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# Predicting fuel research octane number using Fourier-transform infrared absorption spectra of neat hydrocarbons

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ABSTRACT

Liquid transportation fuels require costly and time-consuming tests to characterize metrics, such as Research Octane Number (RON) for gasoline. If fuel sale restrictions requiring use of standard Cooperative Fuel Research (CFR) testing procedures do not apply, these tests may be avoided by using multivariate statistical models to predict RON and other quantities. Existing techniques inform these models using information about existing, similar fuels—for example, training a model for gasoline RON with a large number of characterized gasoline samples. While this yields the most accurate predictive models for these fuels, this approach lacks the ability to predict characteristics of fuels outside the training data set. Here we show that an accurate statistical model for the RON of gasoline and gasoline-like fuels can be constructed by ensuring the representation of key functional groups in the spectroscopic data set are used to train the model. We found that a principal component regression model for RON based on IR absorbance and informed using neat and 134 mixtures of *n*-heptane, isooctane, toluene, ethanol, methylcyclohexane, and 1-hexene could predict RON for the 10 Coordinating Research Council (CRC) Fuels for Advanced Combustion Engine (FACE) gasolines and 12 FACE gasoline blends with ethanol within 34.8 ± 36.1 on average and 51.2 in the worst case. We next studied the effect of adding 28 additional minor components found in the FACE gasolines to the statistical model, and determined that it was necessary to add additional representatives of the branched alkane and aromatics classes to reduce model error. For example, adding 2,3-dimethylpentane and xylene to the previous model allowed it to predict RON for the 22 target fuels within 0.3 ± 4.4 on average and 7.9 in the worst case. However, we determined that the specific choice of fuel in those classes mattered less than ensuring the representation of the relevant functional group. This work builds upon previous efforts by creating models informed by neat and surrogate fuels—rather than complex real fuels—that could predict the performance of complex unknown fuels.



## 1. Introduction

Research octane number (RON), determined by ASTM-CFR standard testing procedure D2699-15 [1], indicates a fuels' resistance to autoignition under specific engine operating conditions. RON and the other ASTM 4814 fuel specifications dictate several attributes necessary to operate in the installed fleet of vehicles. In 2014, 136.78 billion gallons of gasoline were consumed in the US [2]—all of which need to meet those quality specifications. Determining the RON of fuels using a Cooperative Fuels Research (CFR) engine costs over $200,000 for the capital investment (among considerable lab modifications) takes 20 min, and also requires trained technicians/operators.

In an effort to reduce this testing burden, researchers sought out more cost-effective and faster noninvasive optical techniques for determining RON, among other fuel specifications, by way of statistical analysis. Vibrational spectroscopy, such as infrared absorption (IR) and Raman spectroscopy, has proved to be a reliable method for fuel characterization. The work of Kiefer [3] highlights current technical advances in the context of fuel characterization, overviews fundamental theory, and discusses advantages/disadvantages of the various techniques currently in use today. Now, a brief sequential overview of literature utilizing vibrational spectroscopy in conjunction with statistical analysis will be discussed.

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Kelly et al. [4] determined 10 ASTM specifications including RON, Motor Octane Number (MON), vapor pressure, specific gravity, bromine number, and contents of aromatic, alkene, saturate, sulfur, and lead using a short wavelength near infrared (SW-NIR) scanning spectrophotometer (660–1215 nm) and multivariate analysis to correlate the spectra to the performance metrics. For example, the group showed that RON of gasolines can be predicted to a standard error within 0.4–0.5 [4], which is better than the ASTM RON test itself at ±0.7 [1]. The original work of Kelly et al. [4] inspired other investigations to enhance their technique, consider alternate fuels, or to predict other fuel performance metrics. To briefly touch on these alternate studies, Williams et al. [5] instead leveraged FT-Raman spectra (3200–600 $cm^{-1}$) to predict cetane index and cetane number to ±1.22 and 2.19, respectively. Cooper et al. [6] applied a similar methodology as Williams et al. (using Raman spectra at wavenumber ranges of 2510–3278 $cm^{-1}$ and 196–1851 $cm^{-1}$) to predict MON, RON, and pump octane number to within ±0.415, 0.535, and 0.410, respectively. Litani-Barzilai et al. [7] combined near-IR (700–1000 nm) and laser-induced fluorescence (250–500 nm third and fourth harmonic) spectra to predict 10 physical specifications; e.g., RON and MON were predicted to within ±0.33 and 0.27, respectively. The more recent work of Kardamakis and Pasadakis [8] presents an efficient multivariate analysis technique that predicts RON within ±0.26 using a limited data set in comparison to previous studies; this work also provides a succinct history of efforts in this field. There are many additional studies to the short list previously mentioned that consider various optical and multivariate analysis techniques to predict performance parameters of fuels [9–17].

Various commercial devices utilize these principles to rapidly predict relevant properties of gasoline and diesel fuels based on optical characteristics. For example, the Zeltex ZX 101C octane analyzer [18] passes radiation from light emitting diodes through optical filters and gasoline samples (14 static wavelengths ranging from 893–1045 nm). The light is collected on a photodetector and processed for absorbance at the wavelengths of interest, with a total measurement time of 20 s and accuracy of ±0.5 RON units [18]. The IROX Miniscan IRXpert gasoline/diesel analyzer takes a similar approach based on FTIR spectroscopy, collecting a broad absorption spectrum and generating information at 12,900 wavelengths. This allows the prediction of 16 total ASTM specifications, and predicts RON with an accuracy of ±0.5 within 80 s [19]. This equipment costs less than half of a CFR engine and does not require expert technicians/operators.

All the previous approaches using multivariate analysis to predict fuel attributes [4–17] used existing, real-world fuel samples (i.e., existing gasoline, diesel, jet fuels) as the training data set to predict performance attributes of those specific fuels. This work used hydrocarbons—neat or combined as mixtures for gasoline surrogate fuels including up to five neat components—to provide model input for predicting RON of the Fuels for Advanced Combustion Engines (FACE) gasolines designed by the Coordinating Research Council (CRC) and manufactured by ChevronPhillips Chemical Co [20]. With this novel approach, a sensitivity analysis can then target neat hydrocarbons and classes (i.e., functional groups) to develop and optimize spectroscopic surrogates for the FACE gasolines. These spectroscopic surrogates most simply represent the bulk auto-ignition behavior (through statistics) of the FACE gasolines. Researchers and industry alike can then predict RON for future fuels (e.g., new, alternative, regarding advanced engines) that may otherwise not be accurately represented spectroscopically by traditional fuels used today. Here, the statistical models created are robust in that they are informed on a fundamental level. This mitigates the issue of creating a model informed by existing fuels that may be physically and spectroscopically different to future fuels—inaccurate prediction of the future fuel would result.

This work uses the FACE gasoline for the fuel and RON to represent the fuel performance parameter. RON is readily obtained for neat hydrocarbons, surrogate and research-grade gasolines, and has previously been shown extensively in literature to correlate well with optical data of quantified gasoline samples. We test our model by predicting RON for the 10 FACE gasolines and 12 additional blends with ethanol; these represent candidate fuels for advanced internal combustion engines (i.e., future fuels) [20].

The structure of the paper is as follows. Section 2 presents the methodology of the approach. This section includes the neat hydrocarbons and surrogate gasoline mixtures considered in this work, the FTIR spectra collection method, and the development of the statistical model. Section 3 provides the results and discussion of the predicted RON values of FACE gasoline samples from the developed statistical model. Lastly, Section 4 summarizes the findings of this study.

## 2. Methodology

In the current approach, hydrocarbon components (neat or mixtures of up to five components) informed a statistical model rather than characterized gasoline samples as in prior efforts. First, the training data set—i.e., the pure hydrocarbon components and mixtures considered to train the statistical model—is discussed. Second, IR absorbance spectra collection methods and the statistical methodology used in this work are covered. Lastly, with the statistical model created, the methodology to validate the model is discussed.

### 2.1. Neat hydrocarbons considered

Promoted by the literature [21–23] as components most relevant to simple fuel surrogates, we primarily considered mixtures of *n*-heptane, isooctane, toluene, ethanol, methylcyclohexane, and 1-hexene. These six hydrocarbons will be referred to as the "primary" hydrocarbons used in this study. In brief, the first two components are used to measure RON (also called the primary reference fuels, or PRFs) and represent the straight and branched alkane functional groups, respectively. Toluene and ethanol represent aromatics and oxygenates, while methylcyclohexane and 1-hexene represent cycloalkane (naphthene) and alkene (olefin) classes, respectively. This study used the aforementioned neat hydrocarbons in addition to the 134 blends taken from the literature [21–24]. These blends are mixtures of the six hydrocarbons in various combinations ranging from two to five components, primarily consisting of isooctane, *n*-heptane, and a third component; see the supplemental material for the full list.

In addition to the six primary neat hydrocarbons, we also considered hydrocarbons found within the FACE gasolines via detailed hydrocarbon analysis [20]. Table 1 lists these additional 28 pure components, referred to as the "additional" hydrocarbons in this work; they will be used to supplement the "primary" hydrocarbons. The hydrocarbon classes of these additional species overlap with the classes from the primary set. However, an outcome of this study demonstrated that the primary set—common components in gasoline surrogate mixtures [21–23]—was not sufficient to physically and spectroscopically represent the FACE gasolines, and species from the additional set were needed (see Section 3).

### 2.2. IR absorbance spectra collection

Absorption spectra were collected using a ThermoFisher Nicolet iS10 FTIR with a single-bounce, Attenuated Total Reflectance (ATR)