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Optimal octane number correlations for mixtures of toluene reference fuels (TRFs) and ethanol

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ABSTRACT

This paper presents a method for correlating the octane numbers of fuel mixtures, and applies this to the study of toluene reference fuels (TRFs) blended with ethanol. This method combines linear regression and exhaustive (or brute-force) searching for optimal Scheffé polynomials, where optimality is defined as the shortest polynomial that meets a reasonable estimate of the reproducibility limits in the standard, octane number test procedures.

Two correlations for the RON and MON are found to be optimal. These achieve maximum absolute errors (MAE) of less than 2 octane numbers across TRF/ethanol mixtures with a RON between 80 and 120. These two correlations use mole fractions as the correlating variables, are consistent with previously published, linear TRF correlations, and show that binary (non-linear) interactions between iso-octane/ethanol, *n*-heptane/ethanol and toluene/ethanol are all significant. The use of liquid volume fractions is also shown to lead to poor correlation performance, thereby demonstrating the superiority of mole fractions as the correlating variables.

1. Introduction

A fuel's susceptibility to knock in spark ignition engines (SI) is characterized by its octane number (ON). Knock is the result of autoignition of the end-gas and, in general, is affected by the engine design, engine operating condition and the fuel's reactivity. Standard test procedures in Cooperative Fuel Research (CFR) engines are used to determine the *Research Octane Number* (RON) [1] and *Motor Octane Number* (MON) [2].

The octane numbers of pure compounds were extensively measured in the 1950s by the American Petroleum Institute [3]. Some have since been updated. Measurement of the octane numbers of mixtures are less common, however, and the octane blending of mixtures can be quite involved [4,5]. This is particularly the case for oxygenated hydrocarbons, such as ethanol/gasoline mixtures, the use of which has received significant attention in recent years [4,6–10].

Ethanol is commonly blended with gasoline in part because of its low autoignition reactivity and high heat of vaporization, which together result in ethanol's relatively high octane number. Octane number measurements have been conducted for ethanol blended with different commercial gasolines [9,10], primary reference fuels (PRFs) (mixtures of *n*-heptane and isooctane) [4,11–13], and toluene reference fuels (TRFs) (mixtures of PRF and toluene) [4,11–13]. Significant non-linear blending has been reported in some cases.

ON correlations for TRFs [14–16], TRF/ethanol mixtures [13,17] and gasoline distillate blends [18–21] have also been proposed. It is generally agreed that octane numbers of mixtures are better correlated with the fuel components' mole fractions than volume fractions [9,10,14,15]. However, whilst these studies of TRF/ethanol mixtures reported good agreement between measured and correlated octane numbers, the presented correlations did not return the octane numbers of the pure TRF/ethanol components and are relatively complex. These functions are therefore likely to have limited accuracy, particularly when the mixture approaches one of the pure components.

This paper therefore proposes an alternative method for ON correlation. Whilst this method can be generalized to any mixture, we only apply it to the study of TRF/ethanol fuels in this work. This method makes use of Scheffé polynomials [22], which provide a composition-based model for mixture properties. It involves use of linear regression and exhaustive (or brute-force) searching for Scheffe polynomials that result in the best correlation with a given number of polynomial terms. Particular correlations for the RON

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and MON of TRF/ethanol mixtures are identified as being consistent with existing TRF-only correlations [15], sufficiently accurate to be useful and sufficiently simple to provide insight into the most significant component interactions.

2. Method

2.1. Scheffé polynomials

Scheffé polynomials [22] are often used to characterize how a property of a mixture varies with its composition, e.g. [23–25]. The Scheffé polynomial for a four component mixture contains a total of 35 terms, as shown in Table 1, and can be written as

$$\begin{aligned} ON = & \sum_{i=1}^{4}\beta_i x_i + \sum_{i<j}^{3}\sum_{j}^{4}\beta_{ij}x_i x_j + \sum_{i<j}^{3}\sum_{j}^{4}\delta_{ij}x_i x_j(x_i - x_j) \\ & + \sum_{i<j}^{3}\sum_{j}^{4}\gamma_{ij}x_i x_j(x_i - x_j)^2 + \sum_{i<j}^{2}\sum_{j<k}^{3}\sum_{k}^{4}\beta_{ijk}x_i^2 x_j x_k \\ & + \sum_{i<j}^{2}\sum_{j<k}^{3}\sum_{k}^{4}\beta_{ijjk}x_i x_j^2 x_k + \sum_{i<j}^{2}\sum_{j<k}^{3}\sum_{k}^{4}\beta_{ijkk}x_i x_j x_k^2 \\ & + \sum_{i<j}^{1}\sum_{j<k}^{2}\sum_{k<l}^{3}\sum_{l}^{4}\beta_{ijkl}x_i x_j x_k x_l \end{aligned} \quad (1)$$

In this work, x_i denotes the mole or volume fraction for each fuel compound in the mixture, and we define x_1, x_2, x_3 and x_4 as iso-octane, *n*-heptane, toluene and ethanol respectively. This effort is focused on mole-based correlations due to their superior performance in correlating mixture octane numbers, as mentioned in the Introduction and shown later in this work.

The coefficients β_i of the four first-order (linear) terms in Eq. (1) (Table 1) are the octane numbers of the pure components, which for iso-octane and *n*-heptane are 100 and 0 respectively by definition (Table 2). Whilst those for toluene and ethanol could also be fixed, there is some disagreement in the literature as to the RON and MON of toluene in particular, with reported values from different studies varying by roughly 4–5 ON [3,15,26]. We therefore fixed our β_i coefficients for the RON and MON of ethanol to those measured for this study (Table 2), and which were close to previous measurements by ourselves and others [4,27,10], whilst allowing the β_i coefficients for toluene's RON and MON to be part of the correlation method.

The Scheffé polynomial for TRFs can be derived from Eq. (1) by deleting all terms containing x_4. This results in 15 terms, some of which are later shown to be small. Deleting all terms containing x_3 then results in 5 terms remaining in an ON correlation for PRFs. These 5 terms are non-zero when expressed as mole fractions even though the PRF correlation on a liquid volume fraction basis is by definition $ON = 100x_1 + 0x_2$. This is because the molar volumes (m^3/mol) of iso-octane and *n*-heptane are different, thereby inferring that the liquid volume fraction and the mole fraction of any mixture containing these two species must also differ. It is nonetheless straightforward to show that the impact of these non-linear terms in the Scheffé polynomial for PRFs is weak.

Table 2
Coefficients of first order terms in the Scheffé polynomial.

Variable	Compound	β_i/RON	β_i/MON
x_1	Isooctane	100	100
x_2	*n*-heptane	0	0
x_3	Toluene[a]	Variable	Variable
x_4	ethanol	108.0	90.7

[a] RON = 120.0, MON = 103.5 from [3]; RON = 116.0, MON = 101.8 from [15]; RON = 117.2, MON = 110.5 from [26]; RON = 117.4, MON = 106.9 from this work.

2.2. Linear regression

All candidate polynomials are evaluated by linear regression. With *m* different fuel mixtures of known (i.e. measured) ON and a polynomial with *n* terms, this linear regression can be expressed as

$$\boldsymbol{y} = \boldsymbol{X}\boldsymbol{\beta} \quad (2)$$

where $\boldsymbol{y}$ is a vector representing the measured ONs for the *m* fuels, $\boldsymbol{X}$ is an $m \times n$ matrix containing the value of the indeterminate of each of the *n* polynomial terms for these *m* fuels (i.e. $x_1, x_2, \ldots, x_1x_2, \ldots, x_1x_2(x_1 - x_2), \ldots$), and $\boldsymbol{\beta}$ is a vector denoting the *n* coefficients of these polynomial terms. In order to solve for vector $\boldsymbol{\beta}$, the rank of $\boldsymbol{X}$ must be no less than *n* otherwise *rank deficiency* will occur, i.e. the number of fuels of linearly independent composition must be at least equal to the number of polynomial terms. Given the number of fuels ($m > 50$) is considerably larger than the number of polynomial terms commonly considered ($n < 10$), rank deficiency is not an issue in this work.

2.3. Data for correlation development and validation

We use several sets of data to develop and validate our correlations. The development data is made up of ON measurements from ASTM standards for TRFs [1,2], Morgan et al. for TRFs [14], Knop et al. for TRFs [15] and Foong et al. [4] for TRF/ethanol mixtures. The validation data is made up of ON measurements from the present work for TRFs and Lund for TRFs and TRF/ethanol mixtures [11–13]. It is noted that all of this data is restricted to fuels with a RON between 80 and 120, which spans the ONs of plausible, production gasolines.

Fig. 1 shows the development and validation data distributions for ternary mixtures. Note that quaternary mixtures cannot be shown in Fig. 1 but are listed in Appendix A. The contour representing RON = 80 is also shown in Fig. 1(a), (c) and (d). No RON = 80 contour is plotted in Fig. 1(b) since this entire surface has a RON higher than 100. Given the varied data sources used in this study, and their focus on compositions of more engine-representative RONs, it is not surprising to observe unevenly distributed data in $x_1 - x_2 - x_3 - x_4$ parameter space. This is, however, undesirable when developing correlations, since non-uniform data

Table 1
Terms of the Scheffé polynomial with four variables.

No.	Term	No.	Term	No.	Term	No.	Term	No.	Term
1	x_1	8	x_1x_2	15	$x_2x_4(x_2 - x_4)$	22	$x_3x_4(x_3 - x_4)^2$	29	$x_1x_3^2x_4$
2	x_2	9	x_1x_3	16	$x_3x_4(x_3 - x_4)$	23	$x_1^2x_2x_3$	30	$x_2x_3^2x_4$
3	x_3	10	x_2x_3	17	$x_1x_2(x_1 - x_2)^2$	24	$x_1^2x_2x_4$	31	$x_1x_2x_3^2$
4	x_4	11	$x_1x_2(x_1 - x_2)$	18	$x_1x_3(x_1 - x_3)^2$	25	$x_1^2x_3x_4$	32	$x_1x_2x_4^2$
5	x_1x_4	12	$x_1x_3(x_1 - x_3)$	19	$x_1x_4(x_1 - x_4)^2$	26	$x_2^2x_3x_4$	33	$x_1x_3x_4^2$
6	x_2x_4	13	$x_1x_4(x_1 - x_4)$	20	$x_2x_3(x_2 - x_3)^2$	27	$x_1x_2^2x_3$	34	$x_2x_3x_4^2$
7	x_3x_4	14	$x_2x_3(x_2 - x_3)$	21	$x_2x_4(x_2 - x_4)^2$	28	$x_1x_2^2x_4$	35	$x_1x_2x_3x_4$