Fuel 261 (2020) 116243

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Formulating gasoline surrogate for emulating octane blending properties with ethanol

Hao Yuan[a], Zhongyuan Chen[a], Zhenbiao Zhou[a], Yi Yang[a,*], Michael J. Brear[a], James E. Anderson[b]

[a] Department of Mechanical Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia
[b] Ford Research and Advanced Engineering, Ford Motor Company, Dearborn, MI 48121, USA

ARTICLE INFO

Keywords:
Octane number
Gasoline
Ethanol
Surrogate fuel
Non-linear blending

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.

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 Fig. 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

* Corresponding author.
E-mail address: yi.yang@unimelb.edu.au (Y. Yang).

https://doi.org/10.1016/j.fuel.2019.116243
Received 7 August 2019; Received in revised form 17 September 2019; Accepted 18 September 2019

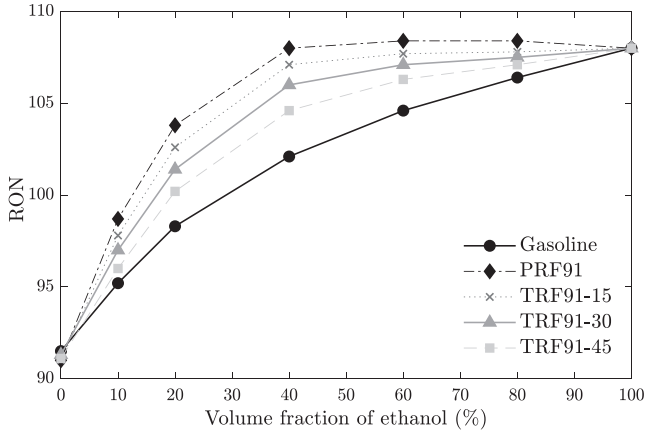

Fig. 1. Measured RONs for an Australian market gasoline, PRF91, and TRF91s blended with ethanol [8]. The reference fuels have the same RON of 91 but contain different amounts of toluene (0%, 15%, 30%, 45% by volume, as indicated). The gasoline contains 31.7 vol% aromatics.

required to emulate the blending behaviour.

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

Figs. 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 Fig. 3 and agree reasonably with the measurements in this study.

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 Fig. 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

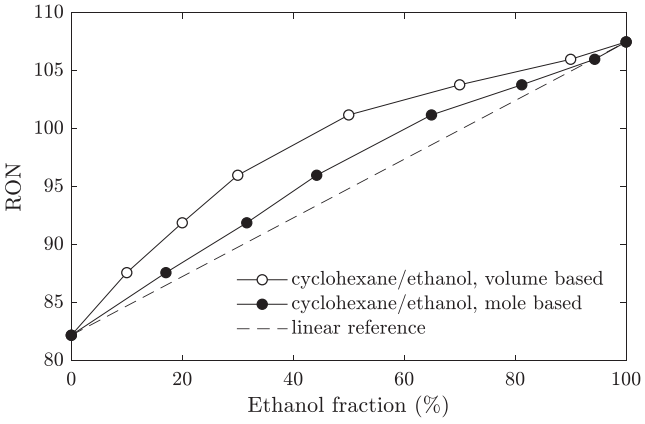

Fig. 2. RONs of ethanol/cyclohexane mixtures.