthenes, and aromatics in the base gasolines that they used. Briefly, the composition of the base gasoline plays a major role in predicting the RON and MON of ethanol blends with gasoline.

The present work first focuses on studying the effect of ethanol blending with eight pure components, namely, n-pentane, n-heptane, *iso*-pentane, *iso*-octane, toluene, 1,2,4-trimethylbenzene, cyclopentane and 1-hexene. These species were selected in a systematic way so they cover the classes of molecules (n-paraffins, *iso*-paraffins, aromatics, naphthenes and olefins) relevant to gasoline fuels, in particular the Fuels for Advanced

Combustion Engines (FACE) gasolines [51], which are also studied herein. The aforementioned molecules have been proposed as palette species for surrogate mixtures of the FACE gasolines [52]. A series of studies on FACE gasolines have been published in recent years. Their fundamental combustion kinetics has been explored in shock tubes, rapid compression machines, jet stirred reactors, and premixed flames [52–56]. Furthermore, engine studies have been performed to assess FACE gasoline combustion characteristics under homogenous charge compression ignition (HCCI) [57], direct inject spark ignition (DISI) [58] and blending effects on SI engine antiknock quality when using various biofuels [59]. The selected surrogate palette species have been subjected to rigorous chemical kinetic modeling studies, including recent state-of-the-art models for n-pentane [60,61], n-heptane [62], iso-pentane [60,61], iso-octane [63], toluene [64], 1,2,4-trimethylbenzene [52], cyclopentane [65–67] and 1-hexene [68,69].

In this work, a non-linear by volume blending model is developed to predict the octane response of ethanol addition to individual gasoline surrogate palette molecules and multi-component gasoline surrogate mixtures. The model is validated against a wide range of octane numbers for various primary reference fuels (PRFs), toluene primary reference fuels (n-heptane/iso-octane/toluene fuels (TPRFs)) and FACE gasoline fuels.

3. RON and MON measurements for pure components and FACE gasolines blended with ethanol

3.1. Experimental methodology

Octane numbers (RON and MON) data are available in literature for blends of ethanol with n-heptane [49], iso-octane [49], toluene [49], PRF [44,49] and TPRF [44,49]. Based on these data, AlRamadan et al. [44] developed a molar based blending rule for PRF and TPRF mixtures with ethanol. To extend that model to include more molecules relevant to gasoline surrogates, new RON and MON measurements were obtained for five additional single components with ethanol. The examined components were chosen based on the different classes of molecules relevant to gasoline surrogates. The ON of n-pentane (n-paraffinic), iso-pentane (iso-paraffinic), 1,2,4-trimethylbenzene (aromatics), cyclopentane (naphthenes) and 1-hexene (olefins) blended with multiple volume fractions (0–60 vol%) of ethanol were measured here following the standard test methods for RON and MON [42,43] using the Saudi Aramco Cooperative Fuel Research (CFR) engine facility. The differences between the ethanol and gasoline physical chemical properties introduce some challenges in the hardware used to measure the RON and MON [42,43]. Ethanol has lower stoichiometric air/fuel ratio compared to gasoline, and hence the standard fuel metering jet for RON and MON tests is inappropriate to supply sufficient fuel flow rate of ethanol [46]. German institute for standardization DIN 51756-7 [70] suggests some modifications to the engine hardware to measure fuels with high alcoholic content. Replacing the original carburetor jet by an adjustable orifice jet

to supply sufficient flow rate of alcohol for both the RON and MON tests is one of the recommendations. This hardware modification has been implemented in this study to ensure sufficient flow rate of ethanol-rich fuels.

In addition, the high heat of vaporization of ethanol [27,43,49] introduces difficulties in maintaining the standard temperatures of the fuel/air mixtures in the RON and MON conditions. An external electric heating system is suggested to be used in the MON test to provide additional heat to compensate for the cooling effect of the ethanol-rich air/fuel mixture. At RON conditions, Foong et al. [49] proposed modifications to the CFR engine to measure RON of ethanol-containing mixtures. They reported standard and modified RON measurements for various ethanol/PRF mixtures and noted that differences up to 4 points can be observed between the standard and modified RON. However, the RON and MON measurements reported in this work are from a standard CFR engine without modifications in the RON test conditions. The ON of pure ethanol in this study are taken from Foong et al. [49] (RON 108, MON 90.7), where they followed the recommendations discussed earlier [42,43,70].

With these new RON and MON measurements, gasoline surrogate mixtures can be formulated using multiple species within a certain hydrocarbon class (as opposed to conventional PRF and TPRF surrogates). For example, n-heptane and n-pentane are available to represent the n-paraffinic class. Similarly, iso-octane and iso-pentane for the iso-paraffinic class, and toluene and 1,2,4-trimethylbenzene for the aromatic classes. In addition, representatives of the naphthenes (cyclopentane) and olefins (1-hexene) are now accessible when formulating surrogates for gasoline fuels.

In addition, six FACE gasolines were blended with ethanol, and their RON and MON were measured to validate the developed blending rule. The FACE gasolines were chosen based on their different compositions. For example, FACE A, C and I were chosen because of their high paraffinic contents (~90 vol%). FACE G and J have high aromatic contents (>30 vol%). Finally, FACE F was selected because of its considerable amounts of naphthenes (~10 vol%) and olefins (~10 vol%). In addition, these FACE gasolines were chosen because some pairs have comparable RON and MON values but different compositions. FACE A and C have similar RON and MON despite the differences in the compositions. The same applies to FACE F and G and to FACE I and J. The compositions and properties of the studied FACE gasolines are listed in Table 1. More details about the FACE gasolines can be found in [51].

3.2. Experimental results

Table 2 summarizes the new CFR engine measurements for the five single components blended with ethanol. These volume and mole based experimental data are presented in Fig. 1 and Fig. 2. The calculated RON and MON using the linear-by-volume or mole method are also shown in Fig. 1 and Fig. 2, respectively. Regarding the volume based experimental data, it is clearly seen from Fig. 1

Table 1
Compositions and the octane ratings of the six tested FACE gasolines. The data are taken from [51].

	FACE					
	A	C	F	G	I	J
RON	83.5	84.7	94.4	96.8	70.3	71.8
MON	83.6	83.6	88.8	85.8	69.6	68.8
n-Paraffins (vol%)	11.7	24.4	4.4	6.8	14.5	31.6
iso-Paraffins (vol%)	86.0	69.7	67.5	39.0	74.6	33.7
Aromatics (vol%)	0.7	3.9	7.7	34.2	1.2	31.8
Naphthenes	1.6	0.7	11.0	11.7	3.3	2.3
Olefins	0.0	1.3	9.4	8.3	6.4	0.6

Table 2

Measured RONs and MONs of different single components blended with ethanol.

Ethanol vol%	n-Pentane		iso-Pentane		1,2,4-Trimethylbenzene		Cyclopentane		1-Hexene	
	RON	MON	RON	MON	RON	MON	RON	MON	RON	MON
0	61.7	58.3	92.0	90.0	109.5	108.0	100.0	85.6	73.6	64.5
10	72.0	66.0	95.5	91.0	107.0	102.0	101.0	85.9	81.0	68.5
25	83.2	78.2	100.0	92.0	105.0	95.5	102.3	86.3	89.2	74.5
40	93.6	86.0	102.4	92.6	104.0	93.5	103.3	86.6	96.5	79.5
60	103.4	92.8	105.5	92.7	105.8	91.0	104.8	87.2	101.7	84.0

Fig. 1. Measured (symbols) and calculated using linear-by-volume or mole (dashed lines) RONs of different single components blended with ethanol. Filled symbols are plotted against the volume fraction of ethanol and open symbols are plotted against the mole fraction of ethanol.

that there are distinct synergistic effects (the measured RON is higher than the estimated using linear-by-volume) when blending ethanol with n-pentane, iso-pentane and 1-hexene. 1,2,4-Trimethylbenzene clearly shows an antagonistic effect (the measured RON is lower than the linear-by-volume) when blended with ethanol. Cyclopentane nearly follows the linear-by-volume RON response with the addition of ethanol. Similar synergistic effects are seen with MON when adding ethanol to n-pentane, iso-pentane and 1-hexene, as shown in Fig. 2. The MON values for blends of 1,2,4-trimethylbenzene with ethanol also show antagonistic effect, as expected. Unlike the linear-by-volume relationship of RON for cyclopentane and ethanol mixtures, antagonis-

tic effects are observed for MON, as shown in Fig. 2. The synergistic and antagonistic responses mostly decrease when plotting the RON and MON experimental data against the mole fraction of ethanol. This is expected because the data points are shifted towards the linear-by-mole line when analyzed on molar basis. In some cases, the slightly synergistic behavior changes to antagonism when plotting the data against the mole fraction of ethanol as can be seen from the cyclopentane/ethanol RON measurements. However, there are still synergistic and antagonistic RON and MON responses when adding ethanol to the five studied molecules. These synergistic and antagonistic effects are quantified and discussed in details in the subsequent sections.

Fig. 2. Measured (symbols) and calculated using linear-by-volume or mole (dashed lines) MONs of different single components blended with ethanol. Filled symbols are plotted against the volume fraction of ethanol and open symbols are plotted against the mole fraction of ethanol.

The RON and MON for the blends of FACE gasolines with ethanol measured in this work are presented in Table 3. The measured RON and MON data along with the linear-by-volume or mole calculations are also presented against the ethanol volume and mole fractions in Fig. 3 and Fig. 4, respectively. Previous RON and MON measurements of FACE gasolines/ethanol blends are reported in literature [51]. However, these measurements are only available for FACE A, B, C and H and with ethanol addition up to 30 vol%. The new measurements reported here serve as an extension of the CRC work and the overlapping measurements are compared in the subsequent plots. The measured RON and MON (Table 3) of the base FACE gasolines are within the reproducibility limits of the values reported in [51] and Table 1. Similarly, excellent agreements are observed between the RON and MON measurements reported here and the ones from [51] for FACE gasolines/ethanol

blends. Regarding the octane response when blending FACE gasolines with ethanol, it is clear that the RON and MON of all tested FACE gasoline fuels exhibit synergistic effects. The scale of this synergy depends on the composition of the base FACE gasoline. For example, the synergistic effect of FACE F with ethanol is higher than that of FACE G despite having similar base RON and MON, as shown in Fig. 3 and Fig. 4, respectively. For example, D_{RON} ($RON_{Measured} - RON_{Linear-by-volume}$) of FACE F with 10, 25 and 40 vol % of ethanol are 3.3, 5.6 and 5, respectively. However, D_{RON} of FACE G with 10, 25 and 40 vol% of ethanol are 1.2, 3.1 and 2, respectively. This is due to the higher aromatics content in FACE G compared to FACE F. Similar to the previous analysis on the RON and MON of pure components/ethanol mixtures, the mole based ON responses are lower than the volume based ones. These distinct effects are also discussed in more details in the subsequent sections.

Table 3
Measured RONs and MONs of FACE gasolines blended with ethanol.

Ethanol vol%	FACE A		FACE C		FACE F		FACE G		FACE I		FACE J	
	RON	MON	RON	MON	RON	MON	RON	MON	RON	MON	RON	MON
0	83.6	82.9	84.4	83.0	94.2	87.4	96.4	84.9	69.5	69.0	71.8	66.9
10	92.0	88.0	92.2	87.1	98.9	88.5	98.8	86.1	79.9	78.0	79.0	73.6
25	100.7	90.6	100.3	90.5	103.2	89.5	102.4	87.9	92.6	85.3	89.8	81.7
40	104.1	91.7	104.1	91.0	104.7	90.3	103.0	88.5	100.4	88.3	98.0	85.9
60	106.0	91.3	105.8	91.3	105.7	90.5	105.0	88.9	104.1	89.7	103.6	88.2

Fig. 3. Measured (symbols) and calculated using linear-by-volume or mole (dashed lines) RONs of different FACE gasoline fuels blended with ethanol. Filled symbols are plotted against the volume fraction of ethanol and open symbols are plotted against the mole fraction of ethanol.

4. Methodology to develop a blending rule of ethanol with PRFs and TPRFs

The development of the blending rule starts with PRF and TPRF mixtures with ethanol, since these are widely used surrogates for gasoline fuels [44,71–76]. Also, establishing an octane number regression model for PRFs/ethanol and TPRFs/ethanol blends would significantly aid the efforts in designing modern engines fuels with optimum ON response due to the addition of ethanol. This is achieved because detailed [38] and reduced [77] chemical kinetic models are available in literature for PRF and TPRF mixtures with ethanol, thereby enabling different types of engine simulations ranging from 0D to 3D. Note, that we recently [44] developed a molar based blending rule for predicting the ON of PRF and TPRF mixture with ethanol; however, the complexity of that model hinders its extension to development of blending rules for other multi-component surrogates with ethanol. The complexity of the molar based model is introduced by the definition of the linear and non-linear sections of the octane response. The transition from linear to the non-linear sections was defined as a function of the PRF number of the simple PRF and TPRF surrogates. The determination of the transition point of multi-component mixtures is not a direct function of the PRF number anymore but rather a complicated parameter because of the unknown interactions between the various species. Therefore, a simpler volume based model with fewer parameters is proposed herein. The following steps were followed to develop the proposed model.

4.1. Scaling parameter (D) of *n*-heptane, *iso*-octane and toluene

As previously noted, there are distinct synergistic and antagonistic effects when blending ethanol with different pure components. Therefore, a variable termed D was defined first. D , similar to the scaling parameter suggested by Anderson et al. [48], is the difference between the measured ON (RON and MON) and the calculated ones using the linear-by-volume or mole method for mixtures of pure *n*-heptane, *iso*-octane and toluene with ethanol as described in Eq. (1).

$$D_{ON,i} = ON_{Measured,i} - ON_{Linear-by-volume\ or\ mole,i} \quad (1)$$

where i refers to the species of interest being *n*-heptane, *iso*-octane or toluene and $ON_{Linear-by-volume\ or\ mole,i}$ is defined as,

$$ON_{Linear-by-volume\ or\ mole,i} = \phi_{eth} \times ON_{eth} + (1 - \phi_{eth}) \times ON_i \quad (2)$$

where ϕ_{eth} is the ethanol volume or mole fraction and ON_{eth} and ON_i are the RON or MON of ethanol and pure component i , respectively. Fig. 5 below shows the volume and mole based D_{RON} and D_{MON} for blends of pure *n*-heptane, *iso*-octane and toluene with ethanol. The data used to calculate the D_{ON} (Fig. 5) are taken from [49] and are listed in Table 4. D is a direct measure of the synergistic and antagonistic effects of the fuel blend with ethanol. In other words, there is a synergistic effect between the fuel and ethanol if D is positive and an antagonistic effect when D is negative. The degree of this synergistic or antagonistic effect is measured by the values

Fig. 4. Measured (symbols) and calculated using linear-by-volume or mole (dashed lines) MONs of different FACE gasoline fuels blended with ethanol. Filled symbols are plotted against the volume fraction of ethanol and open symbols are plotted against the mole fraction of ethanol.

of D. Regarding the volume based RON of ethanol mixtures with n-heptane, iso-octane and toluene, n-heptane and iso-octane have synergistic while toluene has antagonistic effects as can be seen from Fig. 5a. The volume based MON of n-heptane and toluene mixtures with ethanol show similar trends as RON, however, MON of iso-octane blends with ethanol are very close to the linear-by-volume calculations as can be seen from the near zero values (filled symbols) of $D_{MON, iso-octane}$ in Fig. 5b. The mole based D_{RON} and D_{MON} of iso-octane and toluene blends with ethanol are very similar to those the volume based ones with the peak shifting to higher ethanol mole fraction. However, the mole based D_{RON} and D_{MON} of n-heptane/ethanol mixtures are significantly lower than the volume based ones and the peaks are also shifted to higher ethanol mole fractions.

It has been previously shown [27,44,45,48,49] that a linear-by-mole blending may better reproduce octane number response with ethanol addition. Also, it was earlier demonstrated that the degree of synergism and antagonism may change if data is analyzed on molar basis. However, D value trends indicate that both volume and mole based analyses clearly show synergetic and antagonistic responses, albeit the magnitude varies with the method used. D values based on volume blending tend to be larger than those for molar blending for cases when there are large differences between base fuels RON (e.g., n-heptane/ethanol mixtures). Nevertheless, the linear-by-volume is used here as the basis of D definition because qualitative trends are adequately captured and for simpler applicability, especially in industry. The model presented herein is

considered one of the potential simple approaches to analyze the data.

The volume based D values shown in Fig. 5 were fitted using high order polynomial expressions in Microsoft Excel to obtain the highest R^2 values as can be seen from the equation below.

$$D_{ON,i} = a \times \varnothing_{eth}^5 + b \times \varnothing_{eth}^4 + c \times \varnothing_{eth}^3 + d \times \varnothing_{eth}^2 + e \times \varnothing_{eth} + f \quad (3)$$

where a, b, c, d, e and f are the polynomial fitting constants. These polynomial constants of D_{RON} and D_{MON} along with the R^2 values are provided in Table 5. Note that the values for constant f are not zeros and can be noticeable in some cases such as D_{MON} for n-heptane (−1.38). The values of the constants including f were obtained from the simple polynomial fittings while maximizing the R^2 values and having a non-zero value for f does not reflect a modification to the assumed octane rating of the pure component.

A preliminary model for predicting RON and MON of any PRF or TPRF blends with ethanol is proposed.

$$ON_{TPRF+eth} = ON_{Linear-by-volume} + \sum_{i=1}^N (D_{ON,Mix,i}) \quad (4)$$

where i refers to the pure components, N is the number of components present in the base TPRF mixture and $D_{ON,Mix,i}$ is the individual D effect for species i when mixed with ethanol but normalized by the volume fraction of species i in the base TPRF mixture. This term is defined as,

Fig. 5. D_{RON} and D_{MON} for n-heptane, iso-octane and toluene mixtures with ethanol obtained from [49]. Filled symbols are plotted against the volume fraction of ethanol and open symbols are plotted against the mole fraction of ethanol.

Table 4

Measured RONs and MONs of n-heptane, iso-octane and toluene blended with ethanol. The data are taken from [49].

Ethanol vol%	n-Heptane		iso-Octane		Toluene	
	RON	MON	RON	MON	RON	MON
0	0.00	0.00	100.0	100.0	120.0	107.0
10	–	–	106.8	99.9	112.8	101.0
20	–	–	109.4	99.1	110.9	97.0
30	54.3	–	–	–	–	–
40	69.7	64.5	110.2	95.9	108.6	93.3
50	83.8	–	–	–	–	–
60	94.7	83.8	109.2	94.2	108.1	91.9
70	101.6	–	–	–	–	–
80	104.7	88.9	109.0	92.6	107.9	91.1
90	106.5	–	–	–	–	–
100	108.5	90.7	108.5	90.7	108.5	90.7

Table 5

Polynomial fitting constants of D_{RON} and D_{MON} for mixture of ethanol with pure n-heptane, iso-octane and toluene.

Polynomial constants	n-Heptane		iso-Octane		Toluene	
	D_{RON}	D_{MON}	D_{RON}	D_{MON}	D_{RON}	D_{MON}
a	0.00	0.00	–108.34	0.00	–257.40	–608.60
b	153.21	0.00	209.37	–15.57	549.58	1482.80
c	–343.79	39.09	–39.70	40.89	–316.37	–1213.90
d	130.30	–187.89	–127.48	–34.68	35.71	408.30
e	59.96	148.42	66.24	9.28	–11.18	–68.30
f	0.20	–1.38	0.00	0.21	–0.33	0.70
R ² values	0.999	0.994	0.999	0.903	0.991	0.999

$$D_{ON,Mix,i} = \phi_{i,base} \times D_{ON,i} \quad (5)$$

and $\phi_{i,base}$ is the volume fraction of species i in the base TPRF mixture. For example, when 20 vol% of ethanol is added to a base TPRF mixture that contains 50 vol% n-heptane, 30 vol% *iso*-octane and 20 vol% toluene, N would be equal to 3, i is n-heptane, *iso*-octane and toluene, $\phi_{i,base} = 0.5, 0.3$ and 0.2 for n-heptane, *iso*-octane and toluene, respectively and $D_{ON,i}$ is calculated using Eq. (3). $ON_{Linear-by-volume}$ is calculated as,

$$ON_{Linear-by-volume} = \phi_{eth} \times ON_{eth} + (1 - \phi_{eth}) \times ON_{TPRF,base} \quad (6)$$

where $ON_{TPRF,base}$ are the RON and MON of the base TPRF mixture without ethanol addition.

4.2. Interactions between molecules

There are cross-reactions between the different components in TPRF mixtures when blended with ethanol [38,45]. These interactions between the molecules cannot be neglected when developing a blending rule for TPRF+ethanol mixtures and hence need to be accounted for as per the expression below.

$$ON_{TPRF+eth} = ON_{Linear-by-volume} + \sum_{i=1}^N (D_{ON,Mix,i}) + \alpha_{H,I} \sqrt{(D_{ON,Mix,H} \times D_{ON,Mix,I})} + \alpha_{H,T} \sqrt{(D_{ON,Mix,H} \times D_{ON,Mix,T})} + \alpha_{I,T} \sqrt{(D_{ON,Mix,I} \times D_{ON,Mix,T})} \quad (7)$$

where $D_{ON,Mix,H}$, $D_{ON,Mix,I}$ and $D_{ON,Mix,T}$ are calculated using Eq. (5) for n-heptane, *iso*-octane and toluene, respectively. $\alpha_{H,I}$ is the introduced scaling factor for the interactions between n-heptane and

iso-octane when blended with ethanol. Similarly, $\alpha_{H,T}$ is for the interactions between n-heptane and toluene and $\alpha_{I,T}$ accounts for the cross-reactions between *iso*-octane and toluene when blended with ethanol. The interactions between hydrocarbons on ethanol blending are represented by the products of terms from single components to comply with the boundary conditions. In the current form, Eq. (7) can be utilized to predict the ON of pure components/ethanol blends. For example, the RON and MON of n-heptane/ethanol mixture can be calculated using Eq. (7) because the interaction terms are eliminated due to the products nature. The introduced scaling factors are optimized based on the predictions of ON of the various PRF and TPRF blends with ethanol available from literature [44,49]. A manual method to optimize the scaling factors was utilized here. The summation of the octane number errors ($ON_{Measured} - ON_{Predicted}$) was calculated for a range of scaling factors until a local minimum is obtained. The range was then narrowed down around that local minimum until a new minimum is found. First, the $\alpha_{H,I}$ was optimized using the RON and MON data of the various PRF/ethanol mixtures. The optimized $\alpha_{H,I}$ values from the previous step were kept unchanged when optimizing $\alpha_{H,T}$ and $\alpha_{I,T}$ using the same manual approach for the various TPRF/ethanol mixtures. The optimized interaction factors are presented in Table 6.

4.3. Validation of the TPRF+ethanol model

The PRF/TPRF+ethanol model presented in Eq. (7) was validated against the various PRF and TPRF with ethanol data found in literature [44,49]. The RON and MON of all the existing PRF and TPRF blends with ethanol excluding the base PRFs, TPRFs and ethanol were calculated using the developed model. The PRF and TPRF with ethanol data were also predicted using the model proposed by Aronsson et al. [50]. An ON error which is the difference between the measured and predicted ON was defined as a measure of the accuracy of the model. The absolute values of the ON errors are plotted against the measured ON in Fig. 6. The RON and MON reproducibility limits [42,43] are also shown in Fig. 6. The RON predictions using the developed model are very accurate with the majority (91%) of the RON errors being within the reproducibility limits as can be seen from Fig. 6a. MON predictions (Fig. 6b) are not as accurate as RON because of the lesser amount

Table 6
Interaction factors between n-heptane, *iso*-octane and toluene when blended with ethanol.

Interaction factors	RON	MON
$\alpha_{H,I}$	0.52	1.60
$\alpha_{H,T}$	0.55	0.30
$\alpha_{I,T}$	−0.70	−1.55

Fig. 6. Predicted (a) RON and (b) MON errors versus measured RONs and MONs for different PRF and TPRFs/ethanol blends. Filled symbols using the model proposed here and open symbols using Aronsson's blending rule [50].

of data used to calibrate the model for MON. However, the MON errors are almost all less than 2 MON and 31% of the predictions are outside the reproducibility limits. The predictions of the current model are as accurate as the calculations of the previous blending rule [44] despite the fewer number of parameters utilized here. The model proposed here performs better than Aronsson's blending rule where only 70% of the RON predictions are within the reproducibility limits. MON prediction are even worse with 70% are outside the reproducibility limits as can be seen from Fig. 6b. The overall ON errors that are outside the reproducibility limits are smaller using the current model compared to Aronsson's where ON errors of 8 are observed. The ON errors predicted by the current model are all less than 3. The ON errors using Aronsson's model are mainly from the mixtures with high ethanol content. This is expected because they calibrated their model for PRF and TPRF mixtures with ethanol vol% up to 38%. The measured, predicted (using the current model) RON and MON and ON errors for the PRF and TPRF/ethanol blends are provided in Supplementary Material. Note that the PRF and TPRF data used here to test the accuracy of the model were the ones used to optimize the scaling factors as detailed in the previous section. The current test is not intended to predict the ON of the mixtures used to develop and optimize the model but rather a sanity check for the relatively simple model (linear-by-volume with few scaling factors) and its optimization process. It is worth noting that more accurate predictions can be obtained by adding more variables in the model and using a more advanced optimization method. However, the level of accuracy presented in Fig. 6 is considered to be acceptable considering the simplicity of the model and the small number of variables.

5. Model development for multi-component surrogates with ethanol

Similar to the TPRF model, D for the five additional pure components (n-pentane, *iso*-pentane, 1,2,4-trimethylbenzene, cyclopentane and 1-hexene) with ethanol were calculated. The volume and mole based D_{RON} and D_{MON} values for the above-mentioned species blended with ethanol are presented in Fig. 7. As shown previously, the volume based RON and MON responses due to the addition of ethanol to n-pentane, *iso*-pentane and 1-hexene exhibit synergistic trends. Regarding 1,2,4-trimethylbenzene mixtures with ethanol, antagonistic effects are observed for both the RON and MON. The volume based octane response due to the addition of ethanol to cyclopentane closely follows the linear-by-volume line as can be seen from the near zero D values. Interestingly, *iso*-octane and cyclopentane have very different D_{RON} values when blended with ethanol despite having very similar base RON values of 100. D values of around 10 are observed for *iso*-octane/ethanol blends (Fig. 5) while cyclopentane/ethanol mixtures have new zero D_{RON} s. This indicates that variation in D values cannot only be attributed to differences in RON of the base fuels, as was shown earlier for n-heptane/ethanol mixtures. As expected, the mole based D_{RON} and D_{MON} are lower than the volume based ones as can be seen from the open symbols in Fig. 7. Similar to n-heptane, *iso*-octane and toluene, the volume based D values were also fitted using polynomial expressions similar to Eq. (3) and the polynomial constants listed in Table 7 along with the R^2 values.

Based on these additional D values, a new model for any mixture containing some or all of the 8 studied components (n-heptane, n-pentane, *iso*-octane, *iso*-pentane, toluene,

Fig. 7. D_{RON} and D_{MON} for n-pentane, *iso*-pentane, 1,2,4-trimethylbenzene, cyclopentane and 1-hexene mixtures with ethanol. Filled symbols are plotted against the volume fraction of ethanol and open symbols are plotted against the mole fraction of ethanol.

Table 7Polynomial fitting constants of D_{RON} and D_{MON} for mixture of ethanol with pure n-pentane, iso-pentane, 1,2,4-trimethylbenzene, cyclopentane and 1-hexene.

Polynomial constants	n-Pentane		iso-Pentane		1,2,4-Trimethylbenzene		Cyclopentane		1-Hexene	
	D_{RON}	D_{MON}	D_{RON}	D_{MON}	D_{RON}	D_{MON}	D_{RON}	D_{MON}	D_{RON}	D_{MON}
a	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
b	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	30.68	54.17
c	0.00	0.00	11.95	1.03	−30.29	−41.82	4.70	8.23	−33.24	−92.77
d	−56.15	−61.47	−34.77	−11.13	61.06	93.10	−7.22	−7.14	−38.09	26.51
e	56.24	61.55	22.84	10.09	−30.74	−51.32	2.50	−1.09	40.75	12.09
f	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
R ² values	0.995	0.996	0.989	0.999	0.986	0.987	0.972	0.999	0.996	0.999

1,2,4-trimethylbenzene, cyclopentane and 1-hexene) with ethanol is proposed.

$$\begin{aligned}
 ON_{Multi-Comp+eth} = & ON_{Linear-by-volume} + \sum_{i=1}^N (D_{ON,Mix,i}) \\
 & + \alpha_{H,I} \sqrt{(D_{ON,Mix,H} \times D_{ON,Mix,I})} \\
 & + \alpha_{H,T} \sqrt{(D_{ON,Mix,H} \times D_{ON,Mix,T})} \\
 & + \alpha_{I,T} \sqrt{(D_{ON,Mix,I} \times D_{ON,Mix,T})} \quad (8)
 \end{aligned}$$

The proposed model is very similar to the TPRF/ethanol one, however, Eq. (8) accounts for the additional species present in the base multi-component mixture. Only the normalized $D_{ON,Mix,i}$ for the additional five species were considered in the current work. The interactions between the additional components and TPRF species were neglected here because of the unavailability of experimental data of mixtures of the additional pure components with ethanol to calibrate the missing scaling factors. In addition, n-heptane, iso-octane and toluene are usually the major constituents of gasoline fuel surrogates, as shown next, and hence the interactions between them needed to be accounted for in the current model. N is equal to 8 for a base multi-component mixture that contains the studied species and i spans across the molecules present in the mixture.

6. Model validation against FACE gasolines

The RON and MON of the studied FACE gasolines blended with ethanol were predicted using the model developed here (Eq. (8)), and then compared with the measured ones to test the accuracy of the proposed blending rule. However, FACE gasolines are composed of hundreds of species, similar to commercial gasoline fuels. Therefore, surrogate fuels that contain some or all of the 8 studied pure components (n-pentane, n-heptane, iso-pentane, iso-octane, toluene, 1,2,4-trimethylbenzene, cyclopentane and 1-hexene) need to be formulated for each of the FACE gasolines. The objective of the current work is not to develop a methodology to formulate surrogates for FACE gasolines or to test the accuracy of the existing approaches, but rather to predict the octane response when adding ethanol to multi-component mixtures and compare them with those of the real FACE gasolines. Consequently, two different surrogates for each FACE gasoline were formulated based on different methodologies to assess the merits of each. The first surrogate (surrogate #1) is formulated to match RON and MON of the FACE gasoline without any constraints on the molecular class distribution (paraffins, iso-paraffins, olefins, naphthenes and aromatics (PIONA)) while having the 8 available species. The second surrogate (surrogate #2) is developed so it has RON, MON and PIONA compositions close to those of the FACE gasolines. Two additional surrogates termed the TPRF and PIONA surrogates were formulated and tested. The TPRF surrogate is the simplest and contains only n-heptane, iso-octane and toluene (TPRF) to match the RON and MON

of the base FACE gasolines and the PIONA surrogate is formulated to match the hydrocarbon distribution of the base FACE gasolines. These were considered complimentary and their details along with the predictions are provided in [Supplementary Material](#). The logic behind formulating multiple surrogates for each FACE gasoline is to examine the effect of the composition of the surrogates on the octane response due to the addition of ethanol. By definition, the calculated ON of surrogates #2 and the PIONA surrogate ([Supplementary Material](#)) don't exactly match those of the base FACE gasolines. Therefore, the ON increase or decrease due to the addition of ethanol to the surrogates are compared with the measured FACE gasolines/ethanol ones and are used to test the accuracy of the developed model instead of the absolute ON errors. D_{ON} errors defined as $D_{ON, Measured} - D_{ON, Calculated}$ are presented in the subsequent sections against the measured ON. Evaluating the D_{ON} errors instead of the ON errors shifts the focus to the effect of the surrogate composition on the magnitude of the synergistic and antagonistic behavior of gasoline/ethanol blends without being concerned about the deviations between the ON of the base FACE gasolines and their surrogates.

6.1. Surrogate #1: RON and MON multi-components surrogates

This surrogate was formulated to match the RON and MON of the FACE gasolines while taking into consideration all 8 available species. The methodology developed by Ghosh et al. [78] was utilized to formulate surrogates #1 without any constraints on the compositions of these surrogates. Microsoft Excel solver was used to calculate the compositions of surrogates #1. The solver was given initial concentrations of the 8 species based on the PIONA of the FACE gasolines. The compositions of the 8 species were allowed to change freely in order to match the calculated RON and MON of the surrogates with those of the base FACE gasolines. The RON and MON of the 8 species used in the surrogate formulations were taken from the current measurements and from [42,43] and are shown in [Table 8](#). The compositional details as well as the calculated RON and MON of surrogates #1 are shown in [Table 9](#). It can be observed from [Table 9](#) that the compositions of surrogates #1 can be very different than the equivalent FACE gasolines. For example, FACE I #1 has 29.6 vol% n-paraffins and 59.1 vol% iso-

Table 8
RON and MON of the 8 components studied in this work.

Component	RON	MON	Reference
n-Pentane	61.7	58.3	Current work
n-Heptane	0	0	[42,43]
iso-Pentane	92	90	Current work
iso-Octane	100	100	[42,43]
Toluene	118	107	[42,43]
1,2,4-Trimethylbenzene	109.5	108	Current work
Cyclopentane	100	85.6	Current work
1-Hexene	73.6	64.5	Current work

Table 9

FACE gasoline surrogates #1 compositional details.

	n-P vol%	n-H vol%	i-P vol%	i-O vol%	Tol vol%	1,2,4-TMB vol%	C-p vol%	1-H vol%	RON [*]	MON [*]
FACE A#1	10.923	8.650	42.794	33.362	0.429	0.342	2.738	0.763	83.6	83.0
FACE C#1	23.871	6.080	9.293	55.788	0.099	3.570	0.364	0.937	84.4	83.0
FACE F#1	2.386	3.136	17.287	62.191	0.054	4.243	8.793	1.910	94.2	87.4
FACE G#1	5.750	2.780	16.605	34.095	2.028	24.087	11.934	2.722	96.4	84.9
FACE I#1	0.993	28.586	19.040	40.078	1.217	0.059	3.714	6.314	69.5	69.0
FACE J#1	3.899	40.090	21.438	0.000	32.029	0.000	1.806	0.738	71.8	66.9

^{*} The RON and MON are calculated using the method of Ghosh et al. [78].

paraffins compared to 14.4 vol% and 74.7 vol% present in the real FACE I gasoline fuel (Table 1). These discrepancies in matching the PIONA distribution of the FACE gasolines might be due to the inaccuracy of the utilized surrogate formulation blending rule or the lack of additional species available to formulate these surrogates.

The RON and MON of FACE surrogates #1 mixtures with ethanol, excluding the base surrogates and pure ethanol, were predicted using Eq. (8) and the D_{ON} prediction errors are plotted against the measured values and are presented in Fig. 8. The RON predictions of FACE surrogates #1 are acceptable with 37% of the predictions are outside the reproducibility limits. MON predictions are however less accurate than RON with 50% of the prediction are outside the reproducibility limits. The measured D_{ON} for FACE gasolines and the calculated D_{ON} for surrogates #1 are provided in Supplementary Material.

6.2. Surrogate #2: RON, MON and PIONA surrogates

This surrogate was developed so it has RON, MON and PIONA composition values close to the equivalent FACE gasolines. Ghosh et al. [78] blending rule was used to match the RON and MON of the FACE gasolines, however, the PIONA of the surrogate was

allowed to change within 20% of the actual FACE fuel hydrocarbon class composition. The compositional details as well as the ON of FACE surrogates #4 are listed in Table 10. These surrogates were considered as compromises between surrogates #1 and the PIONA surrogates (Supplementary Material). Similar to FACE PIONA surrogates, the RON and MON of surrogates #2 are different than their equivalent FACE gasolines because of the constraints on the PIONA. However, the ON of the base surrogates #2 are closer to their respective FACE gasolines than PIONA surrogates because of the 20% limit on the PIONA. Note that the sensitivity (RON-MON) of FACE A surrogate #2 is negative as per the calculations using Ghosh's method [78]. This highlights some inaccuracy in Ghosh's method because none of the considered components have negative sensitivities.

RON and MON of FACE surrogates #2 blends with ethanol were calculated using the developed model and the D_{ON} errors are presented in Fig. 9. Similar to PIONA surrogates, the D_{RON} predictions are accurate where 71% of the predictions are within the reproducibility limits. Surrogates #2/ethanol D_{MON} prediction are less accurate (55% of D_{MON} errors are outside the reproducibility limits) than surrogates #1 as can be seen from Fig. 9b. The measured D_{ON} for FACE gasolines and the calculated D_{ON} for surrogates #2 are provided in Supplementary Material.

Fig. 8. Predicted (a) D_{RON} and (b) D_{MON} errors versus measured RONs and MONs for FACE surrogates #1/ethanol blends using the developed model.

Table 10

FACE gasoline surrogates #2 compositional details.

	n-P vol%	n-H vol%	i-P vol%	i-O vol%	Tol vol%	1,2,4-TMB vol%	C-p vol%	1-H vol%	RON [*]	MON [*]
FACE A#2	6.203	7.799	20.671	63.480	0.167	0.137	1.290	0.252	88.0	89.1
FACE C#2	23.403	5.998	9.057	56.945	0.079	3.066	0.433	1.019	84.5	82.9
FACE F#2	1.759	1.759	11.665	59.254	0.074	9.183	8.777	7.530	92.7	77.1
FACE G#2	3.720	1.751	10.652	27.792	1.749	38.380	9.364	6.592	96.9	78.7
FACE I#2	1.004	16.310	20.898	49.254	0.882	0.040	3.971	7.641	79.2	72.3
FACE J#2	10.798	27.223	0.606	32.512	1.117	24.270	2.752	0.721	76.3	75.8

^{*} The RON and MON are calculated using the method of Ghosh et al. [78].

Fig. 9. Predicted (a) D_{RON} and (b) D_{MON} errors versus measured RONs and MONs for FACE surrogates #2/ethanol blends using the developed model.

Fig. 10. D_{RON} versus ethanol volume fraction for (a) n-paraffins, (b) iso-paraffins and (c) aromatics studied in this work.

7. Discussion and analysis

The developed model is provided in [Supplementary material](#) as an excel sheet to facilitate the calculation of the octane numbers of any surrogate containing the 8 studied components blended with ethanol. The model can also be utilized via a web-interface on CloudFlame (cloudflame.kaust.edu.sa) [79]. The inputs to the ON predictions are the volume percentages of the 8 components in the base surrogate fuel, the RON and MON of the base mixture and the ethanol volume fraction added to the blend. In general, the proposed model accurately predicts the D_{RON} and D_{MON} of gasoline multi-component surrogates blends with ethanol. The proposed model and the methodologies of formulating the FACE surrogates are possible causes of predicted D_{ON} errors of FACE gasoline fuels/ethanol blends ON that are outside the acceptable limits. One possible way of improving the model is to include more scaling factors to account for the interactions between the various tested components. It was also shown that the volume based D values, especially for n-heptane/ethanol blends, are significantly larger than those of the mole based ones. D is a critical parameter in the presented model, and further comparisons against a mole based model would be useful. However, despite the different compositions of the FACE surrogates, the predicted D_{ON} errors are encouraging and mostly within the reproducibility limits when considering the 8 available species. In fact, only 16%, 20%, 12% and 8% of the D_{RON} errors are more than 2 D_{RON} for TPRF surrogates, surrogates #1, PIONA surrogates and surrogates #2, respectively. Similarly, 25%, 20%, 20% and 25% of the D_{MON} errors are more than 2 D_{MON} for TPRF surrogates, surrogates #1, PIONA surrogates and surrogates #2, respectively. Comparing the predictions of the four surrogates reveals that FACE PIONA surrogates and surrogates #2 result in better predictions than surrogates #1 and TPRF surrogates. This suggests that matching the PIONA of the base FACE gasolines is critical to the accuracy of the predictions. This is expected from the observed synergistic and antagonistic effects of different pure components with the addition of ethanol.

To further elaborate on this, these synergistic and antagonistic effects are compared for the n-paraffinic, iso-paraffinic and aromatics components studied in this work. D_{RON} for the studied n-paraffins (n-pentane and n-heptane), iso-paraffins (iso-pentane and iso-octane) and aromatics (toluene and 1,2,4-trimethylbenzene) are presented in [Fig. 10](#) against the ethanol volume fractions. It is clearly seen that the length of the n-paraffinic carbon chain affects the synergistic effect when blended with ethanol. n-Heptane has higher D_{RON} values than n-pentane, as shown in [Fig. 10a](#). The same is observed for iso-paraffins wherein iso-octane has higher synergistic effect than iso-pentane ([Fig. 10b](#)). Regarding aromatics, [Fig. 10c](#) demonstrates that the addition of two more methyl (CH_3) groups to the benzene ring decreases the antagonistic effects of aromatics/ethanol blends. These findings are critical for the explanation of these synergistic and antagonistic effects and what chemical kinetic roots are causing them. These findings are useful for the optimization of the octane response due to the addition of ethanol to gasoline surrogates. A possible way to improve the octane response per unit addition of ethanol is to reduce the aromatics contents in the base fuel because they generally have antagonistic effects when blended with ethanol. It was shown that a reduction in aromatics facilitates energy and cost savings in gasoline base stock production and enables meeting gasoline pump octane requirement with ethanol addition [80]. Additional costs and energy consumption and poorer fuel economy are possible effects if more ethanol is required to compensate for the decrease in ON due to the reduction of aromatics. In addition, the utilization of longer chain n-paraffins and iso-paraffins

improves the octane response with ethanol blends as can be seen from the D values presented below. Finally, the presence of additional methyl (CH_3) substitutions to the aromatic ring improves the octane response as well. In summary, the octane response due to the addition of ethanol is proportional to the synergistic addition or antagonistic subtraction from the linear line induced by the various base fuel components, and the present analysis enables an optimization of the base fuel composition to maximize the octane number of gasoline/ethanol mixtures.

8. Conclusions

New RON and MON experimental data were measured for five additional pure components and six FACE gasoline fuels with ethanol. These pure components were carefully chosen to cover the classes of molecules relevant to gasoline fuels. A relatively simple volume based blending rule to predict the octane ratings of PRFs, TPRFs and multi-component/ethanol blends was developed in this study. Experimental data from Saudi Aramco's CFR engine and from literature were used to determine the parameters needed for the model. The developed model was based on the pure components synergistic and antagonistic effects when blended with ethanol as well as the introduction of scaling factors to account for the cross-reactions between the different molecules when mixed with ethanol. The model was extended to cover all the studied components and was validated against numerous blends of PRFs/ethanol, TPRFs/ethanol and FACE gasoline fuels/ethanol blends. The predictions were mostly within the experimental reproducibility limits. The proposed model is also applicable for a wide range of ON. Finally, some insights into the variations of the synergistic and antagonistic effects of the studied components with ethanol were provided.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apenergy.2017.06.084>.

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