# Formulating gasoline surrogate for emulating octane blending properties with ethanol

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## Abstract

This work develops a surrogate fuel that reproduces the octane blending of a market gasoline with ethanol. It first extends our previous investigation that reported strong, non-linear blending for ethanol/paraffin and ethanol/aromatic mixtures [Foong et al., Fuel 2014 p. 727] to consider mixtures of ethanol/cycloparaffin, ethanol/olefin, and hydrocarbons from different groups. On the molar basis, ethanol blends synergistically with cyclohexane and 1-hexene, whereas toluene blends antagonistically with ethanol and all hydrocarbons studied.

Various alternative surrogate formulations are then considered given the observed inadequacy of toluene reference fuels (TRFs, mixtures of iso-octane, n-heptane, and toluene) in emulating the octane blending behaviours of a market gasoline with ethanol. These alternative surrogates are formulated to match the market gasoline's Research Octane Number (RON) and its major hydrocarbon group composition. The best performing surrogate, which contains 38% iso-pentane, 12% n-pentane, 30% 1,2,4-trimethylbenzene, 10% cyclohexane, and 10% 1-hexene (all by volume), reproduces the RONs of the market gasoline mixed with ethanol over the entire blending range within 0.5 octane number. This surrogate formulation demonstrates that iso-pentane, n-pentane and 1,2,4-trimethylbenzene are more suitable than TRF compounds for emulating the octane blending of the gasoline/ethanol mixtures used in this study. A RON correlation is then proposed for the developed gasoline surrogate, taking into account the observed, non-linear interactions of ethanol and individual hydrocarbon compounds, which accurately predicts the RON of the surrogate/ethanol mixtures.

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## 1. Introduction

Ethanol is increasingly used as a gasoline blending component around the world. Ethanol production in the United States has increased by two and half times from 2007 to 2017. The use in gasoline reached an average of 10 vol.% (E10) nationally in 2016 and increasing amounts of E15 are being utilized [1]. China recently announced a nationwide mandate of E10 gasoline by 2020 which is expected to triple its ethanol consumption [2]. In Europe, biofuels incorporation obligations were implemented by most its member states in 2018, aiming to achieve a 10% renewable energy share within the transportation sector in 2020 [3].

One major benefit of ethanol blending is the potential to increase the knock resistance of gasoline, which allows more efficient spark-ignition engines [4–6]. Ethanol has a research octane number (RON) of 108-109 and a motor octane number (MON) of 91; both are higher than that of gasoline. In blending with gasoline, ethanol often exhibits significant non-linear response in octane ratings [7–11], and such response is recently found to be strongly affected by the blended fuel. Foong et al. [8] found that ethanol blends superlinearly (or synergistically) with iso-octane and n-heptane but sublinearly (or antagonistically) with toluene. Badra et al. [9] further reported that ethanol blends antagonistically with 1,2,4-trimethylbenzene but synergistically or linearly with nearly all other hydrocarbons tested, including iso-pentane, n-pentane, cyclopentane, and 1-hexene.

The octane response of ethanol/hydrocarbon blending is an important property that needs to be accounted for when developing gasoline surrogates. However, Primary Reference Fuels (PRFs, mixtures of iso-octane and n-heptane) and Toluene Reference Fuels (TRFs, mixtures of PRFs and toluene), although often used as gasoline surrogates, are inadequate for this application. As Figure 1 [8] shows, blending ethanol with PRF91 and three TRFs of the same RON of 91 and different toluene content all produce considerably greater octane increases than the market gasoline, although the aromatic content in the market gasoline (31.7 vol.% [8]) is similar to one of the reference fuels, TRF91-30. This observation demonstrates that more sophisticated surrogates are required to emulate the blending behaviour.

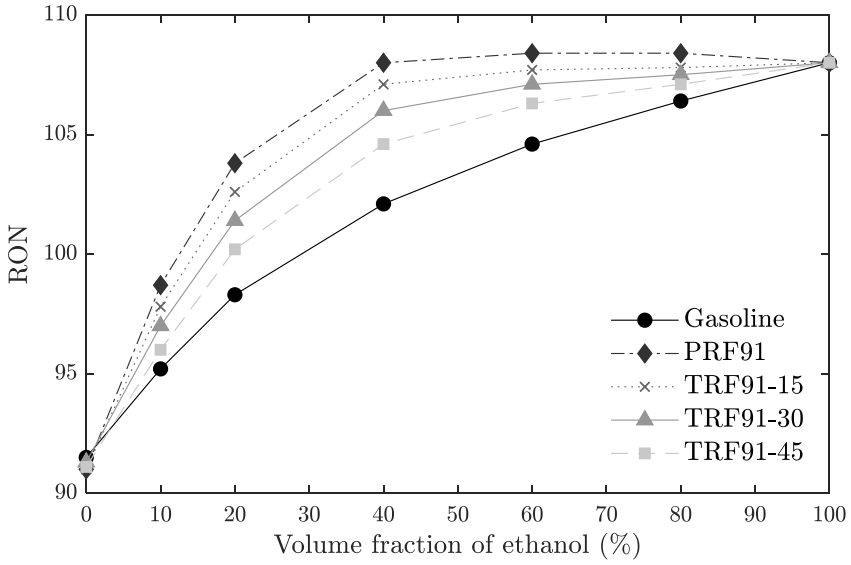



Figure 1: Measured RONs for an Australian market gasoline, PRF91, and TRF91s blended with ethanol [8]. The reference fuels have the same RON of 91 but contain different amounts of toluene (0%, 15%, 30%, 45% by volume, as indicated). The gasoline contains 31.7 vol.% aromatics.

The objective of this work is therefore to develop a methodology for formulating surrogate fuels that reproduce the octane blending of commercial gasolines with ethanol. This approach focuses on the RON which is commonly considered more important than MON for assessing the knock resistance and knock-constrained efficiency of modern SI engines. This work first extends the prior investigation of Foong et al. [8] by measuring the octane number of ethanol mixtures with representative compounds of cycloparaffins and olefins, the other major hydrocarbon groups in gasoline after paraffins and aromatics. Binary mixtures of hydrocarbon compounds from different groups are also assessed for their linearity of blending, which has been rarely investigated in the literature. Based on the hydrocarbon composition of the target gasoline, various surrogate mixtures are then formulated in an attempt to reproduce the octane blending behaviour with ethanol. With one surrogate successfully identified, a correlation is finally developed to quantify the octane blending effects between ethanol and this surrogate.

## 2. Experimental Methods

The octane rating tests (RON and MON) are conducted in a Waukesha CFR engine following the ASTM methods [12,13], with specific engine modifications to enable ethanol blend testing [8]. The engine is a single-cylinder, spark-ignition engine with variable compression ratio. Per the ASTM method, the knock intensity is detected by a 'detonation sensor' which converts measurements of the in-cylinder pressure to readings on a 'knock meter'. Liquid fuels are supplied via a carburettor with the flow rate (and fuel/air ratio) adjusted to achieve the maximum knock intensity at a given condition.

The ASTM standards [12,13] specify the reproducibility limits of RON and MON measurements in terms of the maximum error in 1 out of 20 independent tests of the same fuel. These limits are 0.7 ON for a RON of 90–100, 1.0 for an average RON of 101, 1.2 for an average RON of 102, 1.7 for an average RON of 103, 2.0 for an average RON of 104, and 3.5 for a RON of 104–108. The reproducibility for the MON is 0.9 ON for a MON of 80–90. Limits outside these ranges are not specified.

Test mixtures are prepared by weighing individual fuel components on a laboratory scale and assuming ideal mixing by volume with densities of neat compounds obtained from the literature. The density of the commercial gasoline is determined by weighing 500 ml sample with a volumetric flask.

## 3. Octane Blending Behaviours of Binary Mixtures

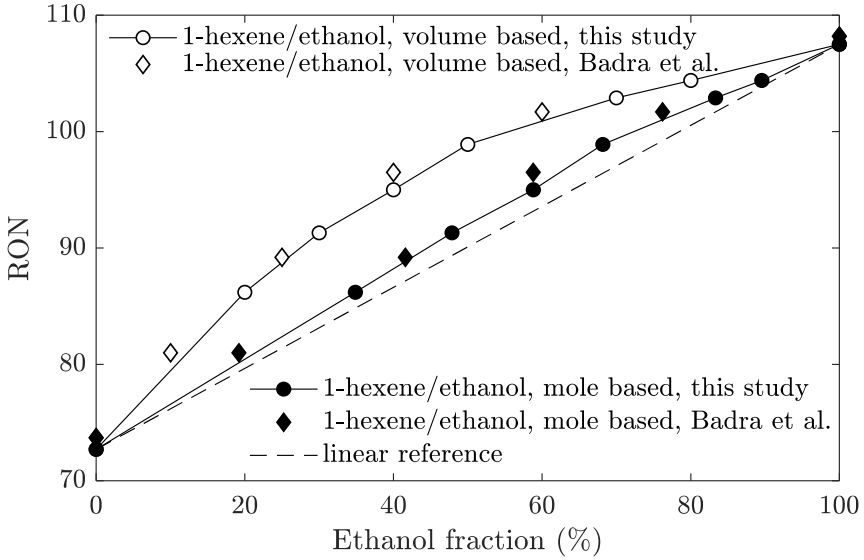
### *3.1 Binary mixtures containing ethanol*

To understand the octane blending behaviours of ethanol with cycloparaffins and olefins, cyclohexane and 1-hexene are selected as representative compounds of these two hydrocarbon groups. Similar selections have also been used by Pitz et al. [14,15] and Sarathy et al. [16] for gasoline surrogate development. Table 1 reports the RONs of neat cyclohexane and 1-hexene measured in this work and from the literature. The RON of cyclohexane measured in this work agrees closely with that from the American Petroleum Institute (API) [17]. The RON of 1-hexene shows a larger discrepancy with the value from API, but is similar to that of Badra [9]. This may be due to

the purity of 1-hexene used in these experiments. This work and that of Badra et al. [9] both used 1-hexene of 97% purity, which is lower than the 99% purity used by API.

Table 1 RONs of cyclohexane and 1-hexene from this study, API [17], and Badra et al. [9].

| Fuel | This study | API | Badra et al. |
|---|---|---|---|
| Cyclohexane | 82.2 | 83.0 | - |
| 1-hexene | 72.7 | 76.4 | 73.6 |




Figures 2 and 3 show the RONs of cyclohexane and 1-hexene blended with ethanol. Synergistic blending is observed for the two sets of binary mixtures on both a volume and a mole basis. In general, ethanol blending appears less synergistic on a mole basis because the molecular volume (molecular weight/density) of ethanol is lower than that of gasoline hydrocarbons. The RONs of 1-hexene/ethanol mixtures from Badra et al. [9] are also plotted in Figure 3 and agree reasonably with the measurements in this study.

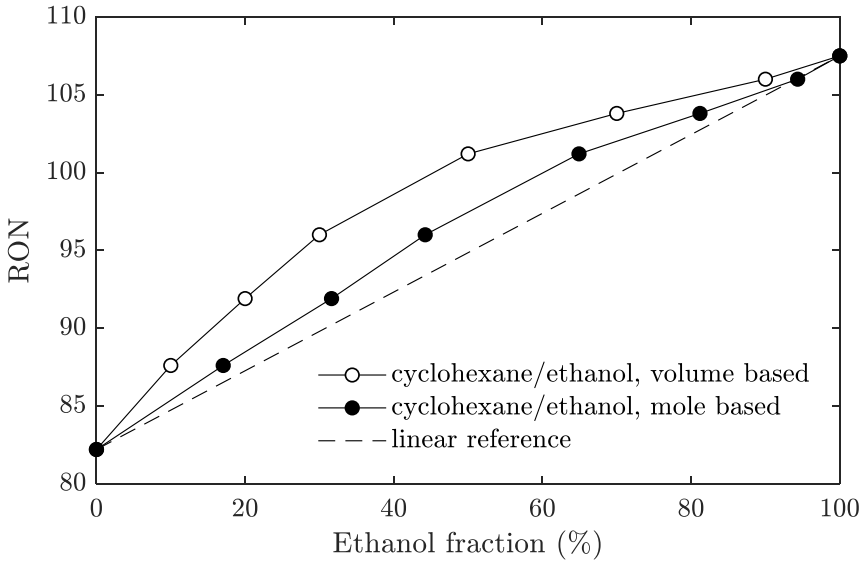



Figure 2: RONs of ethanol/cyclohexane mixtures.

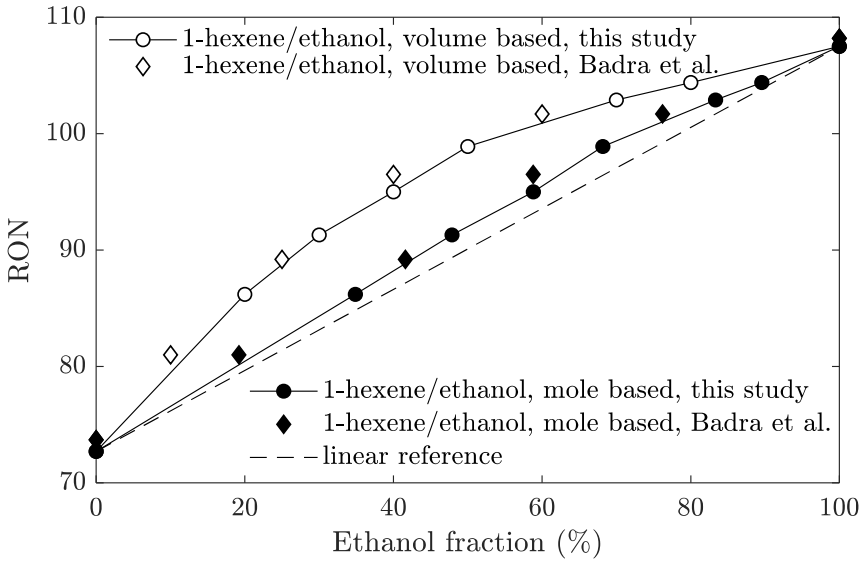



Figure 3: RONs of ethanol/1-hexene mixtures. Data from Badra et al. [9] included.

*3.2 Binary mixtures containing toluene*

Hydrocarbons selected for the study of binary mixtures include iso-octane, n-heptane, toluene, cyclohexane, and 1-hexene. These compounds are commonly used to represent their respective hydrocarbon groups in gasoline.

The RONs of iso-octane and toluene mixtures are shown in Figure 4 on a volume and a mole basis. Linear blending is observed on the volume basis, whereas antagonistic blending is evident on the mole basis. Note that

the RON of toluene is uncertain because its RON approaches the upper limit of the CFR engine method [10,18] and values from 116 to 120 have been reported [8,17,18]. Here the value of 117.4 measured in this work is used.

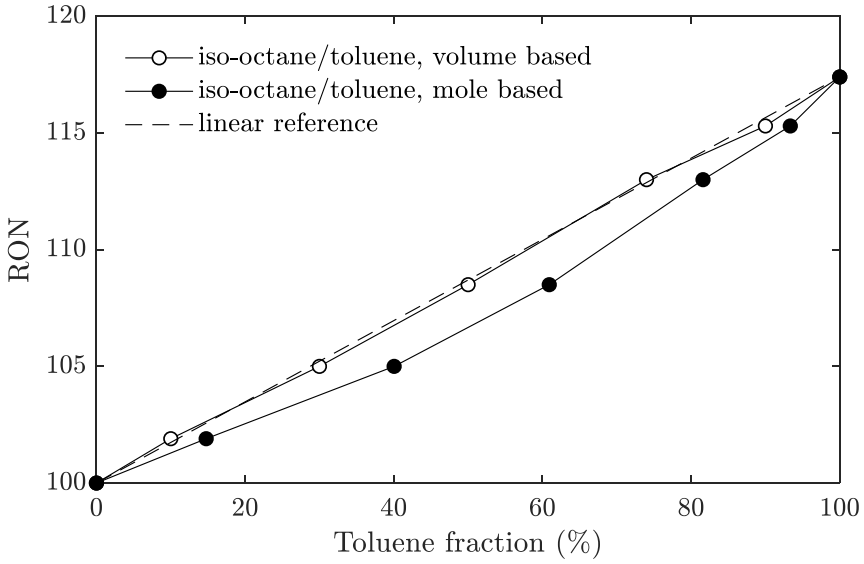



Figure 4: RONs of toluene/iso-octane mixtures.

Figure 5 shows the RONs of n-heptane blended with toluene, where a weak synergistic blending is observed on a volume basis and a weak antagonistic or nearly linear blending is observed on a mole basis. Together, the results in Figures 4 and 5 suggest that antagonistic blending with toluene would be expected for TRFs on a mole basis. However, a weak synergistic blending exists between iso-octane and n-heptane *on a mole basis (their blending is linear by definition on a volume basis)*. For this and other reasons, linear-by-mole correlations have been reported for TRFs by several groups [10,19].

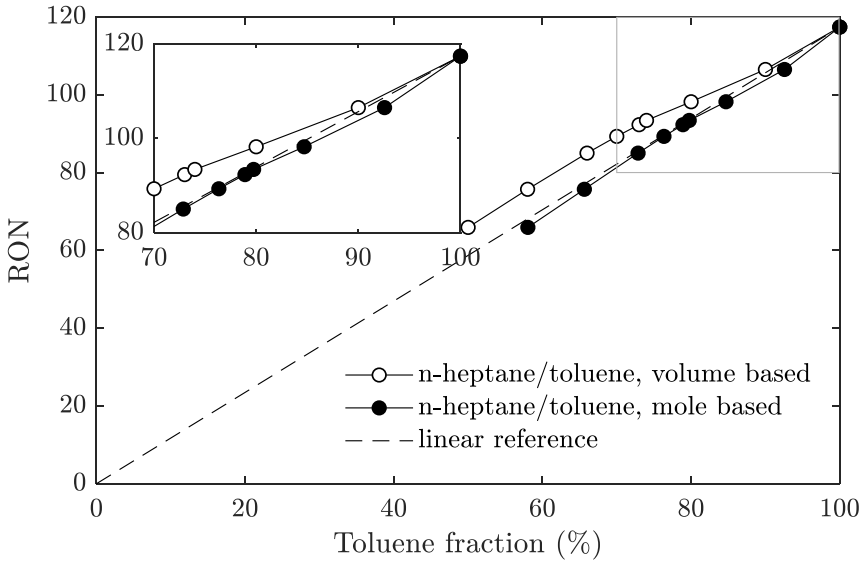



Figure 5: RONs of toluene/n-heptane mixtures.

Figures 6 and 7 show the RONs of cyclohexane and 1-hexene blended with toluene. Both compounds blend antagonistically with toluene on both volume and mole bases. Combining the results from this work with those from Foong et al. [8], it can be concluded that toluene blends antagonistically with all of the non-aromatic compounds (including ethanol) and non-aromatic mixtures tested.

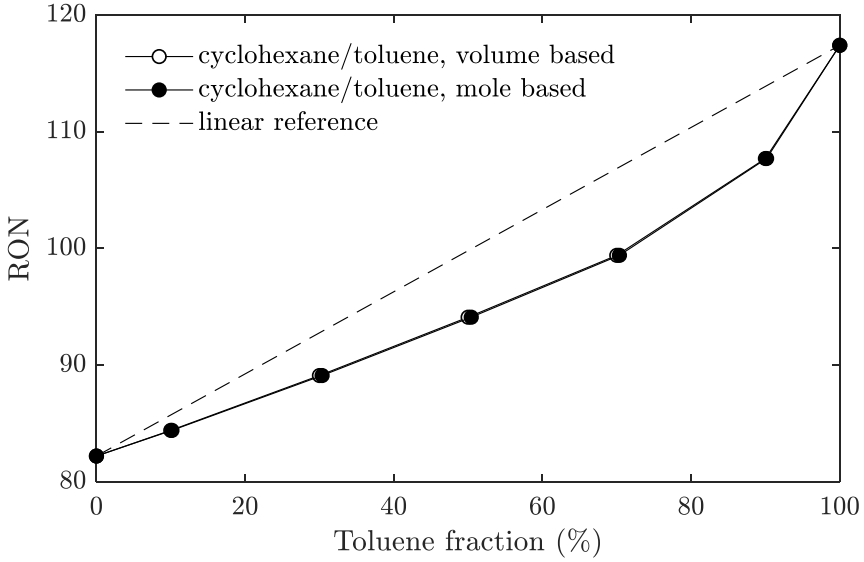



Figure 6: RONs of toluene/cyclohexane mixtures.

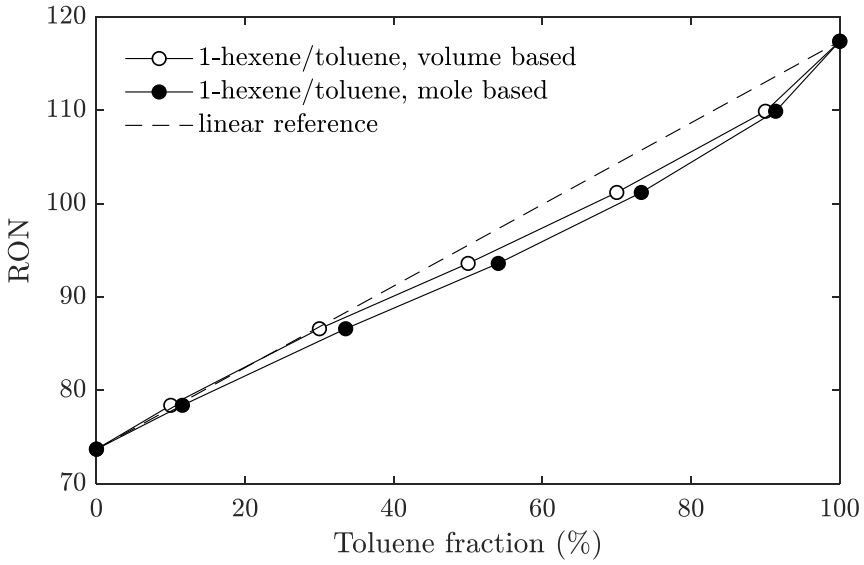



Figure 7: RONs of toluene/1-hexene mixtures.

*3.3 Binary mixtures containing iso-octane*

Binary mixtures of cyclohexane and 1-hexene blended with iso-octane are also tested, with the RONs shown in Figures 8 and 9, respectively. In contrast to the blends with toluene, synergistic blending on a mole basis is observed. Notably, compared with their binary mixtures with ethanol as shown in Figures 2 and 3, the synergistic blending with iso-octane is comparable for cyclohexane and even stronger for 1-hexene. Similar blending responses were also observed by Scott in methylcyclohexane/iso-octane and 2-heptene/iso-octane mixtures [20]. This demonstrates that non-linear blending among hydrocarbons can be important in determining the blending behaviour of gasoline with ethanol and should be considered in developing gasoline surrogates.

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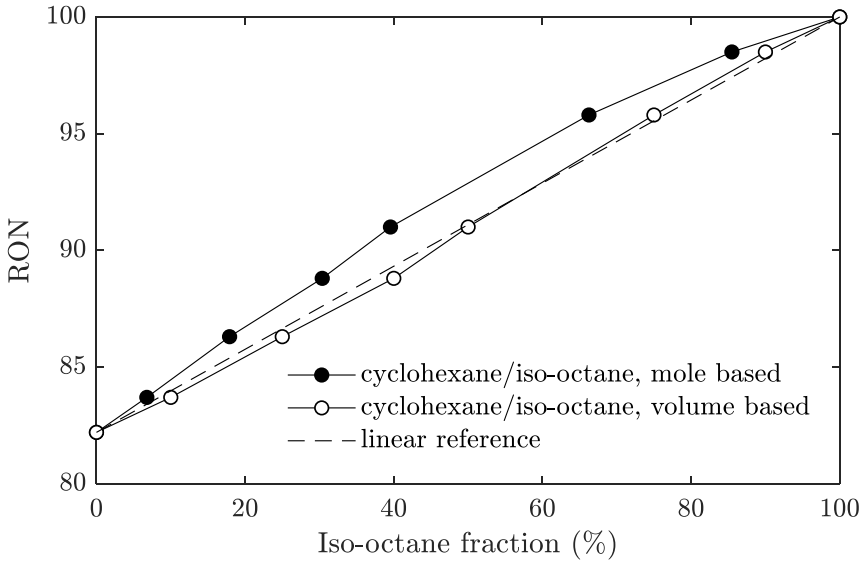



Figure 8: RONs of iso-octane/cyclohexane mixtures.

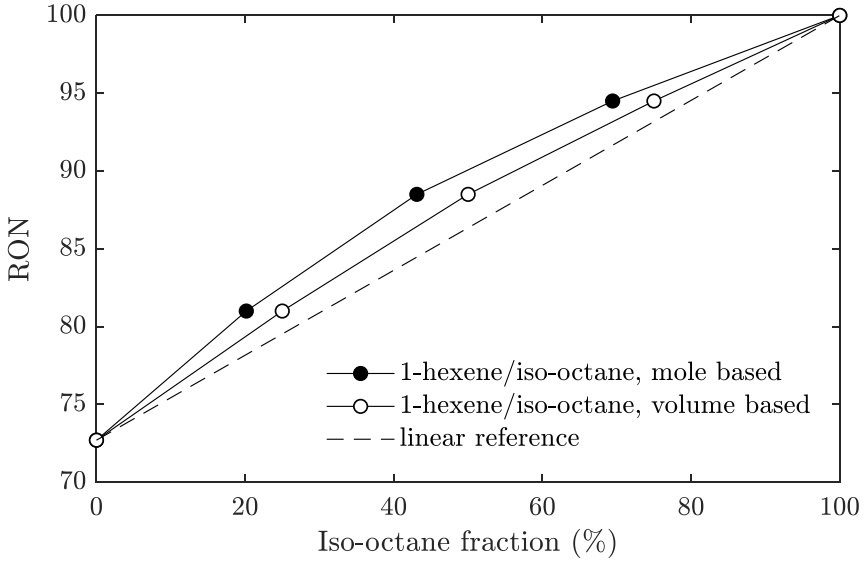



Figure 9: RONs of iso-octane/1-hexene mixtures.

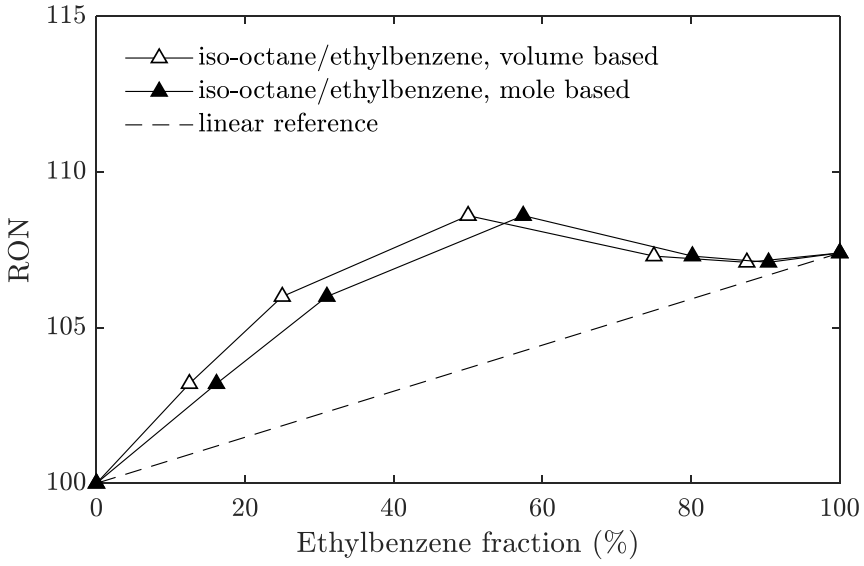
A summary of the octane blending results of binary mixtures on a mole basis is shown in Table 2, based on the data from this work and Foong et al. [8]. It is evident that ethanol blends synergistically with all hydrocarbons tested except toluene, whereas toluene blends antagonistically with all fuel compounds tested. These binary blending behaviours now provide a basis for formulating more sophisticated gasoline surrogates.

Table 2: Interactions of binary mixtures on a mole basis.

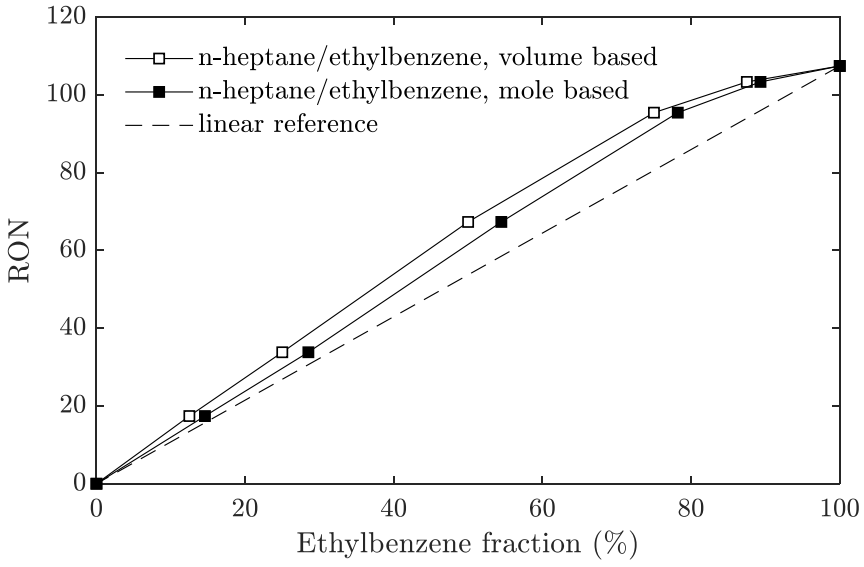
| Fuel | n-heptane | iso-octane | ethanol | toluene | cyclohexane | 1-hexene |
|---|---|---|---|---|---|---|
| n-heptane | | linear | S | A | - | - |
| iso-octane | linear | | S | A | S | S |
| ethanol | S | S | | A | S | S |
| toluene | A | A | A | | A | A |
| cyclohexane | - | S | S | A | | - |
| 1-hexene | - | S | S | A | - | |

"S" synergistic blending
"A" antagonistic blending
"-" not tested

It should be noted that aromatic compounds can produce different octane responses. For example, Scott [20] reported that ethylbenzene blends synergistically with iso-octane and n-heptane on both volume and mole bases, as shown in Figure 10. Consideration is therefore needed regarding which compound is used to represent the aromatic group in octane blending, and toluene may not be the best choice for all applications.



(a)




(b)

Figure 10: RONs of (a) ethylbenzene/iso-octane and (b) ethylbenzene/n-heptane mixtures from Scott [20].

## 4. Formulation of Gasoline Surrogates

### 4.1 *Approach*

The objective of developing the gasoline surrogate is to reproduce the RONs of commercial gasolines when blended with ethanol, for example as shown in Figure 1. The candidate surrogate needs to match two properties of the market gasoline, the RON of 91 and the hydrocarbon group composition, as shown in Table 3. In particular, the aromatic content in the surrogate is set at 30 vol.%, and the contents of cycloparaffin and olefin are both set at 10 vol.%. The contents of normal and iso-paraffins are then varied to satisfy the 91 RON of the mixture. Volume-based blending is used hereafter to follow the practice in gasoline production and also due to the lack of information of molecular weights for the gasoline and its hydrocarbon subgroups. Rather than matching the exact hydrocarbon composition, the surrogate uses a nominal but similar hydrocarbon composition considering the uncertainty in measuring hydrocarbon composition as well as the variation in practical gasoline production.

Table 3: Properties of the market and surrogate gasoline

| RON | Hydrocarbon composition (vol.%) [a] |
|---|---|

| | | n-paraffins | iso-paraffins | olefins | cyclo-paraffins | aromatics |
|---|---|---|---|---|---|---|
| Market gasoline | 91.5 | 13.7 | 35.3 | 8.0 | 11.4 | 31.7 |
| Surrogate | 91.0 ± 0.5 | vary | vary | 10 | 10 | 30 |

[a] The gasoline composition is from PIONA analysis reported in [8].

Representative compounds for each hydrocarbon group are selected. PRFs (iso-octane/n-heptane) and pentanes (iso-pentane/n-pentane) are used to represent the paraffin group. The two pentanes are used because they are often the most abundant paraffins by carbon number in gasoline [21]. Toluene and short-chain alkylbenzenes, including xylenes, ethylbenzene, and 1,2,4-trimethylbenzene, are examined to represent the aromatic group. Cyclohexane and 1-hexene are chosen to represent the cycloparaffin and olefin groups, respectively. Cyclohexane is often the most abundant cycloparaffin compound in gasoline, whereas 1-hexene is selected because most olefins in gasoline have six carbons.

The surrogate development is conducted via extensive, iterative octane number measurements. The empirical, and essentially trial-and-error, approach is adopted to ensure the validity of the developed surrogate because reliable correlations for octane number with ethanol blending are general unavailable, particularly for surrogates containing more than three hydrocarbon compounds.

The surrogate formulation starts from TRF91 containing 30 vol.% toluene (TRF91-30) and incorporates three considerations.

1. Utilizes cyclohexane and 1-hexene in addition to the TRF components (isooctane, n-heptane, and toluene) since cycloparaffins and olefins are significant classes of gasoline hydrocarbons.
2. Includes aromatics other than toluene, considering that different aromatics have different octane blending properties.
3. Uses iso-pentane and n-pentane to replace iso-octane and n-heptane, respectively, considering the significant concentrations of the C5 paraffins in commercial gasoline and the potential different blending properties of paraffinic compounds.

The RONs of these candidate mixtures blended with ethanol are measured and compared against the RONs of the gasoline/ethanol mixtures in Figure 1. To reduce the number of measurements, E40 is chosen as the test ethanol content since Figure 1 shows that TRFs and the gasoline exhibited the largest discrepancy at this blending level. Verification over a broader ethanol concentration range is then conducted after the surrogate is found to perform reasonably for E40.

### *4.2 Adding cyclohexane and 1-hexene to TRF*

The first gasoline surrogate, termed GS1, was formulated by adding cyclohexane and 1-hexene to modify TRF91-30. Since there are no correlation equations to describe the RON of these five-component mixtures, determining the formulation that satisfies the RON of 91 and the hydrocarbon composition (30 vol.% aromatic, 10 vol.% cycloparaffin, 10 vol.% olefin) requires trial and error octane measurement with varying iso-octane and n-heptane proportions for the remaining 50 vol.% of the surrogate. As shown in the later summary table (Table 5), GS1 contains 38.8 vol.% iso-octane and 11.2 vol.% n-heptane. In blending with 40 vol.% ethanol, GS1 produces a RON of 103.7, which is lower than the value with TRF91-30 (105.1) but still higher than that with the gasoline (102.1). This indicates that including cyclohexane and 1-hexene improves the surrogate formulation in terms of octane response to ethanol blending while achieving a match of the overall hydrocarbon composition, but further development is required to match the ethanol blending behaviour.

### *4.3 Replacing toluene with other aromatics*

From the results on binary mixtures, it is evident that toluene is the only component that blends sublinearly with all the test fuels. Other aromatics are therefore studied to determine whether stronger antagonistic octane blending can be found with ethanol, which might help to better replicate the ethanol octane blending with the market gasoline.

Several C8 and C9 aromatics are investigated, including p-, m-, and o-xylene, ethylbenzene, and 1,2,4-trimethylbenzene, which are blended with PRFs to form ternary mixtures as shown in Table 4. No cyclohexane or 1-hexene are included in these mixtures. All blends have a RON of 91, again achieved through extensive engine testing. The varying PRF content in these mixtures reflects differences in the low temperature reactivities of these aromatics (e.g., p-xylene < m-xylene < o-xylene), as reported in other studies [22–25].

The RONs of these mixtures when splash blended with 40 vol.% ethanol are then measured and reported in Table 4 (molar composition data are shown in the Appendix). The E40 blends containing one of these C8 and C9 aromatics all yield a lower RON than when the blend instead contains toluene. Of particular interest is 1,2,4-trimethylbenzene, which produces the lowest RON of 103.6 in blending with 40% ethanol, suggestingthe strongest antagonistic effect with ethanol amongst the aromatics tested.

Table 4: Composition (vol.%) and octane number of PRF + aromatics mixtures

| | iso-octane | n-heptane | aromatic | RON | RON @ E40 |
|---|---|---|---|---|---|
| PRF + toluene (TRF91-30) | 53.2 | 17.0 | 29.8 | 91.3 | 105.1 |
| PRF + p-xylene | 49.0 | 21.0 | 30.0 | 91.0 | 104.2 |
| PRF + m-xylene | 50.4 | 19.6 | 30.0 | 91.2 | 104.5 |
| PRF + o-xylene | 56.7 | 13.3 | 30.0 | 91.3 | 104.7 |
| PRF + ethylbenzene | 51.8 | 18.2 | 30.0 | 91.3 | 104.5 |
| PRF + 1,2,4-trimethylbenzene | 53.2 | 16.8 | 30.0 | 91.2 | 103.6 |

### *4.4 Formulation with 1,2,4-trimethylbenzene and pentanes*

Given the observed strong antagonism, 1,2,4-trimethylbenzene then was used in lieu of toluene in GS1 (iC8/nC7/Tol/CHX/HXN) to form GS2 (iC8/nC7/TMB/CHX/HXN). In addition, iso-pentane and n-pentane are used to replace iso-octane and n-heptane, respectively, which updates GS1 to GS3 (iC5/nC5/Tol/CHX/HXN), and further updates GS2 to GS4 (iC5/nC5/TMB/CHX/HXN). Besides being the most abundant paraffins in gasoline, the two pentanes also have low boiling temperatures (300 K for iso-pentane and 309 K for n-pentane) which help to simulate the front-end volatility of market gasolines.

The resulting compositions of GS2 to GS4 are listed in Table 5, again achieved through extensive engine testing to maintain a RON of 91 for the surrogate. Note that iso-pentane and n-pentane are more difficult to handle due to their boiling points being close to room temperature. In this study, the experiments were conducted at ambient temperature around 280 K and the pentane containers were stored in an ice bath before blending. The prepared mixtures were then tested immediately to minimise evaporative losses. Molar composition data are reported in the Appendix.

Table 5: Composition (vol.%) and octane number of gasoline surrogates [a]

| Surrogate | iC5 | nC5 | iC8 | nC7 | Tol | TMB | CHX | HXN | RON | RON @ E40 | ΔRON @ E40 [b] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| TRF91-30 | - | - | 53.2 | 17 | 29.8 | - | - | - | 91.3 | 105.1 | 3.0 |
| GS1 | - | - | 38.8 | 11.2 | 30.0 | - | 10.0 | 10.0 | 91.2 | 103.7 | 1.6 |
| GS2 | - | - | 38.8 | 11.2 | - | 30.0 | 10.0 | 10.0 | 90.9 | 103.0 | 0.9 |
| GS3 | 32.0 | 18.0 | - | - | 30.0 | - | 10.0 | 10.0 | 91.2 | 103.1 | 1.0 |
| GS4 | 38.0 | 12.0 | - | - | - | 30.0 | 10.0 | 10.0 | 91.1 | 102.1 | 0.0 |

[a] iC5: iso-pentane; nC5: n-pentane; iC8: iso-octane; nC7: n-heptane; Tol: toluene; TMB: 1,2,4-trimethylbenzene; CHX: cyclohexane; HXN: 1-hexen

[b] ΔRON @ E40 = RON (E40 of GS) – RON (E40 of gasoline)

Figure 11 shows the RON of the market gasoline and the four surrogate mixtures blended with 40 vol.% ethanol. For these five-component gasoline surrogates that meet both the RON91 and hydrocarbon composition constraints, GS2 and GS3 produce similar RONs of 103.0 and 103.1 with 40% ethanol, which are lower than GS1. This indicates that replacing PRFs with n- and iso-pentanes, and replacing toluene with 1,2,4-trimethylbenzene, are both helpful in this case. Combining the two favourable effects, GS4 produces a RON of 102.1 with 40% ethanol blended, which is identical to the RON of the market gasoline/ethanol mixture.

Figure 11 also shows the measured RONs of GS4/ethanol mixtures at other ethanol concentrations, demonstrating excellent reproduction of the market gasoline RON blending behaviour over the entire range. The largest difference is 0.5 octane number with 10% ethanol, in part due to the RON of GS4 being lower than that of

the market gasoline by 0.4 octane number (91.1 vs. 91.5). We can therefore consider that GS4 successfully reproduces the RON blending of the commercial gasoline and ethanol. The excellent blending performance of GS4 is likely due to the weaker synergistic interaction of ethanol with pentanes than with PRFs, as seen when comparing GS4 and GS2, as well as the stronger antagonistic interaction of ethanol with 1,2,4-trimethylbenzene than with toluene, as seen from GS4 and GS3.

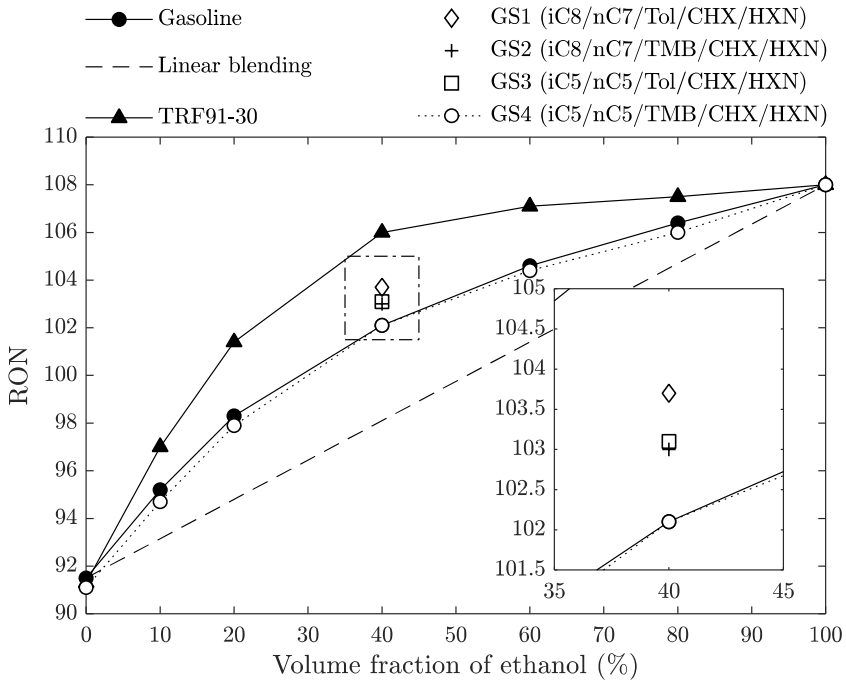



Figure 11: Comparisons between the RONs of the market gasoline and GS1 to GS4 with ethanol added.

Table 6 shows other fuel properties for GS4 and the target gasoline. Perhaps the most significant finding is that the MON of GS4 also closely matches that of the gasoline, both in neat form and in blending with 40% ethanol. The study of MON blending is also the topic of future investigation. Several other fuel properties in Table 6 are matched with modest discrepancies. The charge cooling effect, which is important for fuels containing ethanol, is compared indirectly by the intake mixture temperature measured downstream of the carburettor [26]. The gasoline and GS4 give similar mixture temperatures, indicating similar heat of vaporisation. Finally, the contents

of iso-pentane (38%) and n-pentane (12%) in GS4 (Table 5), which are varied to maintain a RON of 91, are also similar to that of iso-paraffin (35.3%) and n-paraffin (13.7%) in the gasoline (Table 3).

Table 6: Physiochemical properties of the market gasoline and the developed surrogate

| Fuel | density (g/ml) | H/C ratio | RON | RON @ E40 | MON | MON @ E40 | Mixture T at RON test (K) |
|---|---|---|---|---|---|---|---|
| Gasoline | 0.73 | 1.87 [a] | 91.5 | 102.1 | 82.1 | 87.7 | 292 |
| GS4 | 0.72 | 2.03 | 91.1 | 102.1 | 81.6 | 88.0 | 291 |

[a] nominal value.

## 5. RON correlation for gasoline surrogate/ethanol mixtures

Using the measured octane numbers, a correlation is also developed to estimate the RON of ethanol blends with gasoline surrogates that contain the five compounds (n-pentane, iso-pentane, 1,2,4-trimethylbenzene, 1-hexene, and cyclohexane) used in GS4. The development proceeds by adding non-linear blending terms to the linear-by-mole correlation as shown in Equation 1,

$$RON = \sum_{i=1}^{n} RON_i x_i \quad (1)$$

where $x_i$ and $RON_i$ are the molar fraction and research octane number of the $i^{th}$ component respectively. A volume-based equation can also be used; however, volume fractions have been found to correlate much less consistently with octane numbers and would require stronger nonlinear interaction terms [10,27]. Table 7 lists the surrogate compounds and their RON used in developing the correlation. A non-linear blending term is first determined for hydrocarbon mixtures in GS4, then for binary mixtures of ethanol and each of the five components. These six non-linear terms are then added to Equation 1 to obtain the final correlation.

Table 7: Surrogate compounds and their RON.

| Surrogate compound | Molar fraction | RON | Source |
|---|---|---|---|
| n-Pentane | $x_1$ | 61.7 | [9] |
| iso-Pentane | $x_2$ | 92.0 | [9] |
| 1,2,4-Trimethylbenzene | $x_3$ | 109.5 | [9] |
| 1-Hexene | $x_4$ | 72.7 | This work |

| | | | |
|---|---|---|---|
| Cyclohexane | $x_5$ | 82.2 | This work |
| Ethanol | $x_6$ | 108.0 | This work and [8] |

*5.1 Determine non-linear blending term for hydrocarbon mixtures*

Applying the linear-by-mole correlation (Equation 1) to GS4 produces a RON of 89.7, which is lower than the measurement of 91.1. A non-linear term, $x_3(1 - x_3 - x_6)$, is added to account for the difference. This term exists in the generalised Scheffé polynomial for this mixture [10], and captures non-linear blending between the aromatic component ($x_3$) and all the other, non-aromatic hydrocarbon components $x_3(1 - x_3 - x_6)$. Since the blending among non-aromatic compounds is not necessarily linear (as shown in Figures 8 and 9), addition of this term also includes the net non-linear blending amongst the non-aromatic hydrocarbons.

Based on the compositions and the RON of GS4, the following equation is obtained for the RON of the surrogate formulation:

$$RON = 61.7x_1 + 92.0x_2 + 109.5x_3 + 72.7x_4 + 82.2x_5 + 6.7x_3(1 - x_3 - x_6) \quad (2)$$

The coefficient 6.7 in front of the $x_3(1 - x_3 - x_6)$ term is from the single point correction between GS4 and the target gasoline, where the positive value indicates *net* synergistic interaction between 1,2,4-trimethylbeznene and the other hydrocarbons in the mixture (accounting for all non-linear blending among the non-aromatic hydrocarbons).

*5.2 Determine non-linear blending terms for binary mixtures of ethanol and surrogate compounds*

The non-linear, binary blending effect between ethanol and individual hydrocarbons contained in GS4 is quantified using the RON measurements from Badra et al. [9] and this work. The non-linear blending is accounted for by $2^{nd}$ order terms featuring the mole fractions of ethanol and the hydrocarbon of interest. These terms are again contained in the general, Scheffé polynomials of these mixtures [10]. A comparable approach has been adopted by Badra et al. who used higher order of polynomials (up to 5$^{th}$ order) to quantify the volume-based non-

linear interactions between ethanol and hydrocarbons in octane blending. The least-squares best-fit correlation equations are listed in Table 8 and their comparisons with the measurements are shown in Figure 12.

Table 8: RON correlation for binary mixtures of ethanol and surrogate compounds

| Fuel mixture | Optimal correlation | $R^2$ | Max abs. error (MAE) |
|---|---|---|---|
| n-pentane ($x_1$)/ethanol ($x_6$) | $61.7x_1 + 108.0x_6 + 21.4x_1x_6$ | 0.991 | 3.1 |
| iso-pentane ($x_2$)/ethanol ($x_6$) | $92.0x_2 + 108.0x_6 + 6.0x_2x_6$ | 0.998 | 0.4 |
| 1,2,4-TMB ($x_3$)/ethanol ($x_6$) | $109.5x_3 + 108.0x_6 - 16.5x_3x_6$ | 0.959 | 0.7 |
| 1-hexene ($x_4$)/ethanol ($x_6$) | $72.7x_4 + 108.0x_6 + 6.7x_4x_6$ | 0.999 | 0.7 |
| cyclohexane ($x_5$)/ethanol ($x_6$) | $82.2x_5 + 108.0x_6 + 8.0x_5x_6$ | 0.997 | 1.0 |

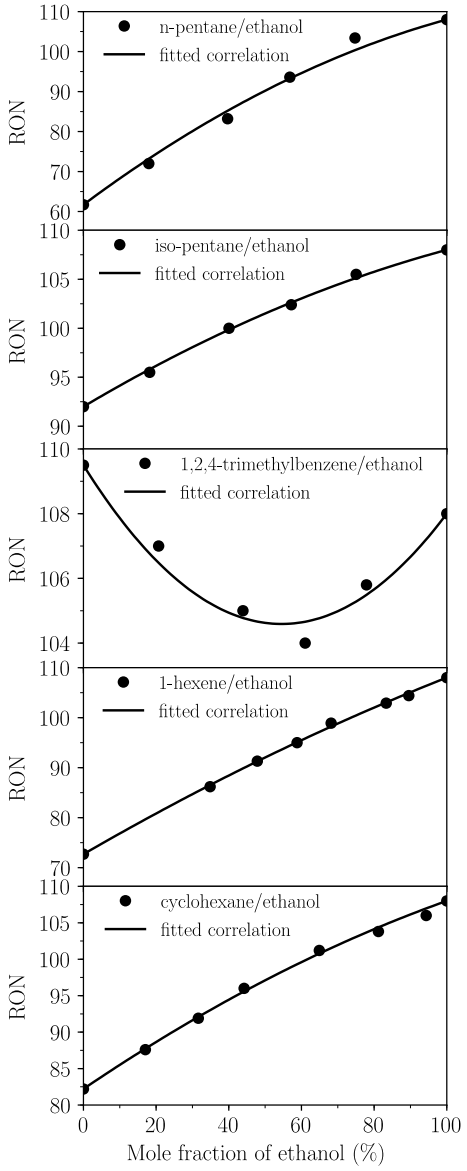



Figure 12: RONs of binary mixtures of ethanol and surrogate compounds used in GS4. Symbols: measurement. Line: best-fit correlation.

*5.3 RON correlation for ethanol and gasoline surrogate mixtures*

The overall correlation of RON for the mixture of ethanol and the five-component gasoline surrogate can therefore be obtained by combining Equation 2 and the equations in Table 8,

$$RON = 61.7x_1 + 92.0x_2 + 109.5x_3 + 72.7x_4 + 82.2x_5 + 108.0x_6$$
$$+ 6.7x_3(1 - x_3 - x_6) + 21.4x_1x_6 + 6.0x_2x_6 - 16.5x_3x_6 + 6.7x_4x_6 + 8.0x_5x_6 \quad (3)$$

This correlation is then tested against the measured RON of various GS4/ethanol mixtures, as shown in Figure 13. Despite the simple formulation summarizing a complicated set of input behaviours, the predicted RON agrees with the measured RON with a maximum absolute error of 0.9 octane number. This close agreement suggests that higher order interactions than that accounted by the 2nd order terms may be insignificant. However, it must be recognised that a small data set is examined here and more octane number measurements for surrogate mixtures containing the five selected compounds are required to test this correlation, such as we have done in other work [10]. More fundamental kinetic studies, e.g. [28–30], are also desirable to understand the underlying chemical kinetics governing these blending behaviours.

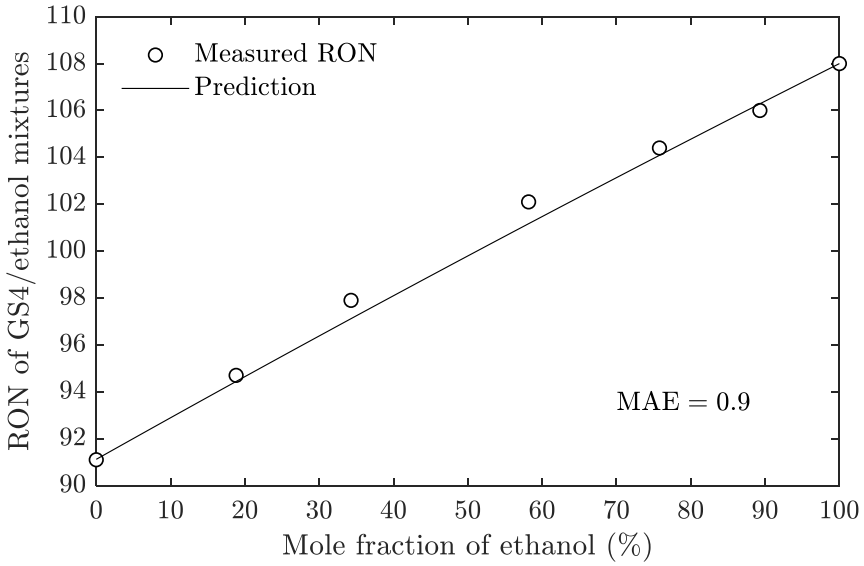



Figure 13: Comparison of the measured RON and predicted RON (Equation 3) for ethanol/GS4 blends.

The excellent agreements in Figure 13 and Figure 11 indicate that Equation 3 can be applied for predicting the RONs of the market gasoline blended with ethanol, as shown in Figure 14. However, caution should be exercised when doing so to other gasolines, particularly when their compositions differ significantly from that used in this work. This is simply because Equation 3 is developed for simple mixtures of the five surrogate compounds and not

for significantly more complex refinery-produced fuels. The major uncertainty lies in the selected surrogate compounds (as well as their assigned contents in the surrogate) where risk always exists with a given surrogate compound being unable to adequately represent the bulk behaviour of the large number of compounds of the intended hydrocarbon group. A separate step is therefore required to validate the developed surrogate against the real fuel for the property in question (e.g. ON from ethanol blending), which as shown in this work is not trivial. Trial and error experiments are generally necessary in this process to make sure that the developed surrogate emulates the target fuel, although certain compositional variations could be tolerated as shown in Appendix B.

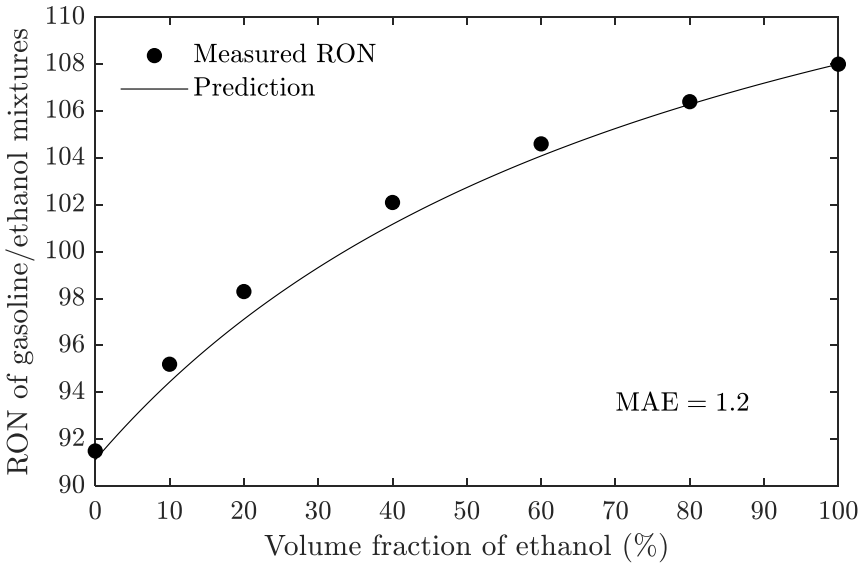



Figure 14: Comparison of the measured RON of ethanol/market gasoline mixtures and the predicted RON of ethanol/GS4 mixtures using Equation 3. Equation 3 is converted to the volume basis using the densities and molecular weights of the five hydrocarbons and ethanol.

## 6. Conclusions

In this work, CFR engine experiments were conducted to investigate the octane blending behaviours of ethanol/hydrocarbon mixtures and to develop a surrogate fuel that reproduced the RON blending for a market gasoline and ethanol. A simple correlation for predicting RON of various formulations of this surrogate and their mixtures with ethanol was proposed.

The following conclusions are drawn from this work.

1. In binary mixtures, toluene blended antagonistically on a mole basis with all fuel compounds studied, including iso-octane, n-heptane, cyclohexane, 1-hexene, and ethanol. Ethanol, in contrast, blended synergistically with all these hydrocarbons except toluene.
2. Hydrocarbons from the same group exhibited different RON blending with ethanol. In particular, as compared to mixtures of iso-octane, n-heptane, and toluene, mixtures of iso-pentane, n-pentane, and 1,2,4,-trimethylbenzene more closely reproduced the RON of the blends with ethanol and the market gasoline considered in this work.
3. A gasoline surrogate containing 38% iso-pentane, 12% n-pentane, 30% 1,2,4-trimethylbenzene, 10% cyclohexane, and 10% 1-hexene (all by volume) reproduced the RON of the market gasoline, as well as RONs of a wide range of blends with ethanol, within 0.5 octane number. The surrogate was developed while matching the 91 RON of the market gasoline without ethanol and maintaining representative hydrocarbon group composition. The MONs of the surrogate and its blend with 40% ethanol were also reproduced well.
4. A simple, non-linear blending equation was developed to estimate the RON of the ethanol/surrogate mixtures over the entire blending range with a maximum error of 0.9 octane number. The non-linear blending was captured by $2^{nd}$ order, binary interaction terms. More octane number measurements on different formulations are needed to fully validate this blending equation.

## Acknowledgements

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**Appendix A**

Table A.1: Measured RON values of ethanol/cyclohexane mixtures

| Ethanol (vol.%) | Ethanol (mol.%) | RON (with cyclohexane) |
|---|---|---|
| 0 | 0 | 82.2 |
| 10 | 17.1 | 87.6 |
| 20 | 31.6 | 91.9 |
| 30 | 44.2 | 96.0 |
| 50 | 64.9 | 101.2 |
| 70 | 81.2 | 103.8 |
| 90 | 94.3 | 106.0 |
| 100 | 100 | 107.5[a] |

[a] RON measured in this work, which is slightly lower than those reported by Foong et al. [8], 108.0-108.5. Same for Table A.2 and A.9.

Table A.2: Measured RON values of ethanol/1-hexene mixtures

| Ethanol (vol.%) | Ethanol (mol.%) | RON (with 1-hexene) |
|---|---|---|
| 0 | 0 | 72.7 |
| 20 | 34.9 | 86.2 |
| 30 | 47.9 | 91.3 |
| 40 | 58.8 | 95.0 |
| 50 | 68.2 | 98.9 |
| 70 | 83.3 | 102.9 |
| 80 | 89.6 | 104.4 |
| 100 | 100 | 107.5 |

Table A.3: Measured RON values of toluene/iso-octane mixtures

| Toluene (vol.%) | Toluene (mol.%) | RON (with iso-octane) |
|---|---|---|
| 0 | 0 | 100.0 |
| 10 | 14.8 | 101.9 |
| 30 | 40.0 | 105.0 |
| 50 | 60.9 | 108.5 |
| 74 | 81.6 | 113.0 |
| 90 | 93.3 | 115.3 |
| 100 | 100 | 117.4 |

Table A.4: Measured RON values of toluene/n-heptane mixtures

| Toluene (vol.%) | Toluene (mol.%) | RON (with n-heptane) |
|---|---|---|
| 50 | 58.0 | 65.9 |

| | | |
|---|---|---|
| 58 | 65.6 | 75.7 |
| 66 | 72.9 | 85.0 |
| 70 | 76.3 | 89.3 |
| 73 | 78.9 | 92.3 |
| 74 | 79.7 | 93.4 |
| 80 | 84.7 | 98.2 |
| 90 | 92.6 | 106.5 |
| 100 | 100 | 117.4 |

Table A.5: Measured RON values of toluene/cyclohexane mixtures

| Toluene (vol.%) | Toluene (mol.%) | RON (with cyclohexane) |
|---|---|---|
| 0 | 0 | 82.2 |
| 10 | 10.2 | 84.4 |
| 30 | 30.3 | 89.1 |
| 50 | 50.4 | 94.1 |
| 70 | 70.4 | 99.4 |
| 90 | 90.2 | 107.7 |
| 100 | 100 | 117.4 |

Table A.6: Measured RON values of toluene/1-hexene mixtures

| Toluene (vol.%) | Toluene (mol.%) | RON (with 1-hexene) |
|---|---|---|
| 0 | 0 | 73.7 |
| 10 | 11.6 | 78.4 |
| 30 | 33.5 | 86.6 |
| 50 | 54.1 | 93.6 |
| 70 | 73.3 | 101.2 |
| 90 | 91.4 | 109.9 |
| 100 | 100 | 117.4 |

Table A.7: Measured RON values of iso-octane/cyclohexane mixtures

| Iso-octane (vol.%) | Iso-octane (mol.%) | RON (with cyclohexane) |
|---|---|---|
| 0 | 0 | 82.2 |
| 10 | 6.8 | 83.7 |
| 25 | 17.9 | 86.3 |
| 40 | 30.4 | 88.8 |
| 50 | 39.6 | 91.0 |
| 75 | 66.3 | 95.8 |
| 90 | 85.5 | 98.5 |

| | | |
|---|---|---|
| 100 | 100 | 100 |

Table A.8: Measured RON values of iso-octane/1-hexene mixtures

| Iso-octane (vol.%) | Iso-octane (mol.%) | RON (with 1-hexene) |
|---|---|---|
| 0 | 0 | 72.7 |
| 25 | 20.2 | 81.0 |
| 50 | 43.1 | 88.5 |
| 75 | 69.4 | 94.5 |
| 100 | 100 | 100 |

Table A.9: Measured RON values of ethanol/GS4 mixtures

| Ethanol (vol.%) | Ethanol (mol.%) | RON (with GS4) |
|---|---|---|
| 0 | 0 | 91.1 |
| 10 | 18.8 | 94.7 |
| 20 | 34.3 | 97.9 |
| 40 | 58.2 | 102.1 |
| 60 | 75.8 | 104.4 |
| 80 | 89.3 | 106.0 |
| 100 | 100 | 107.5 |

Table A.10: Composition (mol.%) and octane number of PRF/aromatic mixtures and their blends with ethanol

| Surrogate | iC8 | nC7 | aromatic | Etoh | density (g/ml) | MW (g/mol) | RON |
|---|---|---|---|---|---|---|---|
| PRF + toluene (TRF91-30) | 44.8 | 16.2 | 39.1 | - | 0.742 | 103.4 | 91.3 |
| PRF + p-xylene | 43.4 | 21.0 | 35.6 | - | 0.740 | 108.4 | 91.0 |
| PRF + m-xylene | 44.7 | 19.6 | 35.7 | - | 0.740 | 108.6 | 91.2 |
| PRF + o-xylene | 50.2 | 13.3 | 36.5 | - | 0.746 | 109.4 | 91.3 |
| PRF + ethylbenzene | 45.9 | 18.2 | 35.9 | - | 0.742 | 108.8 | 91.3 |
| PRF + 1,2,4-trimethylbenzene | 49.1 | 17.5 | 33.4 | - | 0.745 | 113.8 | 91.2 |
| | | | | | | | |
| PRF + toluene (TRF91-30)+Etoh | 17.3 | 6.2 | 15.1 | 61.4 | 0.761 | 68.2 | 105.1 |
| PRF + p-xylene+Etoh | 16.2 | 7.9 | 13.3 | 62.6 | 0.760 | 69.4 | 104.2 |
| PRF + m-xylene+Etoh | 16.7 | 7.4 | 13.3 | 62.6 | 0.759 | 69.4 | 104.5 |
| PRF + o-xylene+Etoh | 18.8 | 5.0 | 13.6 | 62.6 | 0.763 | 69.8 | 104.7 |
| PRF + ethylbenzene+Etoh | 17.2 | 6.8 | 13.4 | 62.6 | 0.761 | 69.5 | 104.5 |
| PRF + 1,2,4-trimethylbenzene+Etoh | 17.9 | 6.4 | 12.2 | 63.5 | 0.762 | 70.8 | 103.6 |

Table A.11: Composition (mol.%) and octane number of gasoline surrogates and their mixtures with ethanol

| Surrogate | iC5 | nC5 | iC8 | nC7 | Tol | TMB | CHX | HXN | Etoh | density (g/ml) | MW (g/mol) | RON |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| GS1 | - | - | 30.5 | 10.0 | 36.8 | - | 12.1 | 10.6 | - | 0.750 | 97.7 | 91.2 |
| GS2 | - | - | 33.3 | 10.9 | - | 31.1 | 13.2 | 11.5 | - | 0.753 | 107.2 | 90.9 |
| GS3 | 30.9 | 17.6 | - | - | 31.9 | - | 10.5 | 9.1 | - | 0.716 | 80.9 | 91.2 |
| GS4 | 39.5 | 12.7 | - | - | - | 26.6 | 11.3 | 9.9 | - | 0.718 | 87.5 | 91.1 |
| GS1/Etoh | - | - | 12.3 | 4.0 | 14.8 | - | 4.9 | 4.2 | 59.8 | 0.766 | 66.9 | 103.7 |
| GS2/Etoh | - | - | 12.7 | 4.1 | - | 11.9 | 5.0 | 4.4 | 61.9 | 0.767 | 69.3 | 103.0 |
| GS3/Etoh | 13.5 | 7.7 | - | - | 13.9 | 0 | 4.6 | 4.0 | 56.3 | 0.745 | 61.3 | 103.1 |
| GS4/Etoh | 16.5 | 5.3 | - | - | - | 11.2 | 4.7 | 4.1 | 58.2 | 0.746 | 63.4 | 102.1 |

**Appendix B**

The applicability of the RON correlation (Equation 3) is tested with another Australian market gasoline of the same grade. In this case, the surrogate is formulated with a lower nominal aromatic content (25 vol.%) to reflect the composition of the target fuel (Table B.1). Results in Figure B.1 show that the predicted RONs (of the five-component surrogate) match closely with the measured RONs (of the market gasoline) for blending with ethanol.

As discussed in the main text, similar agreement may not be expected for gasoline with compositions significantly different from that used in this work.

Table B.1: Properties of the market gasoline #2 and the surrogate

| | | Composition | | | | |
|---|---|---|---|---|---|---|
| | RON | n-paraffins (vol%) | iso-paraffins (vol%) | olefins (vol%) | cyclo-paraffins (vol%) | aromatics (vol%) |
| Market gasoline #2 | 91.1 | 11.3 | 42.3 | 10.5 | 9.6 | 26.3 |

| | RON | n-pentane (vol%/mol%) | iso-pentane (vol%/mol%) | 1-hexene (vol%/mol%) | cyclohexane (vol%/mol%) | 1,2,4-trimethylbenezne (vol%/mol%) |
|---|---|---|---|---|---|---|
| Surrogate | 91.1 | 9.2 / 9.7 | 45.8 / 47.3 | 10.0 / 9.8 | 10.0 / 11.2 | 25.0 / 22.0 |

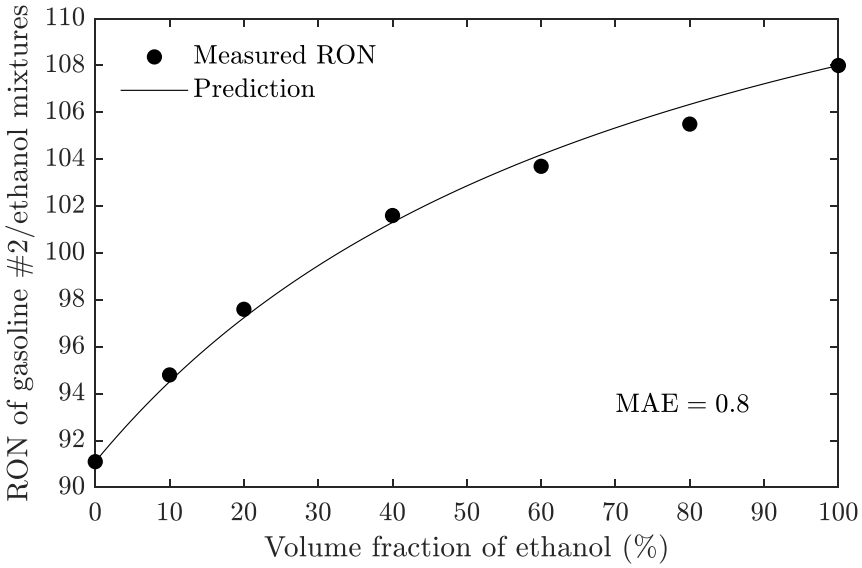


Figure B.1. Comparison of the measured RON of ethanol/market gasoline #2 mixtures and the predicted RON by Equation 3 of ethanol mixtures with the surrogate shown in Table B.1. Equation 3 is converted to the volume basis using the densities and molecular weights of the five hydrocarbons and ethanol.

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