

EXAMINATION OF PHYSICAL PROPERTIES OF FUELS AND MIXTURES WITH
ALTERNATIVE FUELS

By

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ABSTRACT

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The diversity of alternative fuels is increasing due to new second generation biofuels. By modeling alternative fuels and fuel mixtures, types of fuels can be selected based on their properties, without producing and testing large batches. A number of potential alternative fuels have been tested and modeled to determine their impact when blended with traditional diesel and jet fuels. The properties evaluated include cloud point and pour point temperature, cetane number, distillation curve, and speed of sound. This work represents a novel approach to evaluating the properties of alternative fuels and their mixtures with petroleum fuels.

Low temperature properties were evaluated for twelve potential biofuel compounds in mixtures with three diesel fuels and one jet fuel. Functional groups tested included diesters, esters, ketones, and ethers, and alkanes were used for comparison. Alkanes, ethers, esters, and ketones with a low melting point temperature were found to decrease the fuel cloud point temperature. Diesters added to fuels display an upper critical solution temperature, and multiple methods were used to confirm the presence of liquid-liquid immiscibility. These behaviors are independent of chain length and branching, as long as the melting point temperature of the additive is not significantly higher than the cloud point temperature of the fuel.

Physical properties were estimated for several potential fuel additive molecules using group contribution methods. Quantum chemical calculations were used for ideal gas heat capacities.

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Fuel surrogates for three petroleum based fuels and six alternative fuels were developed. The cloud point temperature, distillation curve, cetane number, and average molecular weight for different fuel surrogates were simultaneously represented. The proposed surrogates use the experimental mass fractions of paraffins, and the experimental concentrations of mono- and di-aromatics, isoparaffins, and naphthenics. The surrogates represent both low and high temperature properties better than most surrogates in the literature.

Three different methods were developed to predict the cetane number of alternative fuels and their mixtures with JP-8, a military jet fuel. The same six alternative fuels were distilled, as well as blended with JP-8, and the cetane numbers measured. The Ghosh and Jaffe model represented the neat fuels with pseudocomponents to predict the cetane numbers of blends. This model worked well for the neat fuels, but the mixture behavior was predicted with incorrect curvature. The second and third methods used near infrared (NIR) and Fourier transform infrared (FTIR) spectroscopy to correlate the cetane number. The correlation provides prediction of the cetane numbers of the blends based on spectral measurements. Both the FTIR and NIR correlations are able to predict mixture cetane numbers within experimental error, but the NIR model was found to be the most reliable of all three methods.

Finally, the SAFT-BACK and ESD equations of state were used to model the density and speed of sound for hydrocarbons at elevated pressures. The SAFT-BACK equation was found to be more accurate, and the model was extended to predicting the speed of sound. Mixtures of hydrocarbons were also predicted, but the SAFT-BACK is limited in capability for representing compressed alkanes heavier than octane.

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CHAPTER 1

Introduction and Background

1.1 Introduction

The production of biofuels and alternative fuels is a rapidly expanding area of research. Wide varieties of molecules and production schemes are being developed for many different applications. These fuels range from traditional first generation biofuels like ethanol to second generation fuels like Fischer-Tropsch isoparaffins. Many logistical issues can arise during the consideration of fuels and fuel blends ranging from fuel standards to acceptability in distribution and combustion systems. Fuel properties which need be addressed for biofuels to be considered compatible include energy content, vapor pressure, octane/cetane number, materials compatibility, and cold flow properties.

First generation biofuels are made primarily from starches, sugars, or vegetable oils. These include ethanol from corn and fatty acid methyl esters (FAMES) produced from soybean oil or animal fats. While FAMES from soybean oil are the most commonly used form of biodiesel in the United States [1], the use of this fuel is limited in cold climates due to its high cloud point temperature, even when in mixtures with petroleum diesel [1-3]. Traditional FAMES biodiesel is unacceptable as a bio-based jet fuel, due to the low temperatures encountered at high flight altitudes [4]. Without additional processing, such as distillation [5] or the use of urea to precipitate the saturated esters [6], FAME fuel is not able to achieve the required low cloud point temperatures [7-9].

Second generation biofuels are biofuels made from non-food feedstocks. This classification includes ethanol from corn stover and other lignocellulosic sources, Fischer-Tropsch liquids, and butanol or mixed alcohols from renewable sources [10]. In addition, these fuels can be reacted together or upgraded to produce fuels with more desirable qualities [11, 12].

These processes create molecules with a wide variety of functional groups and oxygen content, and can usually be tailored to produce a specific molecule type.

In order to streamline the production of these fuels, and to identify which types of molecules would be desirable as fuels, evaluations of the molecule's effects on cloud points and other fuel properties are needed. Often, these molecules are fairly new to large scale production, and as such have limited physical property data. Thermodynamic property models can be used to extrapolate property data from a limited experimental data [13].

Because of the wide variety of possible fuel components, physical testing of every possible molecule would be labor and cost intensive. Models for the physical properties of these biofuels in mixtures with traditional fuels facilitates the screening of biofuel components without the need for large production batches or extensive testing. Traditional petroleum fuels contain hundreds of different components. Figure 1.1 shows a GC-MS spectrum for JP-8, a military jet fuel. The vast majority of components are not baseline resolved and are too similar to be identified easily. In particular, isoparaffins and naphthenic species can not be resolved from one another in the analysis below, due to very similar fragmentation patterns. GC-MS is also unable to distinguish between a carbon fragment that has broken off from an aromatic ring and a fragment from another isoparaffin, thus these species cannot be resolved. GCxGC testing can determine the differences between isoparaffin and naphthenic species, but can only give a carbon number, not the specific structure of each component.

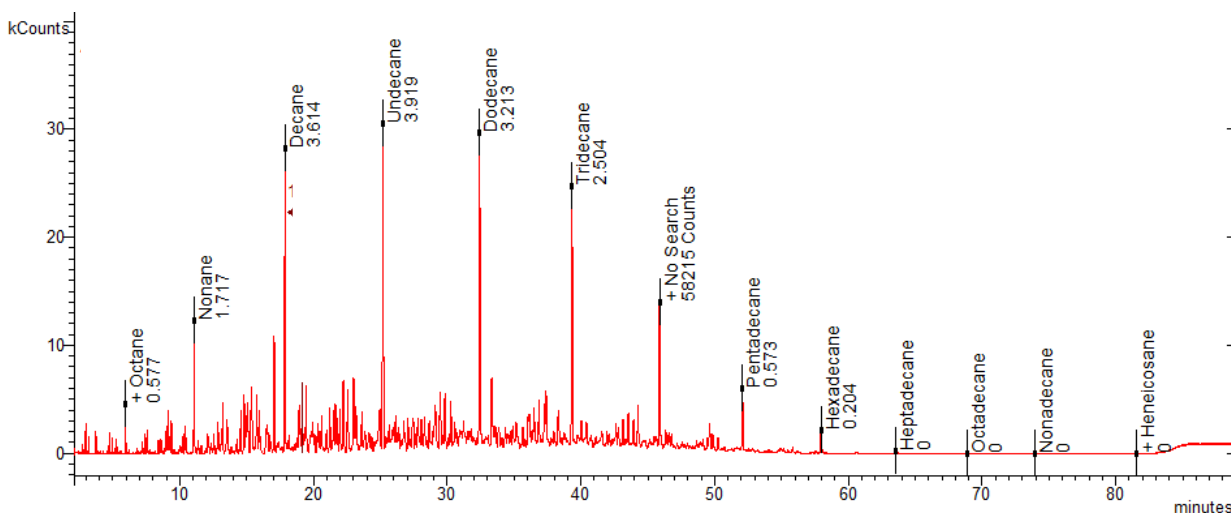


Figure 1.1. GC-MS spectra for JP-8 jet fuel.

It is uncommon to identify and quantify all the components in a traditional fuel. Instead, surrogate mixtures are developed for petroleum fuels. A fuel surrogate uses a limited number of compounds with known physical properties that when mixed mimic the properties of a specific fuel. This surrogate can then be used to calculate properties such as cetane number, distillation curve, cloud point temperature, and compressibility.

This work represents a novel approach to predicting the properties of bio- or alternative fuels based on their properties in mixtures with petroleum fuels. By modeling fuel mixtures, potential biofuels can be identified based on their properties without producing and testing large batches. The objective of this research is to evaluate different methods of developing a fuel surrogate which can predict both low and high temperature fuel properties. The fuel surrogates could then be used to predict the properties of alternative fuel mixtures.

A number of potential biofuels have been tested to determine their impact on the cloud point temperature of different fuels. A model was developed to simultaneously optimize the surrogate composition to match the cloud point temperature, distillation curve, cetane number, and average molecular weight. A surrogate model is used to relate the composition of the fuel to cetane number, and those surrogates are used to predict the cetane numbers of mixtures of fuels.

Near-infrared and Fourier transform infrared spectroscopy is also used to predict the cetane number of fuels. Finally, the speed of sound of pure component and mixtures are predicted using an equation of state.

1.2 Background

The methods for designing a surrogate can vary depending on the type of property that will be predicted and the model used to perform the predictions. Most surrogates are designed to match one or two related fuel properties, such as boiling curve [14, 15], cloud point [16-22], spray formation [23], combustion kinetics [24], or cetane number [25-32]. Cetane number does not need to meet a minimum value for jet fuels, but due to the one fuel for the battlefield program, JP-8 is being used in diesel engines as well [33-35]. When these surrogates are used to model a property for which they weren't designed, they give very inaccurate results, with errors usually in the range of 150-250%. For example, a diesel fuel surrogate with a focus on cetane number and combustion was developed by simply adjusting the ratio of cetane to methyl naphthalene until the cetane number was correct [24]. This surrogate, however, exhibits a cloud point temperature of -38°C, when the actual temperature is -12°C.

These deviations are likely due to the difference in approach and focus of each model. In some cases, components are picked from a database guided by a small amount of compositional information and the concentrations are adjusted until the prediction is correct [14, 15]. Other surrogates use partial compositional data for the paraffin content and only use one or two components to represent the rest of the fuel [17]. For cloud point modeling, some surrogates use a solid solution model [17, 18, 20] or a pure solid model [19], while others use a sequential precipitation technique [16, 21, 22]. For cetane number surrogates, either compositional data is used [25, 26] or components of the fuel spectrum are fit to an empirical equation [27-31].

Compressibility is another fuel property which can affect the performance of biofuels in mixtures. If a fuel is too compressible, the mass of fuel injected for a given injection volume can be different based on the injection pressure. These differences can cause incomplete or insufficient combustion, which can lead to an increase in wear on the engine and higher emissions. The compressibility of a fuel is usually calculated by experimentally determining the speed of sound and density of the fuel at a wide variety of temperatures and pressures [36-38]. For some mixtures, the speed of sound can be predicted by assuming a direct relationship between the pure component speed of sound and the mole fraction [37, 39-41]. An equation of state model can also be used to predict the speed of sound of a pure fluid. This has been done for pure alkanes and binary mixtures using various modifications of the SAFT equation, as well as the Peng-Robinson equation [42-46]. To use an equation of state model, a surrogate would also need to be used.

Thermodynamic models are preferable to empirical models because they represent the chemical interactions in the surrogates rather than other correlations which require a large number of tests to fit or are not accurate if the composition changes. By using thermodynamic models, all predictions are sensitive to changes in composition and the optimized surrogate is more likely to be widely applicable. Different production batches of fuels can meet the required specifications but can have different compositions [47, 48]. The surrogates implemented in this work take elements of some of the above methods and combine them. This approach allows for better representation of the fuel across both low and high temperature properties.

CHAPTER 2

Cold Flow Properties for Blends of Biofuels with Diesel and Jet Fuels

Portions of this chapter have been previously published as Lown A.L., Peereboom L., Mueller S.A., Anderson J.E., Miller D.J., Lira C.T., Cold flow properties for blends of biofuels with diesel and jet fuels, Fuel, 117, Part A (2014) 544-51.

2.1 Introduction

By the year 2022, it is projected that 60 billion gallons of biofuel will be required worldwide to meet government mandates [49]. There are many logistical issues for consideration of fuel blends ranging from fuel standards to acceptability in distribution and combustion systems. Various fuel properties must be evaluated for biofuels to be considered compatible, including energy content, octane/cetane number, materials compatibility, volatility and cold flow properties. In this chapter, an expanded view of possible biofuels is taken, and compounds that contain oxygen in different functional groups are considered.

First-generation biofuels are made primarily from starches, sugars, or vegetable oils. This includes ethanol from corn and fatty acid methyl esters (FAME) produced from vegetable oil or animal fats. While FAME from soybean oil is the most commonly used form of biodiesel in the United States [1], the use of this fuel is limited in cold climates due to its high cloud point temperature, even when mixed with petroleum diesel [1-3]. FAME biodiesel is more problematic as a bio-jet fuel, due to the low temperatures encountered at high flight altitudes [4]. Without additional processing, such as distillation [5] or the use of urea to precipitate the saturated esters [6], FAME is not able to achieve the required low cloud point temperatures. There are many papers in the literature which describe the effects of biodiesel on the low temperature and various fuel properties of diesel fuels [7-9].

Second-generation biofuels are often defined as biofuels made from non-food feedstocks, including ethanol from corn stover and other lignocellulosic sources, Fischer-Tropsch oils from wood, and butanol or mixed alcohols from renewable sources [10]. In addition, these fuels can be reacted together or upgraded to produce fuels with more desirable qualities [11, 12, 50]. Chemical reactions create compounds with a wide variety of functional groups and oxygen

content, and can usually be tailored to produce a specific molecule type. Dibutyl succinate has previously been considered as a diesel-range oxygenate [51], as well as other ethers [52].

Evaluations of the functional group's effects on cloud points and other cold flow properties are needed to streamline the development of these fuels, and to identify which types of molecules would be desirable as fuels.

Twelve compounds representing different chemical classes (alkanes, ethers, esters, ketones, and diesters) were examined in fuel blends, to develop an understanding of the impact of molecular functionality on cold flow properties. ASTM D7683 and D2500 were to determine cloud point temperatures, and ASTM D6371 was used for cold filter plugging point temperatures. Multiple types of both diesel and jet fuels were used to determine the effects of the molecule types across fuel specifications. The compounds evaluated have the potential to be produced through bio-derived pathways. Most are usually not produced directly by fermentation, but are envisioned as products of the upgrading of fermentation products.

2.2 Materials and Methods

2.2.1 Materials

Three petroleum diesel fuels and one jet fuel with properties shown in Table 2.1 were used, covering a range of intended application temperatures. These fuels include a representative US standard #2 diesel (USD), a representative European standard diesel (ESD), and a diesel with comparatively high aromatic content, denoted high aromatic diesel (HAD). Three samples of HAD fuel were used, obtained from three fuel batches prepared to the same specifications, but with slightly different measured properties. HAD was the initial sample, HAD+ was obtained 2 months later, and HAD* was obtained 4 months after the first sample. The same batch of HAD used in these cloud point studies was previously characterized by Windom et. al. [15]. The JP-8

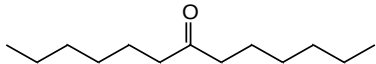
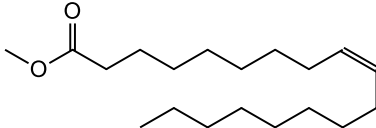
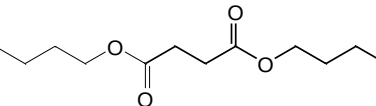
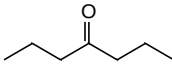
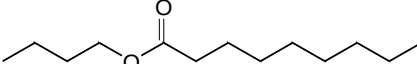
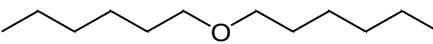
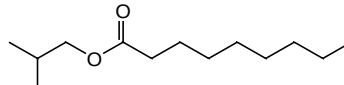
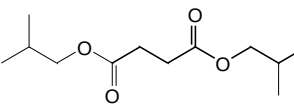
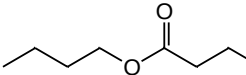
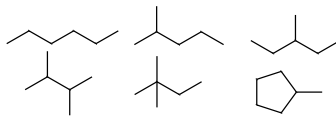
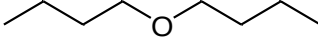
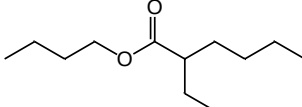
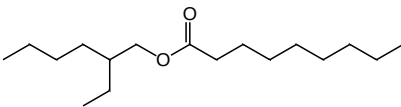
jet fuel was donated by the US Air Force. JP-8 is the petroleum-based fuel used by the US military and it is very similar in specifications to the commercially available fuel Jet A1. However, JP-8 contains an additional additive package including a corrosion inhibitor, a lubricity enhancer, an icing inhibitor, and a static dissipater.

Table 2.1. Base petroleum fuel characteristics. USD – US standard #2 diesel; ESD – European standard diesel; HAD – high aromatic diesel.

	USD	ESD	HAD	JP-8	Test Method
Cloud point (°C)	-15	-23	-27	-52	ASTM D2500
Cold filter plugging point (°C)	n/a	-33	-36	n/a	ASTM D6371
Specific gravity at 15.6 °C	0.847	0.834	0.859	0.798	ASTM D4052
Distillation T10 (°C)	207	209	214	177	ASTM D86
Distillation T50 (°C)	256	263	253	203	
Distillation T90 (°C)	313	332	312	241	
Aromatics (%vol)	29	22	34	15.7	ASTM D1319 ASTM D5291
Saturates (%vol)	68	74	63	n/a	
Olefins (%vol)	3	4	3	0.8	
Cetane Number	44	52	41	n/a	ASTM D613

Chemical classes for the selected biofuel compounds include diesters, esters, ketones, ethers, and alkanes. Table 2.2 summarizes all compounds tested, their structures, and their melting temperatures. For FAME, the structure of methyl oleate is shown as a representative component. All melting points are either from NIST Chemistry Webbook [53], or the DIPPR database [54] and for FAME the cloud point is tabulated. The compounds can be divided into two classes based on molecular weight. The lighter components contain 7 or 8 carbons, and the heavier components contain from 12 to 17 carbons.

Table 2.2. Evaluated compounds, their structures, and melting points. *a)* FAME is a mixture of multiple esters, represented here with methyl oleate, the main component in canola FAME. For FAME only, the cloud point is given, rather than the melting temperature.

Compound Name	Structure	Melting Point (T _m) (°C)	Chemical Class
Dihexyl ketone		30	Ketone
FAME (see note <i>a</i>)		3.0	Ester
Dibutyl succinate		-29	Diester
4-Heptanone		-32.5	Ketone
Butyl nonanoate		-38	Ester
Dihexyl ether		-43	Ether
Isobutyl nonanoate		-48	Ester
Diisobutyl succinate		-55	Diester
Butyl butyrate		-92	Ester
Hexanes (mixture of isomers)		-95	Alkane
Dibutyl ether		-97.9	Ether
Butyl ethyl hexanoate		< -65	Ester
Ethyl hexyl nonanoate		< -65	Ester

Hexanes (99.8% purity), butyl butyrate (98% purity), dibutyl ether (99.3% purity), dihexyl ketone (97% purity), and dihexyl ether (97% purity) were obtained from Sigma Aldrich. All other chemical compounds were synthesized in the MSU laboratories and purities were

confirmed using gas chromatography. Water contents were analyzed using Karl-Fisher titration. All compounds had $\geq 97\%$ purity and $< 0.1\%$ water.

Dibutyl succinate (DBS) is a possible biofuel component because it can be made from succinic acid and butanol, which are both potential products of fermentation. Dibutyl succinate and diisobutyl succinate were produced adapting the method of Kolah et al. [55], using n-butanol or isobutanol, respectively, instead of ethanol. Dibutyl ether, 4-heptanone, and butyl butyrate were selected because they can be made from butanol and butyric acid. Butyric acid is also a fermentation product [56]. Dibutyl ether can be made by acid-catalyzed dehydration of n-butanol, 4-heptanone by ketonization of butanol [57, 58], and butyl butyrate can be produced by esterification of n-butanol with butyric acid [59].

The cetane numbers (CN) of certain compounds such as DBS (CN = 15-20 [60]) or butyl butyrate (CN = 17.5 [61]) are too low to be viable as a diesel fuel in their own, but could be envisioned as blending components to provide other beneficial properties (e.g., oxygen content, reduction in exhaust particulates). The DBS CN = 15 is based on extrapolation of ASTM D613 testing DBS/FAME blends by Paragon Laboratories, Livonia, MI. The experimental cetane numbers are listed here in the format of (v/v% DBS, CN): (0%, 59.3), (20%, 46.5); (40%, 40.1), (50%, 35.6). Larger compounds (CNs measured by Paragon Laboratories, ASTM D613) such as butyl nonanoate (CN = 51), isobutyl nonanoate (CN = 45), and ethylhexyl nonanoate (CN = 59) have higher cetane numbers that are more typical of diesel fuel and thus are more desirable for diesel blending.

Dihexyl ketone and dihexyl ether are included to evaluate whether the trends exhibited by esters, ethers, and ketones continue into the higher molecular weight range. Butyl ethyl hexanoate and ethyl hexyl nonanoate can be made from other biofuel intermediates and are

included to evaluate the effect of side chain branching for higher molecular weight compounds. 2-Ethylhexanol can be produced by the Guerbet reaction of n-butanol [62], which can then be esterified with nonanoic acid to produce ethyl hexyl nonanoate. Nonanoic acid can be produced by ozonolysis of oleic acid [63]. 2-Ethylhexanoic acid can be made by oxidizing 2-ethylhexanol, which can then be esterified with n-butanol to produce butyl ethyl hexanoate.

Fatty acid methyl esters (FAME) are currently blended with diesel and are included here to compare the trends in cloud point temperatures with cold filter plugging point (CFPP) temperatures. The FAME was produced from canola oil using a standard acid-catalyzed esterification. The resulting fuel had >97% purity and was not distilled to decrease the cloud point temperature.

2.2.2 Experimental methods

2.2.2.1 Gas chromatography method

A Varian 450 gas chromatograph was used with helium carrier gas at 10 mL/min. The column was a J&W Scientific DB-WAX 30 m x 0.54 mm with a film thickness of 1 μ m, with on-column injection of 0.2 μ L at 250 °C. The oven temperature program consisted of a hold at 40 °C for 2 min, a ramp of 10 °C/min to 150 °C, a ramp of 30 °C/min to 230 °C, and a hold for 2 min. Detection was by thermal conductivity with a 240 °C operating temperature.

2.2.2.2 Cloud point testing (ASTM D7683)

Cloud point (CP) testing was conducted at Michigan State University (MSU), and Ford Motor Company. Data in all figures except some series in Figure 2.5 and Figure 2.9 were collected using ASTM D7683 in the MSU laboratory, as indicated in the captions. Data in Figure 2.5 and Figure 2.9 were collected at Ford Motor Company using ASTM D2500 as outlined in section 2.2.2.3. The two methods were used for convenience due to the equipment availability at

the physical locations of the collaborating groups. Comparison of the methods using round-robin testing shows a small systematic difference in cloud point results of 1.68 °C as reported in ASTM D7683. Because the majority of the data in this study was collected using ASTM D7683, the data from ASTM D2500 have been shifted to ASTM D7683 values using $CP(D7683) = CP(D2500) - 1.68$ to facilitate comparison in the figures. The original measurements are tabulated in Appendix A.

Cloud point tests at MSU were performed using ASTM method D7683 with a Tanaka Mini-Pour/Cloud Point Tester (Model MPC-102A/102L). The cloud point temperature is defined as the temperature at which the first solid appears in the liquid. The commercial unit includes a sample chamber into which a cylindrical vial is inserted. The vial holds a 3.5 mL sample with 3 cm of head space above the sample. After loading the sample, the temperature decreases at a programmed rate. The unit monitors light reflected from a source in the top of the sample via a reflector on the bottom of the sample chamber. The cloud point is identified as the temperature at which the formation of a second phase in the solution scatters the light and decreases the reflected light by a predefined amount.

The commercial apparatus was modified using a Varian Star 800 module interface to log data every 0.27 seconds. Data included the temperature of the bath, sample temperatures at both the lower and middle positions in the sample chamber, and the light sensor voltage response. The lower temperature sensor is used to determine the cloud point temperature, and the middle position is used to determine the pour point temperature. The absence of stirring in the apparatus causes a small temperature gradient. The solution at the bottom of the chamber becomes colder slightly faster than in the center of the chamber, thus the cloud point is visible at the bottom of

the chamber first. The temperature difference between the two locations was on average 4 °C when the cooling rate was 1.0 °C/minute.

Figure 2.1 shows the light detection for both a successful run and a run which displays interference. The unmodified commercial apparatus self-determines and displays the cloud and pour point temperatures of the sample. However, the self-reporting was susceptible to erroneous results. Logging of the light scattering showed that several downward steps occasionally occurred in the plateau of the light scattering trace, and a step was occasionally misinterpreted by the instrument as the cloud point. The sources of the errors were suspected to be electrical interference from other instruments on the same electrical circuit, electrical noise, issues with reflectors, or physical interference, but they were not reproducible. By logging the signals and comparing results from multiple runs, it was determined that runs with this behavior did result in accurate cloud points when the trace was manually interpreted.

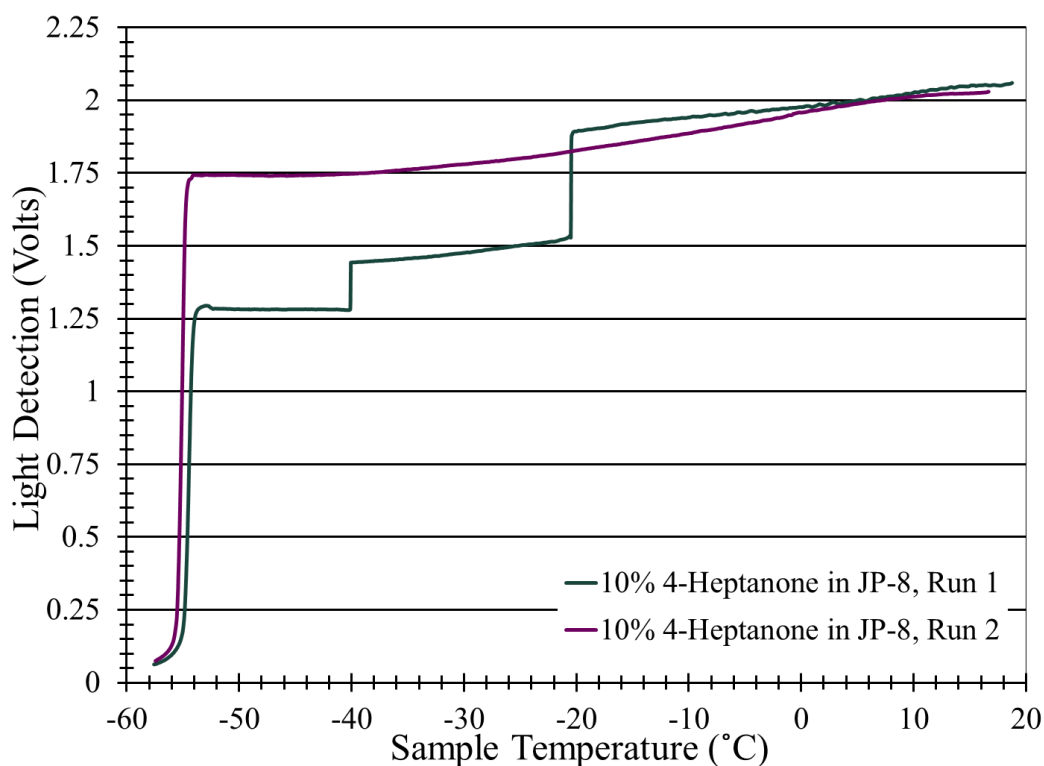


Figure 2.1. Examples of experimental cloud point runs. Run 1 shows interference, while run 2 show typical cloud point behavior.

All cloud points reported were determined using the logged data from the light sensor and the lower sample temperature sensor. Data were collected at a uniform cooling rate of 1.0 °C/min. To decrease the run time for some samples, a variable cooling rate was used, usually 5 °C/min until the sample temperature was 30 °C warmer than the expected cloud point, and then 1 °C/min afterwards. A minimum of 3 runs were performed to determine the cloud point at each concentration. Before the cloud point was reached, the light detection reached a plateau. The cloud point temperature was taken to be the temperature at which the light detection was at 90% of the plateau value, and only when the decrease was a smooth curve. Figure 2.2-Figure 2.7 and Figure 2.9 display data measured using this method. When there was no evidence of supercooling, the repeatability of the measurements was ± 0.22 °C, and the error of the thermocouple was less than ± 1 °C.

Supercooling was observed in some runs, predominately with nearly pure, or pure compounds. Supercooling is caused by a lack of nucleation sites for the formation of a solid phase, and the sample cools as a liquid below the freezing point. When nucleation occurs, the exothermic heat of fusion warms the sample back to the cloud point/freezing temperature. If supercooling was observed in a test reported here, and the solution warmed by less than 1 °C after nucleation occurred, the cloud point was reported as normal. When behavior other than supercooling was observed, additional runs were performed. A consistent cloud point could not be found for compositions of >85% butyl butyrate in JP-8 and therefore, these runs were excluded from the analysis.

2.2.2.3 Cloud point testing (ASTM D2500)

At Ford Motor Company, cloud point was determined using an automated cloud point analyzer (Lawler model DR-14L automated CP and CFPP analyzer, Lawler Manufacturing

Corp., Edison, NJ) per ASTM D2500 specifications. The fuel sample was cooled at the specified rate and examined in 1 °C increments for the formation of insoluble materials as measured by light scattering. The cloud point was identified as the temperature at which the insoluble materials were first detected at the bottom of the sample vial. The repeatability for these measurements is ± 2.0 °C.

2.2.2.4 Cold filter plugging point (ASTM D6371)

Cold filter plugging point (CFPP) testing was performed at Ford Motor Company. The CFPP temperature was determined by an automated analyzer (Lawler model DR-14L automated CP and CFPP analyzer, Lawler Manufacturing Corp., Edison, NJ) following ASTM D6371. The CFPP temperature is defined as the temperature at which the fuel has solidified or gelled enough to plug the fuel filter. As the fuel sample was cooled at intervals of 1 °C, an attempt was made to draw 20 mL of the fuel sample into a pipette under a controlled vacuum through a standard wire mesh filter. If successful, the procedure was repeated at the next lower temperature. As the sample cools, insoluble materials (e.g., wax crystals) form and begin to inhibit flow through the filter. The cold filter plugging point is defined as the temperature for which the time taken to fill the pipette exceeds 60 seconds. The repeatability for these measurements is ± 1.76 °C.

2.3 Results and Discussion

2.3.1 Pure compounds

Pure components do not display a cloud point temperature. There is often significant supercooling when a pure component freezes. Supercooling is detected when the temperature increases after the first solid forms. For Figure 2.2-Figure 2.7, the cloud point temperature shown for the pure added compound is represented by that compound's melting point temperature as listed in Table 2.2.

2.3.2 Functional group effect on cloud point temperature

For most mixtures tested, the cloud point decreases with addition of esters, ethers, and alkanes. For diesters, a maximum is seen in the cloud point curve, with cloud points that are higher than the cloud point of the base fuel or the melting point of the pure component, which is indicative of a liquid-liquid phase separation.

Figure 2.2 - Figure 2.4 compare the low molecular weight compounds with different compounds added to USD, HAD, and JP-8, respectively. When hexanes are added to USD, HAD, and JP-8, the cloud point decreases steadily with the increasing mass fraction of hexanes from the base fuel's cloud point, though remaining considerably higher than the melting temperature for the hexanes, even at high mass fractions. The hexanes are expected to exhibit approximately ideal solution behavior in the petroleum base fuel, with the cloud point decreasing due to dilution of the high molecular weight n-paraffin content of the base fuel.

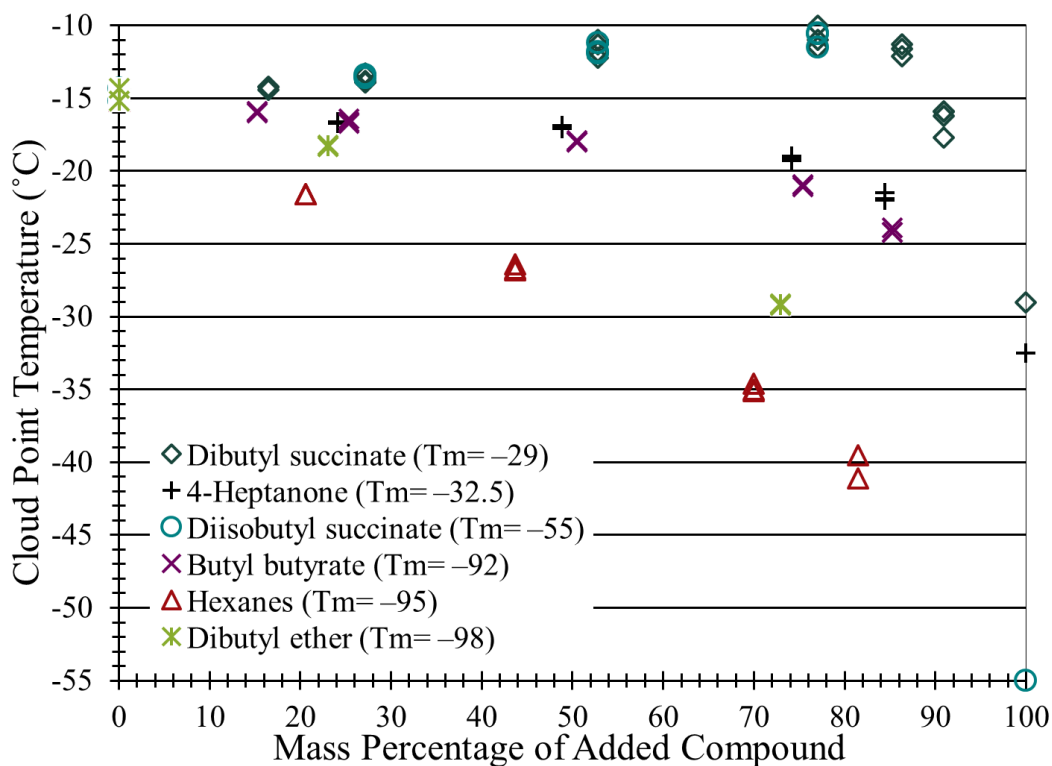


Figure 2.2. Cloud point temperature for USD in mixtures with various low molecular weight compounds. The uncertainty in these measurements is ± 1.2 °C.

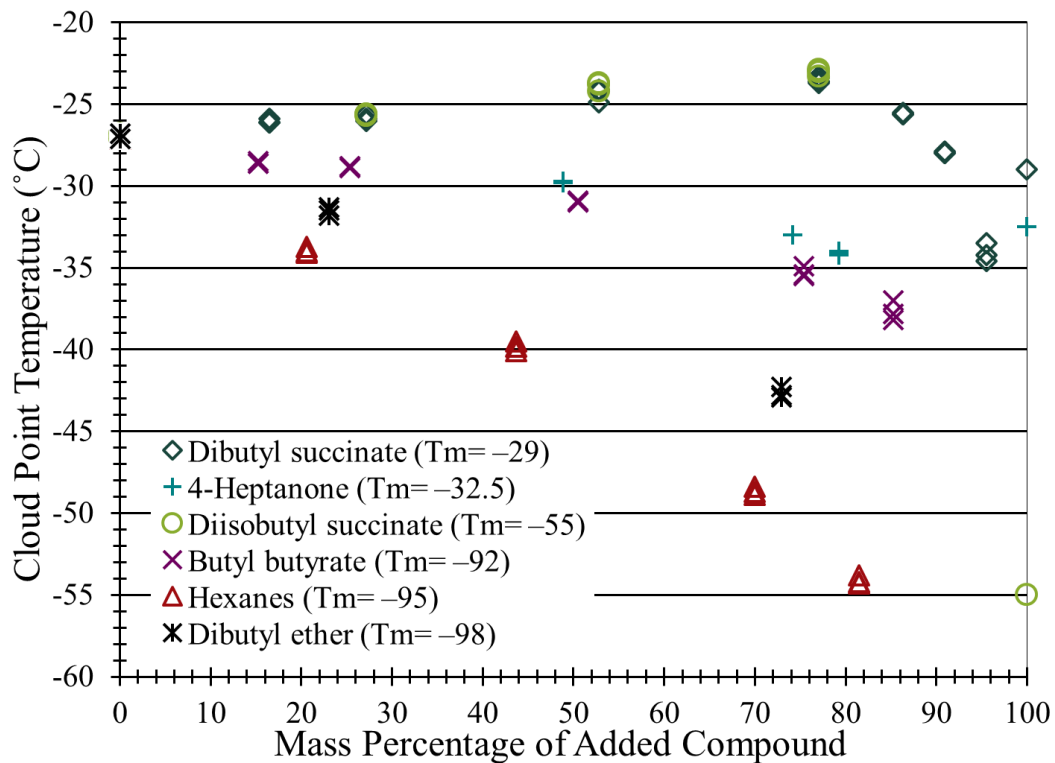


Figure 2.3. Cloud point temperatures for HAD in mixtures with various low molecular weight compounds. The uncertainty in these measurements is ± 1.2 °C.

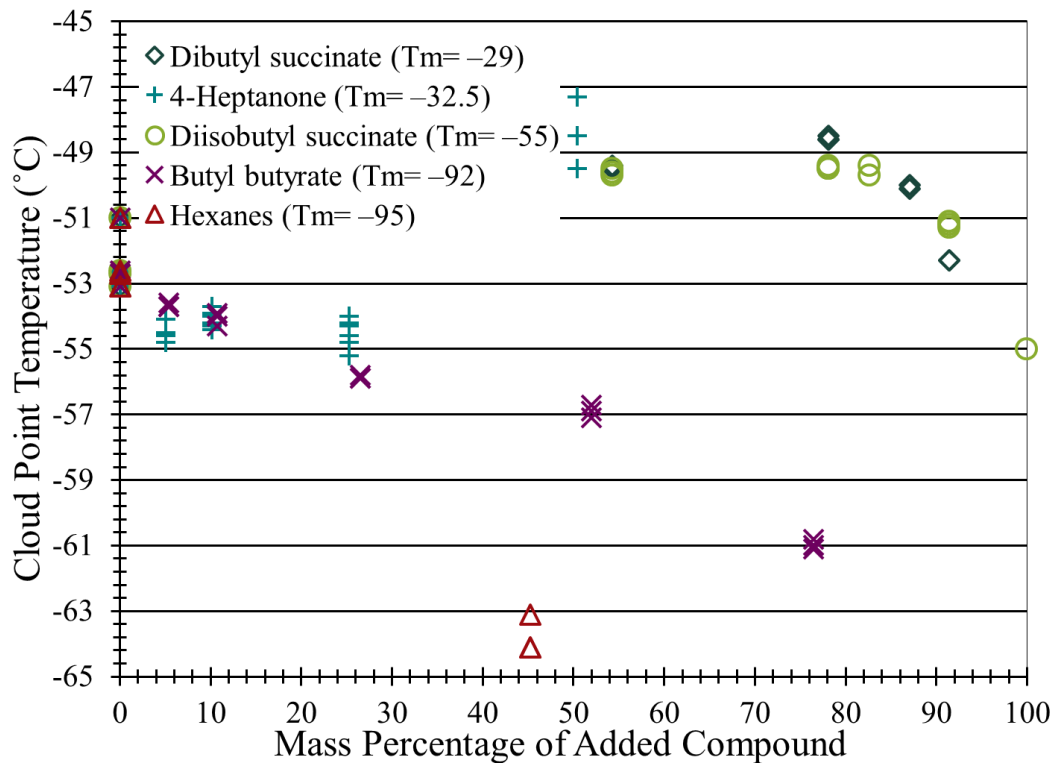


Figure 2.4. Cloud point temperatures for JP-8 in mixtures with various low molecular weight compounds. The uncertainty in these measurements is ± 1.2 °C.

In Figure 2.2 and Figure 2.3, dibutyl ether also decreases the cloud point temperature, but to a lesser extent than hexane in blends. Comparison of the behavior indicates that the activity coefficient of the fuel paraffins in dibutyl ether is greater than in hexanes. Butyl butyrate shows a greater departure from ideal behavior than dibutyl ether, possibly due to the higher oxygen-to-carbon ratio and/or the greater polarity.

For the two ketones tested (4-heptanone and dihexyl ketone), the behavior depends on the relative properties of the ketone and the base fuel. The ketones tested display a eutectic point which shifts based on the difference between the compound's melting point temperature and the base fuel's cloud point temperature. When the ketone's melting point temperature was lower than or close to the cloud point temperature of the base fuel, the ketone in small additions behaves the same as the esters, as shown by 4-heptanone in Figure 2.2 - Figure 2.4. In Figure 2.2, the eutectic is expected to be very near pure 4-heptanone composition and melting temperature, though the composition is not determined explicitly by the experimental data. In Figure 2.3, the eutectic is at concentrations greater than or equal to 85 wt% 4-heptanone. For 4-heptanone in mixtures with JP-8 (Figure 2.4), the eutectic point has shifted to approximately 25 mass% 4-heptanone. To the left of the eutectic point, in the absence of solid solutions, the base fuel's n-paraffins are expected to be the precipitating component, whereas to the right of the eutectic the 4-heptanone is precipitating. In general, the eutectic point of the mixture shifts towards the lower concentrations of the added compound as the cloud point of the base fuel decreases.

Dibutyl succinate (DBS), a di-ester, in mixtures with the three base fuels (Figure 2.2-Figure 2.4) shows a maximum cloud point that is greater than the cloud point of the base fuel, despite the fact that the melting point temperature of DBS is lower than the three base fuels. Typically, when a compound is added to a fuel, the cloud point temperature of the resulting

mixture is between that of the pure fuel and the melting temperature of the compound for a solid solution, or below the cloud point temperature of the two when the system displays eutectic behavior. The observed maximum in cloud point is attributed to a liquid-liquid phase separation as discussed in detail in section 2.3.4.

This behavior was seen for DBS mixtures with five different base diesel fuels, including three different HAD fuel batches (HAD, HAD*, and HAD+), as shown in Figure 2.5. Fuel distillation and blending can produce products with multiple compositions which all meet specifications, but with different cloud point results [48, 64]. Each of these fuels displayed the same tendency of increased cloud point temperatures with addition of DBS, despite the low melting temperature of DBS. As shown in Figure 2.5, the differences in the cloud points of these three base fuel samples (-27 °C for HAD, -26 °C for HAD+, and -24 °C for HAD*) were reflected as differences in the cloud points of their mixtures with DBS.

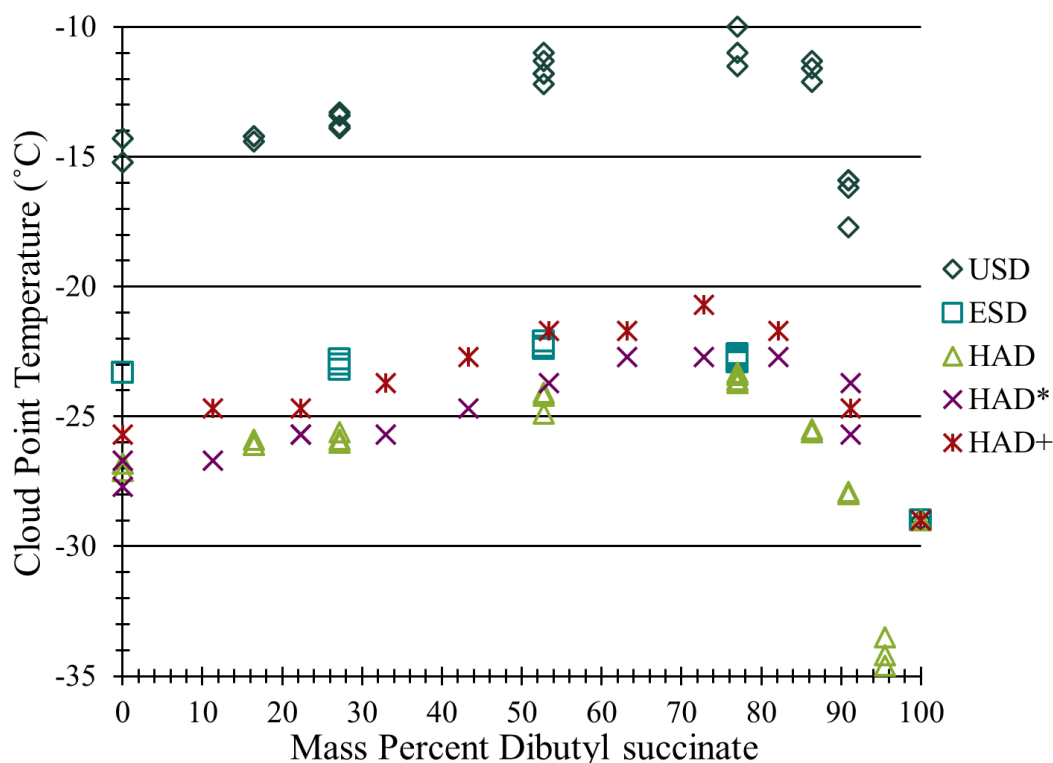


Figure 2.5. Cloud point temperatures for mixtures of various diesel fuels and dibutyl succinate. Differences between HAD, HAD* and HAD+ are described in section 2.1. HAD* and HAD+ measured by ASTM D2500 and shifted as described in the text; all other cloud points were measured by ASTM D7683. The uncertainty in these measurements from ASTM D7683 is ± 1.2 °C and for ASTM D2500 is ± 2.0 °C.

2.3.3 Effect of branching and chain length on cloud point temperature

Figure 2.6 and Figure 2.7 show the cloud points of higher molecular weight esters, ketones, and ethers in mixtures with USD and HAD respectively. With the exception of dihexyl ketone which has a considerably higher melting point temperature than the others, the behavior of the high molecular weight compounds is similar, showing a gradual reduction in cloud point with increasing concentration of the added compound. In Figure 2.6 and Figure 2.7, the eutectic point for the dihexyl ketone system ($T_m = +30$ °C) has shifted almost to the neat base fuel. Because the melting temperature of the ketone is so high, it precipitates at the cloud point instead of fuel paraffins.

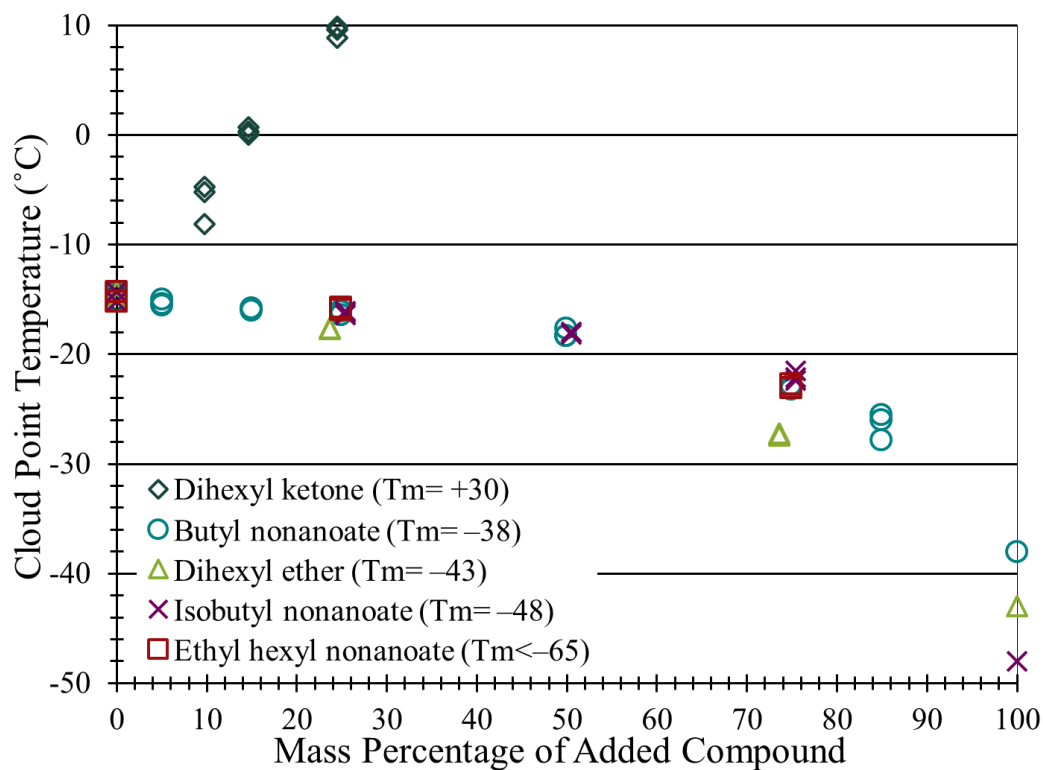


Figure 2.6. Cloud point temperatures for USD in mixtures with high molecular weight compounds. The uncertainty in these measurements is ± 1.2 °C.

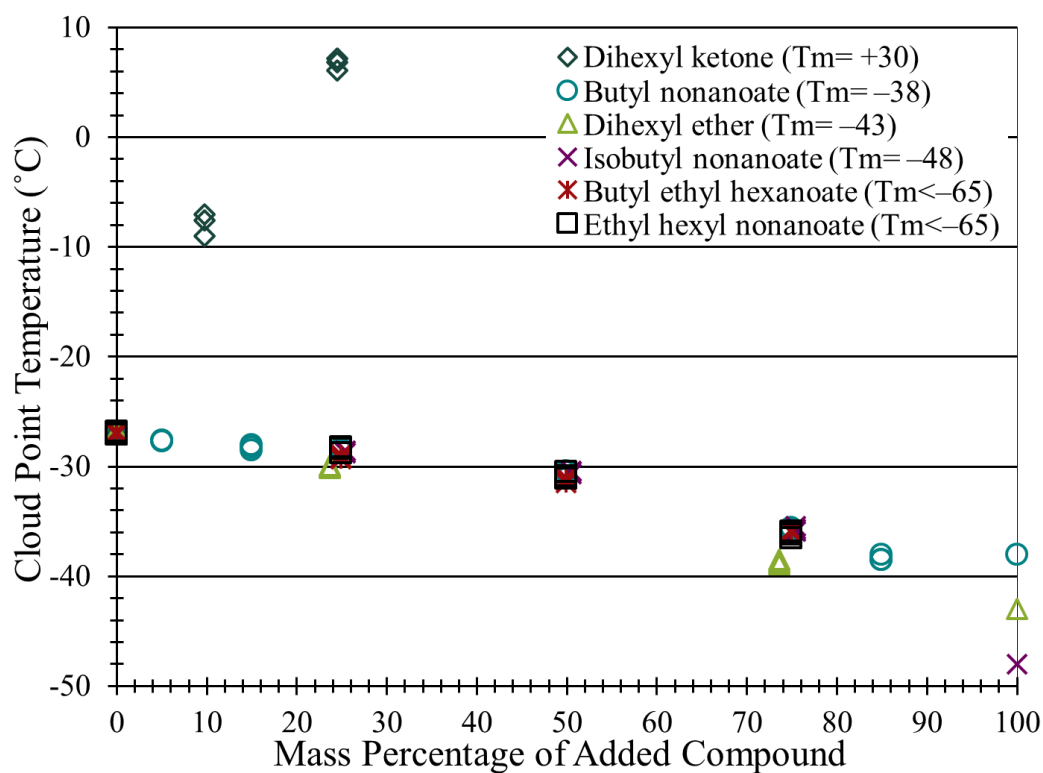


Figure 2.7. Cloud point temperatures for HAD in mixtures with high molecular weight compounds. The uncertainty in these measurements is ± 1.2 °C.

Diisobutyl succinate (DIBS) exhibits behavior almost identical to DBS (Figure 2.2-Figure 2.4), despite a difference of ~ 30 °C in melting temperatures between the succinates. The monoesters (butyl nonanoate, isobutyl nonanoate, butyl ethyl hexanoate, and ethyl hexyl nonanoate) all show very similar cloud point temperatures in mixtures with USD and HAD (Figure 2.6 and Figure 2.7). The cloud point temperature of butyl butyrate in mixtures with USD and HAD (Figure 2.2 and Figure 2.4) are also indistinguishable (within experimental error) from the mixtures with the higher molecular weight esters. The data suggests that the degree of branching and the length of the chain in the alkane side groups have less of an impact on the cloud point than the oxygen-containing functional group.

2.3.4 Dibutyl succinate blends and liquid-liquid phase formation

When DBS or DIBS was added to the base fuel, the measured cloud points of the mixtures at intermediate compositions are higher than the melting temperature of each component and the cloud point of the base fuels. Figure 2.5 shows DBS in mixtures with a variety of base fuels with different properties and hydrocarbon compositions. This elevated cloud point for mixtures is indicative of a liquid-liquid phase separation rather than the normal solid-liquid phase separation expected at a cloud point. The measurement is reported as a cloud point because the liquid-liquid phase behavior creates light scattering. The behavior is different from other cloud point data reported in this study where solids form at the cloud point temperature. Multiple methods were pursued to confirm the existence of two liquid phases.

2.3.4.1 Visual observation

Mixtures were placed in a test tube and allowed to equilibrate in a low temperature bath at varying temperatures to determine the phase behavior for these systems. The HAD, ESD, and USD fuels were mixed with DBS:fuel volume ratios of 50:50 and 25:75. The samples were

cycled from $-10\text{ }^{\circ}\text{C}$ to $-35\text{ }^{\circ}\text{C}$ in $2.5\text{ }^{\circ}\text{C}$ intervals with 2 to 48 hours at each temperature, then warmed to $-10\text{ }^{\circ}\text{C}$ and then cooled again to $-35\text{ }^{\circ}\text{C}$ as before. When equilibrating for 12-24 hours at temperatures lower than the instrument-reported cloud point temperature, the mixtures separated into two liquid phases, with a cloudy phase on top and clear phase below (Figure 2.8a). The phases had similar densities and required long settling times for complete phase separation. This two-phase behavior was highly temperature-dependent; when removed from the bath, the phases homogenized within 10-15 seconds starting from the outside edges of the test tube (Figure 2.8b). As the equilibrium temperature was decreased, the upper cloudy phase became more opaque and increased in volume (Figure 2.8c) with each step until the entire test tube volume was a single cloudy phase. Once the entire solution was cloudy, the solution gelled and then solidified within an additional $5\text{ }^{\circ}\text{C}$ cooling as the temperature decrease continued.

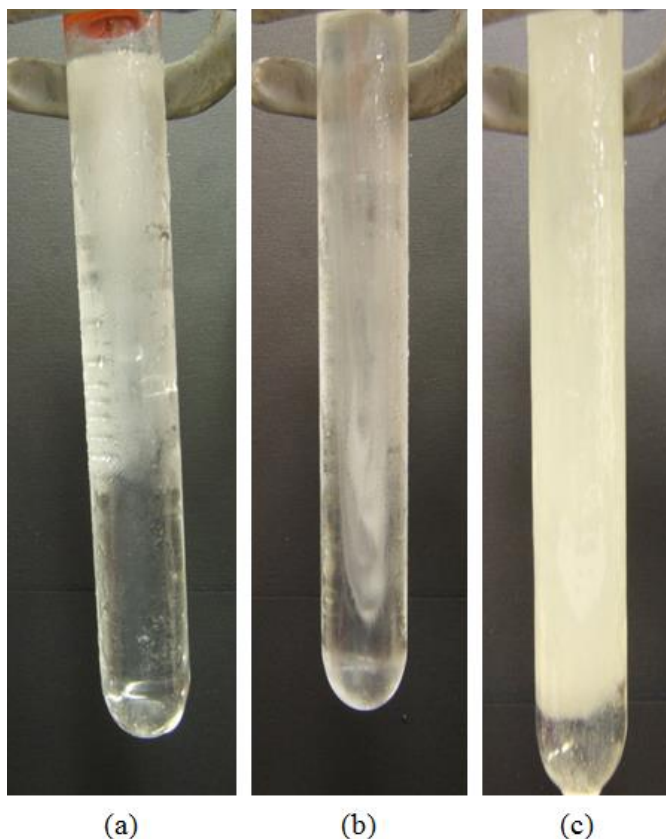


Figure 2.8. Liquid-liquid phase separation in mixtures of diesel fuel and DBS, initially at -25°C . (a) 75% DBS and 25% HAD. (b) 75% DBS and 25% HAD, 10 seconds after picture (a) was taken. (c) 75% DBS and 25% HAD.

2.3.4.2 Testing a system with a known liquid-liquid phase separation

Dimethyl succinate in n-heptane, a mixture that exhibits a known liquid-liquid phase separation [65], was tested to experimentally demonstrate that the cloud point instrument could detect a liquid-liquid separation as a cloud point. The phase envelope [65] was determined by placing samples in a bath and chilling or heating the well-stirred sample at a rate of 0.1 °C/min. The experimental data shown in Figure 2.9 are in good agreement with the data of Manzini and Crescenzi [65], but exhibit some scatter, which is attributed to the faster cooling rate (1.0 °C/min) and lack of stirring in the cloud point instrument used in the present study. Overall, the similarity in behavior demonstrates that the cloud point instrument used in this study can identify a liquid-liquid phase separation and report it as a cloud point.

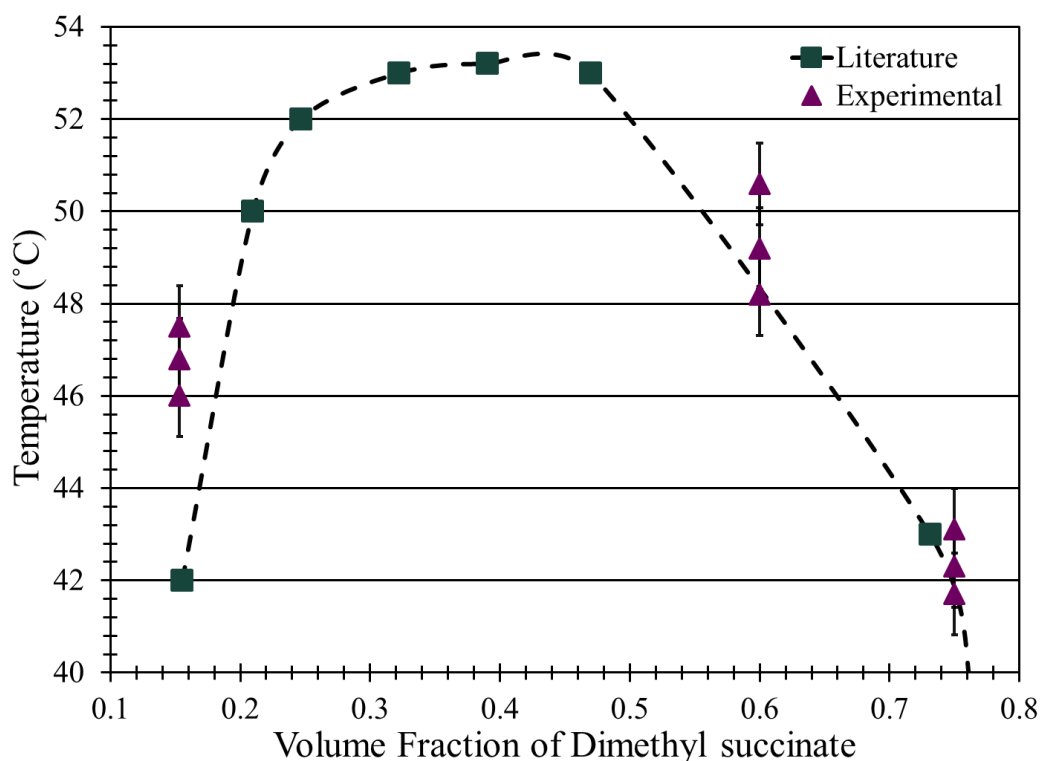


Figure 2.9. Comparison of cloud point experimental data and literature data [65] for dimethyl succinate in n-heptane.

2.3.4.3 Comparison of cloud point and cold filter plugging point temperatures

When canola oil FAME was mixed with the base diesel fuel, both the cloud point and CFPP increased (Figure 2.10a), consistent with the cloud point of canola oil FAME being higher than the cloud point of the diesel fuel. When butyl nonanoate (having a lower melting point) was added, the opposite trend was observed (Figure 2.10b). In the case of canola oil FAME-diesel fuel blend, a component of the FAME precipitated at the cloud point rather than the paraffins present in the diesel fuel because the melting temperatures for saturated FAME components (in the range of 30-38 °C) are very high compared to the base diesel fuel. For butyl nonanoate, the cloud point and CFPP decreased because the paraffins in the diesel precipitate on cooling, and were diluted by the added compound. When DBS was added to the same fuel, however, the cloud point increased (Figure 2.10c), but the CFPP remained approximately constant over the entire concentration range. This data supports the hypothesis that the instrument-detected cloud point for these DBS-diesel mixtures was actually a liquid-liquid phase separation.

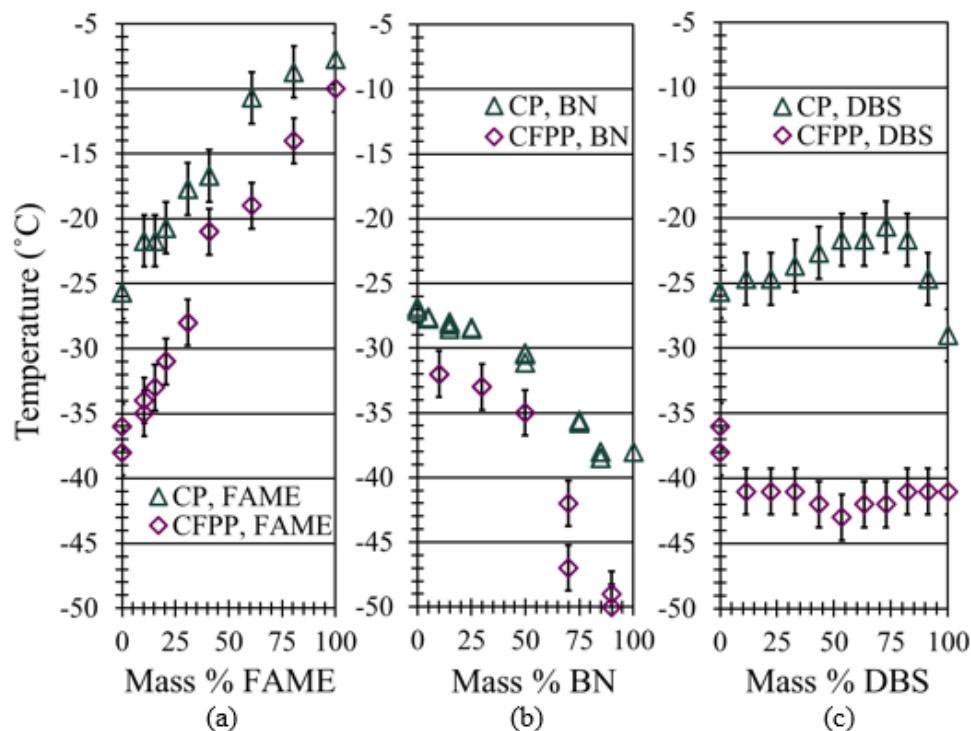


Figure 2.10. Cloud point (CP) and cold filter plug point (CFPP) temperatures for HAD in mixtures with: (a) fatty acid methyl esters (FAME) of Canola oil; (b) dibutyl succinate (DBS); and (c) butyl nonanoate (BN). CP, BN measured by ASTM D7683 (uncertainty = ± 1.2 °C); CP, FAMES and CP, DBS measured by ASTM D2500 and shifted as described in the text.

2.3.5 Discussion summary

Compounds with melting point temperatures lower than the petroleum fuel to which they were added generally decreased the cloud point temperature of the mixtures by dilution of the relatively high-melting temperature paraffins in the fuel. Addition of lower molecular weight compounds resulted in cloud point depressions that were dependent on functionality. Cloud point depressions at a given weight percent increased in the following order: ketone < ester < ether < small alkane. When the molecular weight of the added compound was greater, all behaved similarly. When the melting temperature of the added compound was similar to or higher than the cloud point of the base fuel, eutectic behavior sometimes interfered with the precipitation of the paraffins and/or the added compound precipitated instead. Diesters exhibited liquid-liquid

phase immiscibility and the cloud points of their mixtures with these diesel fuels were higher than both the cloud point of the neat diesel fuel and the melting point of the diester.

2.4 Conclusions

Potential biofuel compounds have been studied in blends with petroleum diesel and jet fuels to increase understanding of blend behavior. For mixtures of diesel fuels and diesters, the diester functionality caused liquid-liquid immiscibility over the small range of carbon chain length tested here. When diesel fuels were mixed with compounds of low molecular weight, the oxygen moieties present had more effect on miscibility than the degree of branching of the carbon chains. Functional groups in order from most effective to least effective at decreasing cloud point were alkanes, ethers, esters, ketones, and diesters. Higher molecular weight compounds exhibited more consistent effects, despite up to 60 °C differences in melting temperatures, over the composition range until the eutectic temperature was encountered.

CHAPTER 3

Physical Property Prediction Methods for Fuels and Fuel Components

3.1 Introduction

The diversity of the molecules used as second generation biofuels is continually expanding. Second generation biofuels are often defined as biofuels made from non-food feedstocks. This classification includes ethanol from corn stover and other lignocellulosic sources, Fischer-Tropsch hydrocarbons from wood, and butanol or mixed alcohols from renewable sources [10]. In addition, fuel quality can be improved by blending or reacting these fuels to produce fuels with more desirable qualities [11, 12]. These processes create molecules with a wide variety of functional groups and oxygen content, and can usually be tailored to produce a specific molecule type.

In order to streamline the production of these fuels, and to identify which types of molecules would be desirable as fuels, evaluations of the molecule's physical properties such as freezing point, vapor pressure, and density are needed. Often, these molecules are fairly new to large scale production, and as such have limited physical property data. Testing of these properties at a number of temperatures and pressures can be time and resource consuming, especially when there are multiple potential biomolecules. Thermodynamic property evaluation can be used to extrapolate property data from a limited experimental data [13]. Then, these properties can be used to predict the behavior of the new biomolecules in mixtures with traditional fuels.

This chapter will apply predictive methods for fuel components. Section 3.2 discusses the method for the prediction of the properties of dibutyl succinate, as well as the extension of the properties for other fuel surrogate components to the critical point. Second 3.2.2 discusses gas phase properties, while section 3.2.3 discusses liquid phase and critical properties.

3.2 Property development and extension

3.2.1 Overview

Collaborators at Ford Motor Company requested properties to be used in predicting combustion and spray formation of alternative fuels. Property data was requested for dibutyl succinate (DBS), methyl oleate, methyl stearate, cetane, 2,2,4,4,6,8,8-heptamethylnonane (HMN), and tripropylene glycol monomethyl ether (TGME). Heptamethylnonane is used in mixtures with cetane to create the scale used for determination of cetane numbers in diesel fuels. Ideal gas phase heat capacity, enthalpy, and entropy were requested in the temperature range of 300-5,000 K, and fitted based on a 4th degree heat capacity polynomial equation for all compounds. Liquid phase viscosity, surface tension, heat of vaporization, vapor pressure, thermal conductivity, density, and heat capacity data were requested from 0 K to the critical point for each compound.

For methyl oleate, methyl stearate, cetane, HMN, and TGME, data was available for all liquid phase properties in the DIPPR database [54]. DBS has very limited literature data and is not included in the DIPPR database. Reaxys was used to find additional literature data for DBS [66]. The properties available in the literature were either experimental or predicted values, or some combination thereof. Table 3.1 details which properties are experimental and predicted, and the source for each property. For the liquid phase, the properties are given for the temperature range that is given in DIPPR. If the data did not go all the way to the critical temperature, it was because there either was no experimental data in that range, or the predictive equations used are not valid above the temperature given. In these cases, properties were extended to the critical point using the same prediction methods as those for DBS. In addition,

gas phase data for heat capacity for these compounds was available up to ~1200 K. Quantum calculations from Gaussian [67] extended the gas phase heat capacity to the requested 5000 K.

Table 3.1. Availability of literature data for the requested properties. Abbreviations: x – no data available in the literature. M – measured in our lab at ambient temperature and pressure. D – data available through DIPPR database [54]. P – data available from a predicted method. E – data available from experimental methods. R – data available through Reaxys [66]. #T – number of temperature points available. RT – range of temperature points available. CT – critical temperature.

	Dibutyl succinate	Methyl Oleate	Methyl Stearate	Cetane	2,2,4,4,6,8,8-Heptamethylnonane	Tripropylene glycol monomethyl ether
Gas phase Cp	x	D - P	D - P	D - P	D - P	D - P
Gas phase H	x	x	x	x	x	x
Gas phase S	x	x	x	x	x	x
Viscosity	x	D - E	D - E	D - E	D - E	D - P
Surface Tension	R - RT	D - E&P	D - E	D - E	D - E&P	D - E&P
Heat of Vaporization	R - 2T	D - P	D - P	D - E&P	D - P	D - P
Vapor pressure	R - RT	D - E&P	D - E	D - E	D - E&P	D - E&P
Thermal Conductivity	x	D - P	D - P	D - E	D - P	D - E&P
Density	M	D - E	D - E	D - E&P	D - E	D - E
Liquid heat capacity	x	D - P	D - E	D - E&P	D - P	D - P

3.2.2 Gas phase properties

For the high temperature ideal gas heat capacity data, Gaussian was used [67]. The structure of each molecule was minimized using the BY3LP method and the 6-31G(d) basis set. Then the minimum energy structure was used to find the frequencies and thermochemical properties. The equation to calculate the statistical-mechanical heat capacity for a linear molecule [68] is

$$C_V = C_t + C_r + C_v = \frac{5}{2}R + R \sum_K e^{\theta_{v,K}/T} \left(\frac{\theta_{v,K}/T}{e^{\theta_{v,K}/T} - 1} \right)^2 \quad (3.1)$$

where C_V is the total constant volume heat capacity (J/kg), C_t is the translational contribution to the heat capacity (J/kg), C_r is the rotational contribution to the heat capacity (J/kg), C_v is the vibrational contribution to the heat capacity (J/kg), R is the ideal gas constant (J/kg K), K is the number of vibrational modes, $\theta_{v,k}$ is the characteristic vibrational temperature (K), and T is the

temperature of the system (K). For equation (3.1), the value of $^{5/2}$ is replaced with 3 for a non-linear molecule.

The relationship between C_V (constant volume heat capacity) and C_P (constant pressure heat capacity) for an ideal gas is $C_P = C_V + R$. The built-in Gaussian utility “freqchk” was used to calculate heat capacity values at multiple temperatures. The deviations in the overlapping region between the low temperature DIPPR data and the high temperature Gaussian was less than 5% for all molecules. The Gaussian data could be scaled to allow for a better alignment.

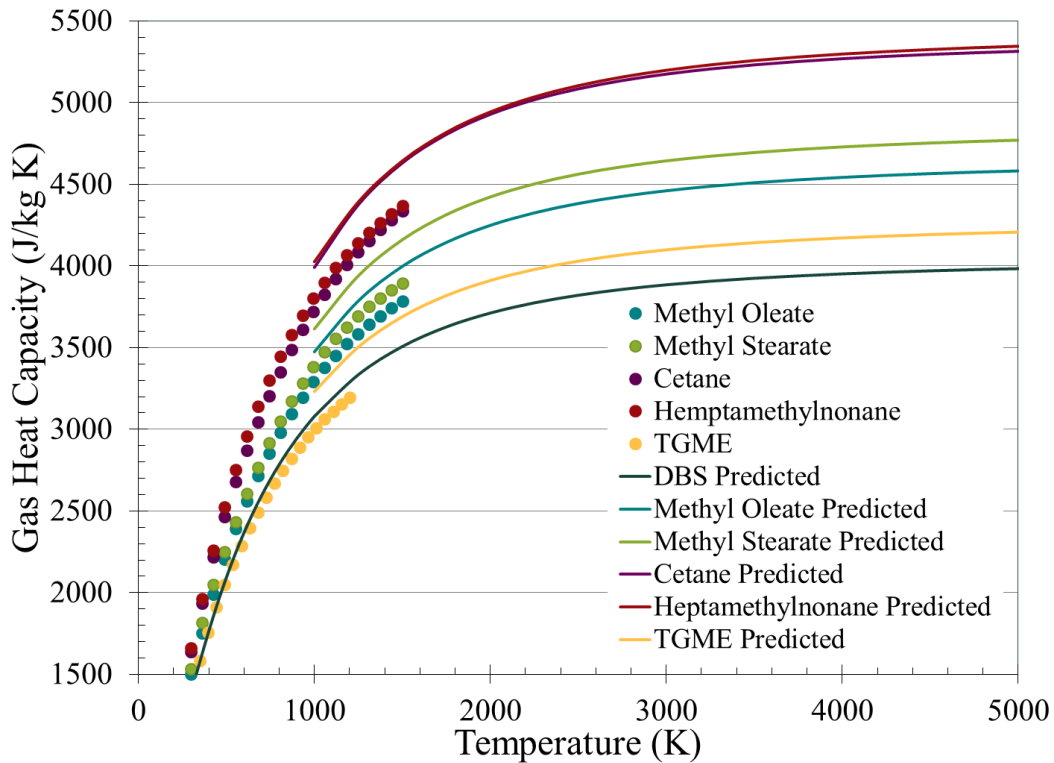


Figure 3.1. Gas phase heat capacity for all molecules. DIPPR data is shown as points, Gaussian predictions are shown as lines.

Entropy and enthalpy constants were found using their standard relationship to heat capacity [69]. The heat capacity values were fitted to the following equation:

$$\frac{C_P}{R} = A_1 + A_2T + A_3T^2 + A_4T^3 + A_5T^4 \quad (3.2)$$

where C_P is the constant pressure heat capacity (J/kg K) and A_{1-5} are the fitted constants.

Ideal gas enthalpy was calculated relative to 298.15 K. The equation for enthalpy:

$$\frac{H}{RT} = \frac{1}{T} \int_{T_{ref}}^T C_p dT = A_1 + \frac{A_2}{2} T + \frac{A_3}{3} T^2 + \frac{A_4}{4} T^3 + \frac{A_5}{5} T^4 + \frac{A_6}{T} \quad (3.3)$$

$$A_6 = -A_1 T_{ref} - \frac{A_2}{2} T_{ref}^2 - \frac{A_3}{3} T_{ref}^3 - \frac{A_4}{4} T_{ref}^4 - \frac{A_5}{5} T_{ref}^5 \quad (3.4)$$

where H is the enthalpy (J/kg), A_{1-5} are the same constants as equation (3.2). T_{ref} is the reference temperature (298.15 K), A_6 is the integration constant, which has the form shown in equation (3.4).

Ideal gas entropy is also calculated using a reference state of 298.15 K. The equation for entropy:

$$\frac{S}{R} = \int_{T_{ref}}^T \frac{C_p}{T} dT = A_1 \ln T + A_2 T + \frac{A_3}{2} T^2 + \frac{A_4}{3} T^3 + \frac{A_5}{4} T^4 + A_7 \quad (3.5)$$

$$A_7 = -A_1 \ln T_{ref} - A_2 T_{ref} - \frac{A_3}{2} T_{ref}^2 - \frac{A_4}{3} T_{ref}^3 - \frac{A_5}{4} T_{ref}^4 \quad (3.6)$$

where S is the entropy (J/kgK), and A_7 is the integration constant with the form shown in equation (3.6).

3.2.3 Liquid phase properties

Very few property data are available for DBS in the literature. Data for a small range of temperatures was found for liquid phase heat of vaporization, surface tension, and vapor pressure. Density was also measured at one temperature, with an experimental error of less than 1%. Group contribution methods were used to find data for all liquid phase properties. When literature values were available, they were compared to the group contribution method to estimate the percent error in the estimation method. Data was also not available for all compounds for viscosity, liquid heat capacity, and thermal conductivity all the way to the critical point. The same methods that are described below are used to extend these properties to the critical point.

Critical properties for DBS were estimated using the method of Constantinou and Gani [13]. For all the other compounds, the values presented in the DIPPR database are used [54]. This is a group contribution method with errors generally <10%. While the acentric factor is not a critical property, it is included in this section because the same method was used. The critical temperature for DBS was found to be 715.4 K, the critical pressure 17.7 bar, the critical volume 753 cm³/mol, and the acentric factor 0.8179. The equations for each property are:

$$T_C = 181.128 \ln \left[\sum_k N_k(tc1k) + W \sum_j M_j(tc2j) \right] \quad (3.7)$$

where T_C is the critical temperature (K), k is the type of first order component, N_k is the number of k -type first order components, $tc1k$ is the first order constant, W is set to 0 for first order only calculations, and 1 to include second order calculations, j is the type of second order component, and $tc2j$ is the second order constant.

$$P_C = \left[\sum_k N_k(pc1k) + W \sum_j M_j(pc2j) + 0.10022 \right]^{-2} + 1.3705 \quad (3.8)$$

where P_C is the critical pressure (bar), $pc1k$ is the first order constant, and $pc2j$ is the second order constant.

$$V_C = -0.00435 + \left[\sum_k N_k(vc1k) + W \sum_j M_j(vc2j) \right] \quad (3.9)$$

where V_C is the critical volume (cm³/mol), $vc1k$ is the first order constant, and $vc2j$ is the second order constant.

$$\omega = 0.4085 \left\{ \ln \left[\sum_k N_k(w1k) + W \sum_j M_j(w2j) + 1.1507 \right] \right\}^{1/0.5050} \quad (3.10)$$

where ω is the acentric factor, $w1k$ is the first order constant, and $w2j$ is the second order constant.

The Brock and Bird method [13] was used to calculate surface tension. This method can give higher errors for polar molecules than for non-polar. Comparison of the predicted values to the experimental data from the literature shows an approximate error of $\sim 3\%$ for DBS. The trend and shape of the predicted data also matches the trends for the experimental data for the other molecules (Figure 3.2).

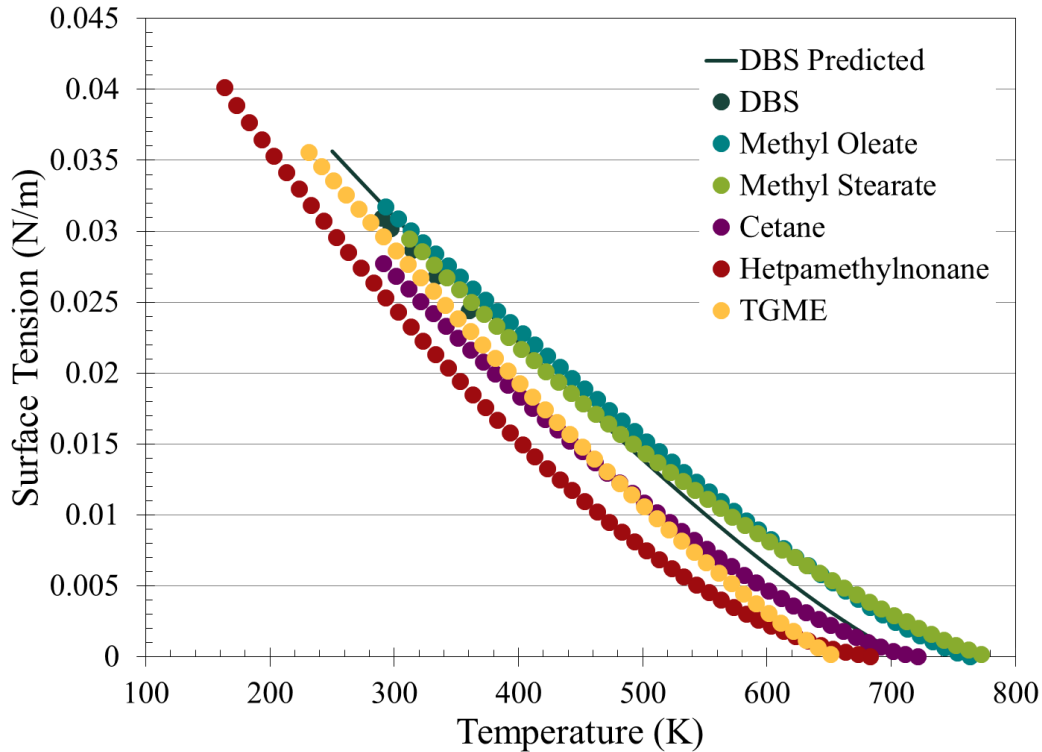


Figure 3.2. Surface tension for all molecules. DIPPR [54] data is shown as points, and predicted values are shown as lines.

The correlation is:

$$\sigma = P_C^{2/3} T_C^{1/3} (0.132\alpha_c - 0.279)(1 - T_r)^{11/9} \quad (3.11)$$

$$\alpha_c = 0.9076 \left[1 + \frac{T_{br} \ln(P_C/1.01325)}{1 - T_{br}} \right] \quad (3.12)$$

where σ is the surface tension (dyn/cm), T_r is the reduced temperature (T/T_c), and T_{br} is the reduced boiling temperature (T_b/T_c).

Viscosity was calculated using the Orrick and Erbar [13] method. For monoesters, the deviation between the predicted values and the literature show an approximate error of 15%. The prediction values for the highly branched compounds deviate more from experimental data than the components with linear chains (Figure 3.3).

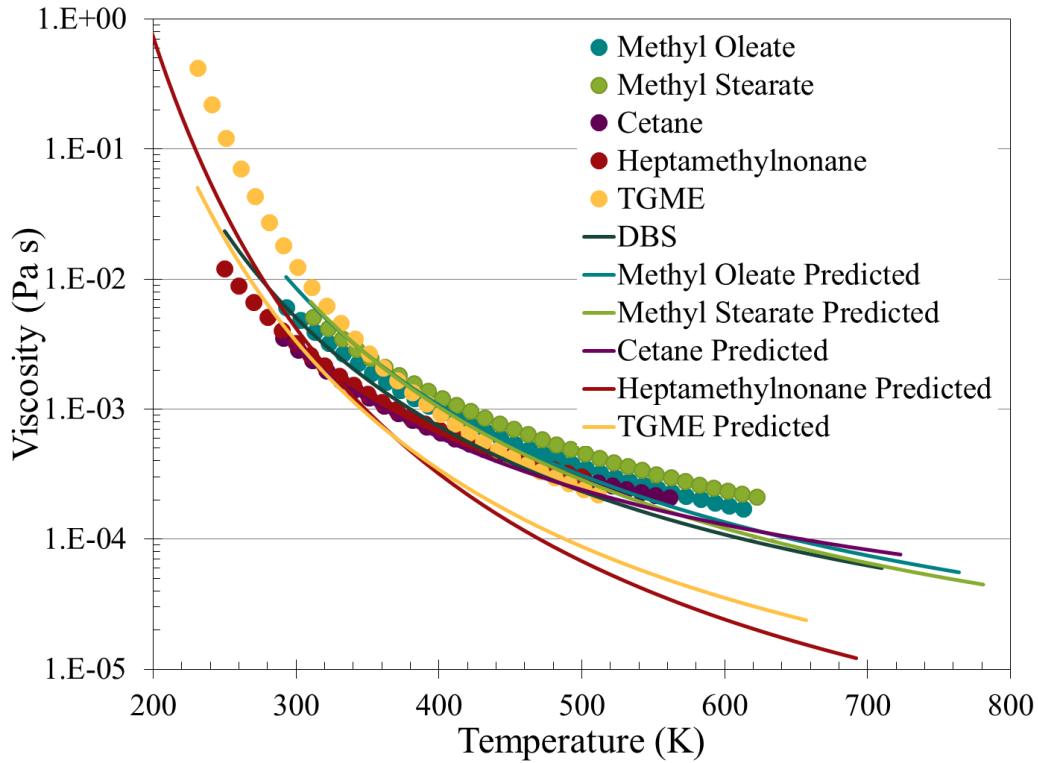


Figure 3.3. Viscosity for all molecules. DIPPR [54] data is shown as points, and predicted values are shown as lines.

The equation for viscosity is:

$$\eta_L = \rho_L M e^{A + \frac{B}{T}} \quad (3.13)$$

where η_L is the liquid phase viscosity (cP), ρ_L is the liquid phase density at 20 °C (g/cm³), M is the molecular weight (g/mol), and A and B are constants based off of group contribution constants.

The Watson relation was used to calculate the heat of vaporization, with an approximate error of 10%. The predictions for DBS again match the shape and trend of the experimental data (Figure 3.4).

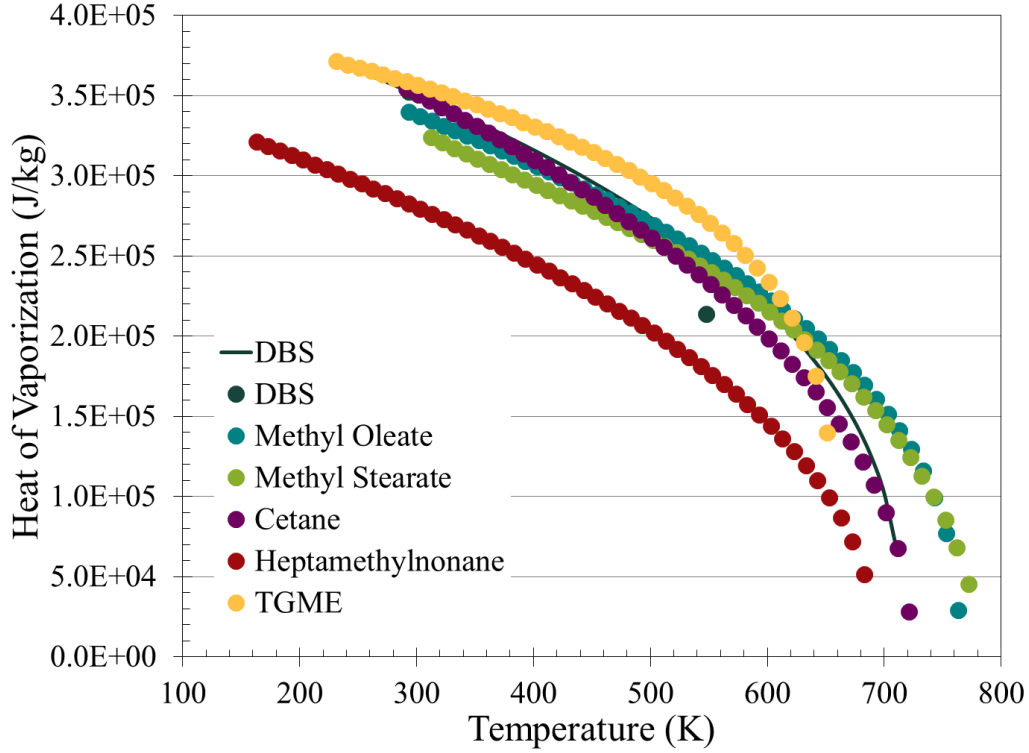


Figure 3.4. Heat of vaporization for all molecules. DIPPR [54] data is shown as points, and predicted values are shown as lines.

There were two data points in the literature for DBS. The first is used as the reference point for the relation below, and the second used to evaluate the error. The relation is:

$$\Delta H_{v,2} = \Delta H_{v,1} \left(\frac{1 - T_{r,2}}{1 - T_{r,1}} \right)^n \quad (3.14)$$

where $\Delta H_{v,2}$ is the heat of vaporization at temperature 2, $\Delta H_{v,1}$ is the heat of vaporization at temperature 1 (the reference temperature), $T_{r,2}$ is the reduced temperature 2, $T_{r,1}$ is the reduced temperature 1, and n is a constant (0.375).

A shortcut estimation was used to find the vapor pressure [69], because no data was available for the heat of vaporization, so the Clausius-Clapeyron equation could not be used. The

shortcut method assumes there is a linear relationship between the natural log of the vapor pressure and the inverse of the temperature, at low temperatures. The available data has that linear trend, but the model is only a good approximation when the reduced temperature is greater than 0.5 and the vapor pressure is greater than 2 bar or 200,000 Pa. The accuracy of the correlation also depends upon prediction of the critical conditions and the acentric factor. The literature data is outside these limits, and the predictions exhibit an error of 30-300% for DBS in the low pressure range (Figure 3.5).

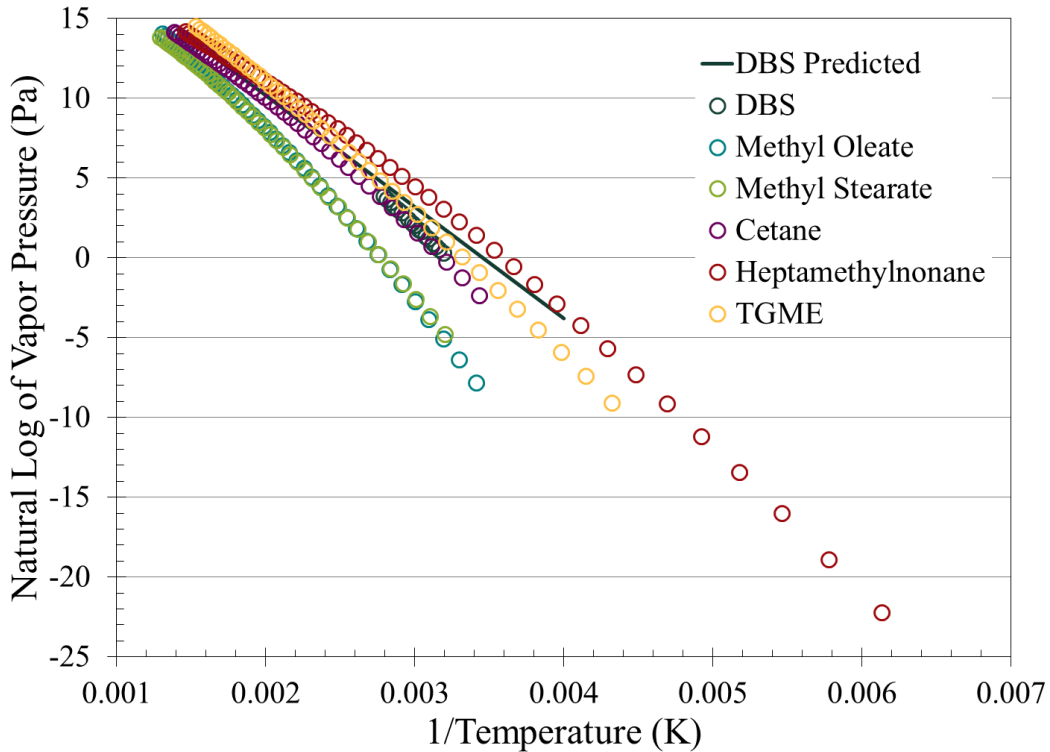


Figure 3.5. Vapor pressure for all molecules. DIPPR [54] data is shown as points, and predicted values are shown as lines.

The relation is:

$$\log_{10} P_r^{sat} = \frac{7}{3}(\omega + 1) \left(1 - \frac{1}{T_r}\right) \quad (3.15)$$

where P_r^{sat} is the reduced vapor pressure (P^{sat}/P_C).

The modified Rackett equation was used to estimate the liquid phase density [13]. Because one density was measured, this density could be used as a reference point. The equation gives the density as the molar volume, which has units of cm^3/mol . To get density in the same units as the literature data, the inverse of the molar volume is taken, and converted from moles to mass. The literature indicates the error in this method to be generally less than 1%, but no compounds from their set were as large as DBS, so the error could be larger. The shape and trend of the DBS curve matches the trend of the literature data, however (Figure 3.6).

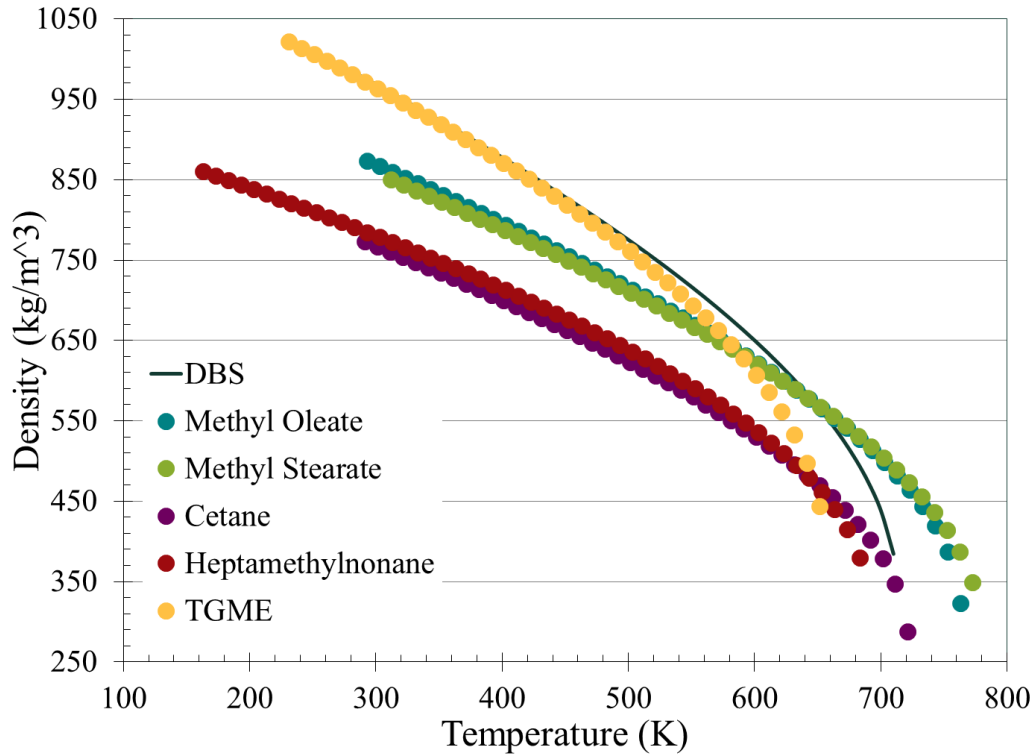


Figure 3.6. Density for all molecules. DIPPR [54] data is shown as points, and predicted values are shown as lines.

The Rackett equation is:

$$V_s = V_s^{ref} (0.29056 - 0.08775\omega)^\phi \quad (3.16)$$

$$\phi = \left(1 - \frac{T}{T_c}\right)^{2/7} - \left(1 - \frac{T_{ref}}{T_c}\right)^{2/7} \quad (3.17)$$

where V_s is the molar volume at the specified temperature (cm^3/mol), and V_s^{ref} is the molar volume at T_{ref} .

A modified Bondi method [13] was used for the liquid phase heat capacity. This method is good for liquids which do not associate, and is better for larger molecules. An estimated error would be <5% based on alcohols and monoesters found in the literature. However, the HMN shows errors of ~12% at higher temperatures, while the other molecules have errors less than 5%. The shapes of the curves are also consistent with the literature data (Figure 3.7).

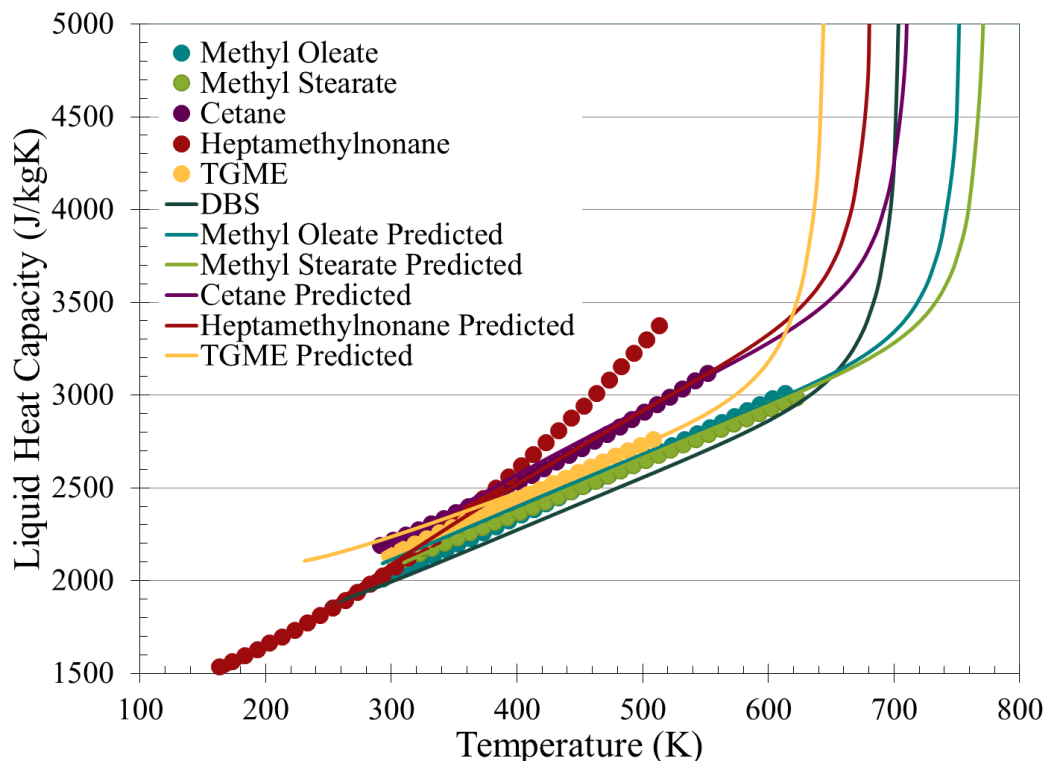


Figure 3.7. Liquid phase heat capacity for all molecules. DIPPR [54] data is shown as points, and predicted values are shown as lines.

The Bondi method is:

$$\frac{C_P - C_P^\circ}{R} = 1.586 + \frac{0.49}{1 - T_r} + \omega \left[4.2775 + \frac{6.3(1 - T_r)^{1/3}}{T_r} + \frac{0.4355}{1 - T_r} \right] \quad (3.18)$$

where C_P° is the ideal gas heat capacity at the calculation temperature.

Thermal conductivity was estimated using both the Latini method and the Sastri method [13]. According to the literature, both methods can have errors as high as 15% for organic molecules. For methyl oleate and cetane, the Latini method and the DIPPR data are in good

agreement. For methyl stearate, HMN, and TGME, there is considerable uncertainty in the predictions from DIPPR, and neither estimation method provides good agreement. For methyl stearate, the Latini and Sastri methods bracket the DIPPR prediction (Figure 3.8). The Sastri method is closer to the DIPPR prediction for HMN, but is still outside DIPPR's uncertainty (Figure 3.9). For TGME, the Latini method is within DIPPR's stated uncertainty (Figure 3.10).

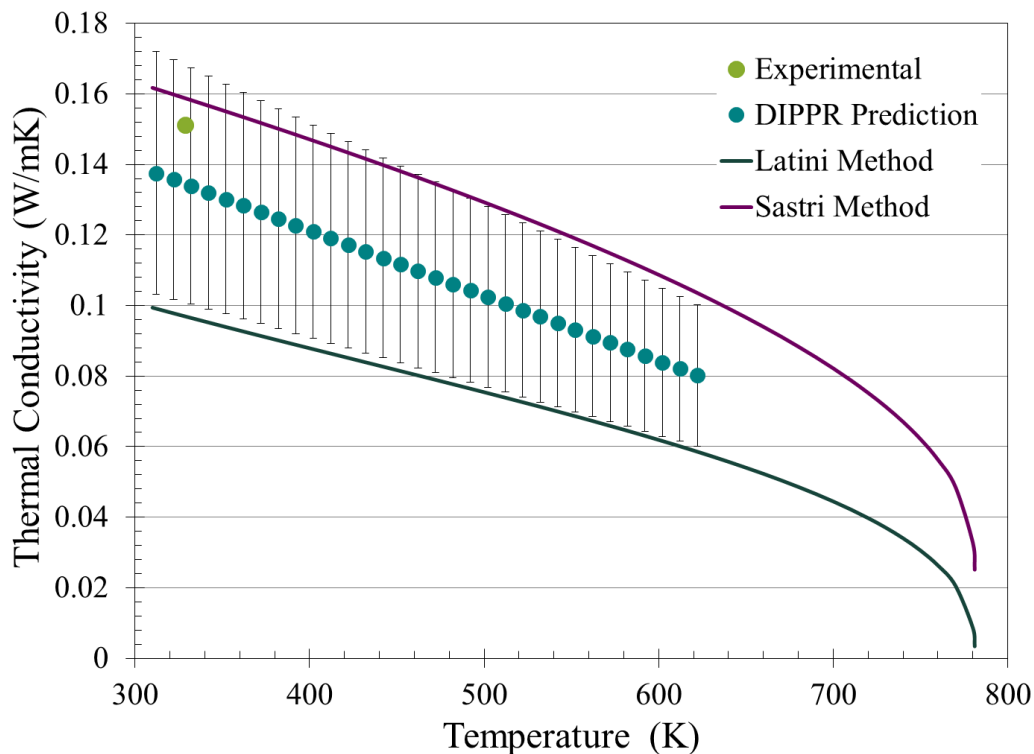


Figure 3.8. Thermal conductivity prediction using two methods, and comparison to the DIPPR [54] values for methyl stearate.

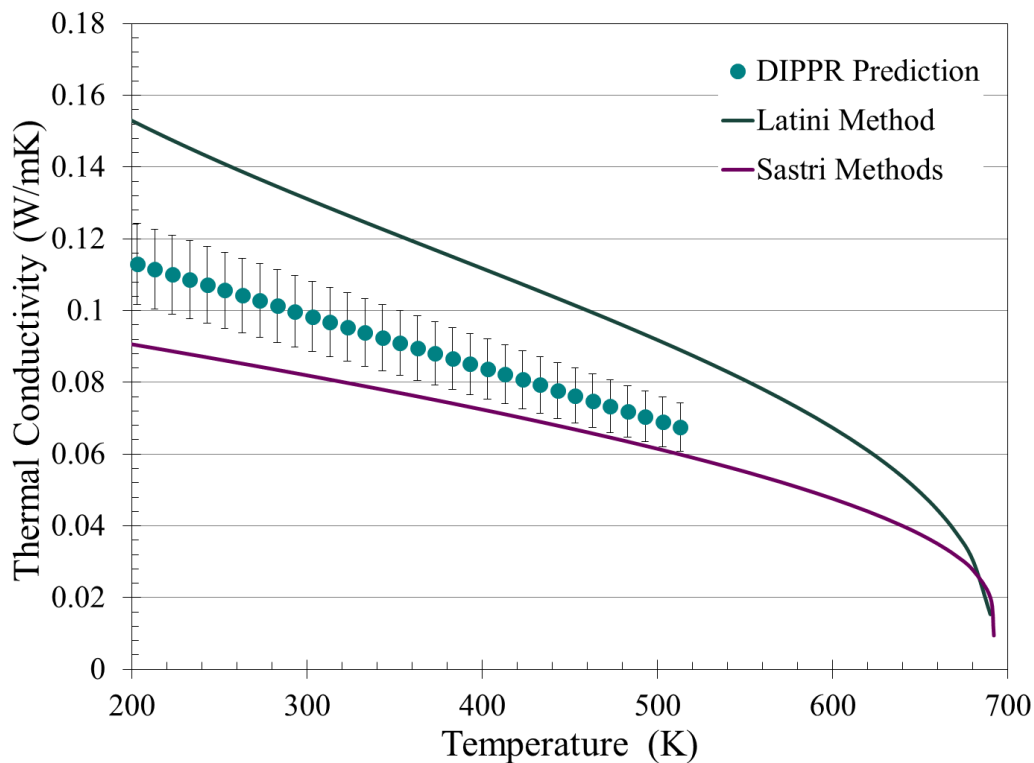


Figure 3.9. Thermal conductivity prediction using two methods, and comparison to the DIPPR [54] values for heptamethylnonane.

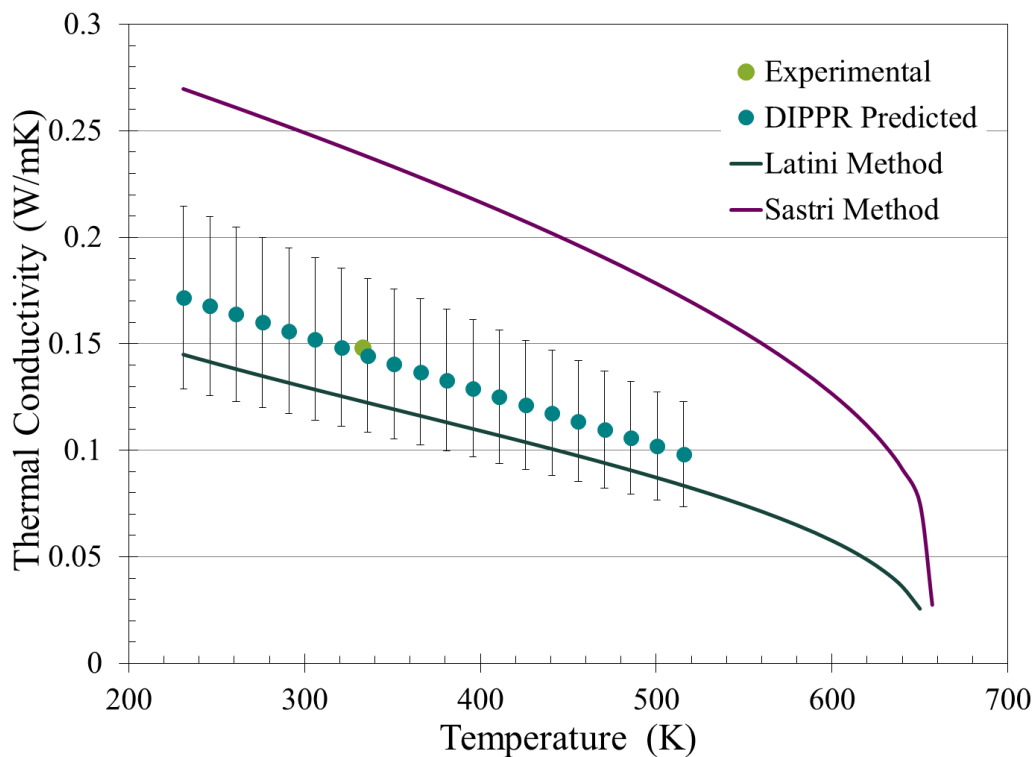


Figure 3.10. Thermal conductivity prediction using two methods, and comparison to the DIPPR [54] values for TGME.

There is significant uncertainty inherent in the prediction of the thermal conductivity, so the uncertainty could be as high as 30%. The values shown in Figure 3.11 were found using the prediction method that was closest to the experimental values. Again, the errors for the highly branched compounds were worse than the linear compounds (Figure 3.11).

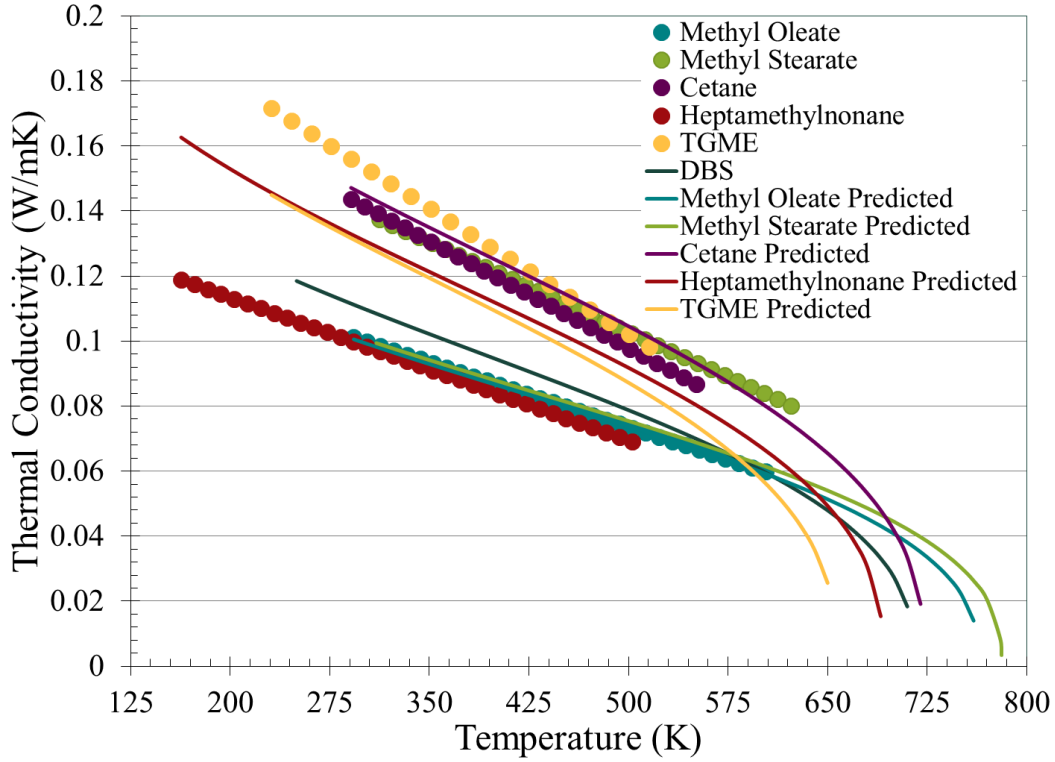


Figure 3.11. Thermal conductivity for all molecules. DIPPR [54] data is shown as points, and predicted values are shown as lines.

The Latini method is:

$$\lambda_L = \frac{A(1 - T_r)^{0.38}}{T_r^{1/6}} \quad (3.19)$$

$$A = \frac{A^* T_b^\alpha}{M^\beta T_c^\gamma} \quad (3.20)$$

where λ_L is the liquid phase thermal conductivity (W/m K), T_b is the normal boiling point (K), and A^* , α , β , γ are all group contribution constants.

The Sastri method is:

$$\lambda_L = \lambda_b a^m \quad (3.21)$$

$$m = 1 - \left(\frac{1 - T_r}{1 - T_{br}} \right)^n \quad (3.22)$$

where λ_b is the thermal conductivity at the normal boiling point (determined by group contribution methods), a is a structure dependent constant (0.16), and n is a structure dependent constant (0.2).

3.3 Summary

Multiple methods were used to predict the physical properties of various molecules for use in fuel modeling. Most of the compounds evaluated had substantial literature data and only needed extending of the data to the critical point. DBS has very limited literature data available, and more extensive methods were required to predict its properties, including critical properties. Properties were estimated for the linear and monoester compounds with errors of less than 15%. Branched and diester compounds had larger errors, usually of less than 30%.

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CHAPTER 4

Development of an Adaptable and Widely Applicable Fuel Surrogate

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4.1 Introduction

A wide variety of different alternative fuels are currently being produced. These can range in composition from esters from oils and fats to paraffins and isoparaffins from Fischer-Tropsch synthesis. These processes create molecules with a wide variety of functional groups and oxygen content, and usually are tailored to produce specific molecules. Often, these molecules are fairly new to large scale production and characterization, and thus physical property data are limited. Because of the wide variety of possible fuel components, physical testing of every possible blend of new molecules would be labor and cost intensive. Creating models for the physical properties of these biofuels in mixtures with traditional fuels would allow for potential biofuel components to be identified without large production batches or extensive testing.

It is uncommon to both identify and quantify all the components in a traditional fuel, making rigorous computer modeling of these fuels difficult [70]. Instead, petroleum fuels are represented with either surrogate mixtures or pseudocomponents. A fuel surrogate uses a limited number of compounds with known physical properties that when mixed approximate the properties of the target fuel. The pseudocomponent method differs from the surrogate method in that the components used to make up the surrogate are not real compounds. They are instead theoretical compounds which are given properties to meet the desired results. The surrogate method is used here because it more closely relates to the real fuel by using real components.

The methods for designing a surrogate can vary depending on the type of property that will be predicted and the model used to perform the predictions [14, 15, 17-21, 23-31]. Most surrogates are designed to match one or two related fuel properties, such as boiling curve and viscosity [14, 15], cloud point [17-21], spray formation [23], combustion kinetics [24], or cetane

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number [25-32]. Cetane number is required to be reported for jet fuels, but does not need to meet a certain value. Due to the one fuel for the battlefield program, JP-8 is being used in diesel engines as well [33-35], thus the cetane value is important in the field. When surrogates are used to model a property for which they weren't designed, they give very inaccurate results, with errors usually in the range of 150-250%. For example, a diesel fuel surrogate with a focus on cetane number and combustion was developed by adjusting the ratio of cetane to methyl naphthalene until the cetane number was correct [24]. This surrogate, however, gives a cloud point temperature of -38 °C, when the actual temperature is -12 °C.

Surrogates are developed using a variety of methods for the selection of surrogate components and compositions. In some cases, components are picked from a database guided by a small amount of compositional information until the property is matched [14, 15]. Other surrogates use partial compositional data for the paraffin content and use physical prediction methods but only use one or two components to represent the remainder of the fuel [17]. The method of property prediction can also impact the surrogate design. For cloud point modeling, some surrogates use a solid solution model [17, 18, 20] or a pure solid model [19], while others use a sequential precipitation technique [21]. For cetane number surrogates, either compositional data is used [25, 26] or components of the fuel spectrum are fit to an empirical equation [27-31].

This work combines established methods to develop a surrogate which correctly predicts multiple fuel properties simultaneously. Physical property calculations are combined with empirical adjustment of certain component concentrations to optimize a surrogate composition. Both low and high temperature properties are used for fitting. A single JP-8 fuel as well as two fuel groups were assessed at different times during research. The first group, Group A, are diesel fuels: a high aromatic diesel (HAD), and a US standard diesel (USD). The second group, Group

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B, is made up of alternative jet fuels. Group A fuels were tested with GC-MS to determine paraffin content and HPLC for aromatic content. Group B fuel surrogate design was guided by GCxGC testing. The same JP-8 fuel has been tested with both Group A and Group B methods and JP-8 surrogates were developed based on compositions for each test. The resulting two JP-8 surrogates developed in this work are extremely similar.

4.2 Materials and Methods

4.2.1 Materials

4.2.1.1 Group A fuels

The properties of two petroleum diesel fuels and one JP-8 fuel with properties shown in Table 4.1 were used for surrogate development. These fuels include a representative US standard #2 diesel (USD), and a diesel with comparatively high aromatic content, denoted high aromatic diesel (HAD). The USD and HAD fuels were both donated by Ford Motor Company, Dearborn, MI, and are the same fuels that are discussed in Chapter 2, section 2.2.1. The same batch of HAD used in these cloud point studies was previously characterized by Windom et. al. [15]. The JP-8 jet fuel was donated by the US Air Force Research Lab at Wright Patterson Air Force Base. The same batch of JP-8 (POSF 6169, also designated POSF 11732 during a repeat test) was used for all testing and characterization. JP-8 is a traditional petroleum-based fuel used by the US military and it is very similar in specifications to the commercially available fuel Jet A1. However, JP-8 contains an additional additive package including a corrosion inhibitor, a lubricity enhancer, an icing inhibitor, and a static dissipater.

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Table 4.1: Base petroleum fuel characteristics. USD – US standard #2 diesel; HAD – high aromatic diesel.

	JP-8	USD	HAD	Test Method
Cloud point (°C)	-52	-15	-27	ASTM D2500
Distillation T10 (°C)	177	207	214	ASTM D86
Distillation T50 (°C)	203	256	253	
Distillation T90 (°C)	241	313	312	
Aromatics (%v)	15.5	29	34	ASTM D1319
Saturates (%v)	83.2	68	63	ASTM D5291
Olefins (%v)	1.3	3	3	
Cetane Number	45.78	44	41	ASTM D613

4.2.1.2 Group B fuels

Six different group B fuels were evaluated. They were all given designated names which relate to their composition or manufacturing process. The IPK (POSF 7629 and POSF 11736) and HRJ (POSF 7635 and POSF 11734) fuels were donated by Wright Patterson Air Force Base, Dayton, Ohio, and the SPK2 (POSF 11737), HRJ-8 (POSF 11735), SPK (POSF 11738), and HRD (POSF 11733) fuels were provided by the US Army Tank Automotive Research, Development, and Engineering Center (TARDEC) (Table 4.2 and Table 4.3). The HRJ fuel is a mixture of multiple batches of fuel, one of which is the HRJ-8 fuel. Select fuel characteristics are listed in Table 4.3. Dynamic Fuels and Syntroleum are part of the Renewable Energy Group at the time of this writing.

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Table 4.2. Table of fuel name, supplier, source, and production method for each fuel of interest.

Fuel	Fuel Designation	Supplier	Production Method and Source
Isoparaffin Kerosene	IPK	Sasol	Fischer-Tropsch, natural gas
Hydrotreated Renewable Jet	HRJ	Dynamic Fuels	Hydrotreating and isomerization, mixture of sources
Synthetic Paraffin Kerosene	SPK2	Shell	Fischer-Tropsch, natural gas
Hydrotreated Renewable Jet	HRJ-8	UOP	Hydrotreating, camelina oil
Synthetic Paraffin Kerosene	SPK	Syntroleum	Fischer-Tropsch, natural gas
Hydrotreated Renewable Diesel	HRD	Dynamic Fuels	Hydrotreating and isomerization, waste fat and oil

Table 4.3. Alternative fuels characteristics. All tests were performed at TARDEC in Warren, MI. Note a) No wax formation was found for IPK down to -78 °C.

	IPK	HRJ	SPK2	HRJ-8	SPK	HRD	Test Method
Freeze point (°C)	<-78 ^a	-49.2	-53.5	-53.6	-58.9	-10.2	ASTM D7153
Distillation T10 (°C)	164.6	180.2	161.6	164.5	169.6	228.0	
Distillation T50 (°C)	177.4	222.2	169.0	216.4	205.1	279.0	ASTM D86
Distillation T90 (°C)	201.2	258.5	184.5	271.8	256.6	297.7	
Aromatics (%v)	0.5	1.4	0.6	0.4	0.6	5.1	
Saturates (%v)	99.1	95.8	98.6	98.8	98.8	93.6	ASTM D1319
Olefins (%v)	0.4	2.8	0.8	0.8	0.6	1.3	ASTM D5291
Derived Cetane Number	31.59	57.99	58.11	56.88	60.05	64.65	ASTM D6890

4.2.2 Analytical testing

4.2.2.1 GC-MS for *n*-paraffin content

Gas chromatography coupled with mass spectroscopy (GC-MS) was used to quantify the paraffin content. Linear paraffins create sharp, well resolved peaks on GC-MS. Standards can be used to determine response factors for various paraffins, which allows the paraffin content to be quantified, both for mass fraction and carbon number. A Varian 3800 GC was used, coupled to a Varian 2000 MS using an ion trap detector. The column used in the GC was a Supelco SLB-5ms

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30 m x 0.25 mm with a film thickness of 0.25 μm . The GC temperature program was: 40 $^{\circ}\text{C}$ for 5 min, ramp to 190 $^{\circ}\text{C}$ at 2 $^{\circ}\text{C}/\text{min}$, ramp to 325 $^{\circ}\text{C}$ at 30 $^{\circ}\text{C}/\text{min}$, and hold at 325 $^{\circ}\text{C}$ for 5.5 min.

Three paraffin standards were obtained from Sigma Aldrich. One standard contained n-pentane through n-octane, one contained n-heptane through n-decane, and the final contained n-decane, n-dodecane, n-tetradecane, and n-hexadecane. These standards had a linear relationship for the response factors, and the values were extrapolated to the higher carbon numbers. The GC-MS for JP-8 is shown in Figure 4.1. The middle range of the spectrum has so many different peaks that they are unable to be baseline resolved. For the paraffins in that section, valley-to-valley integration is used, so potentially the paraffins are underestimated.

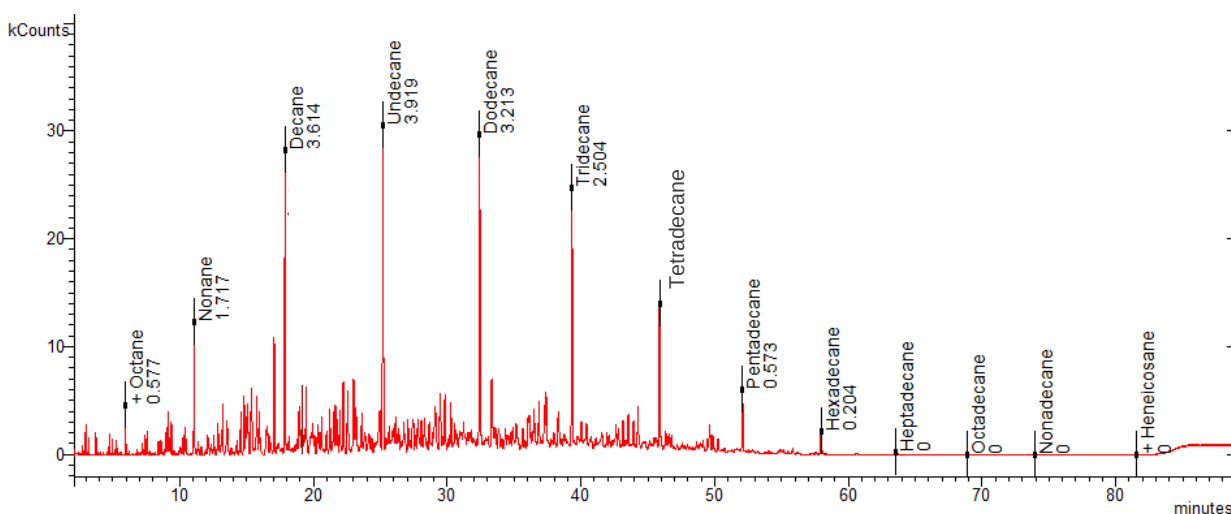


Figure 4.1. GC-MS of JP-8, with the n-paraffins labeled.

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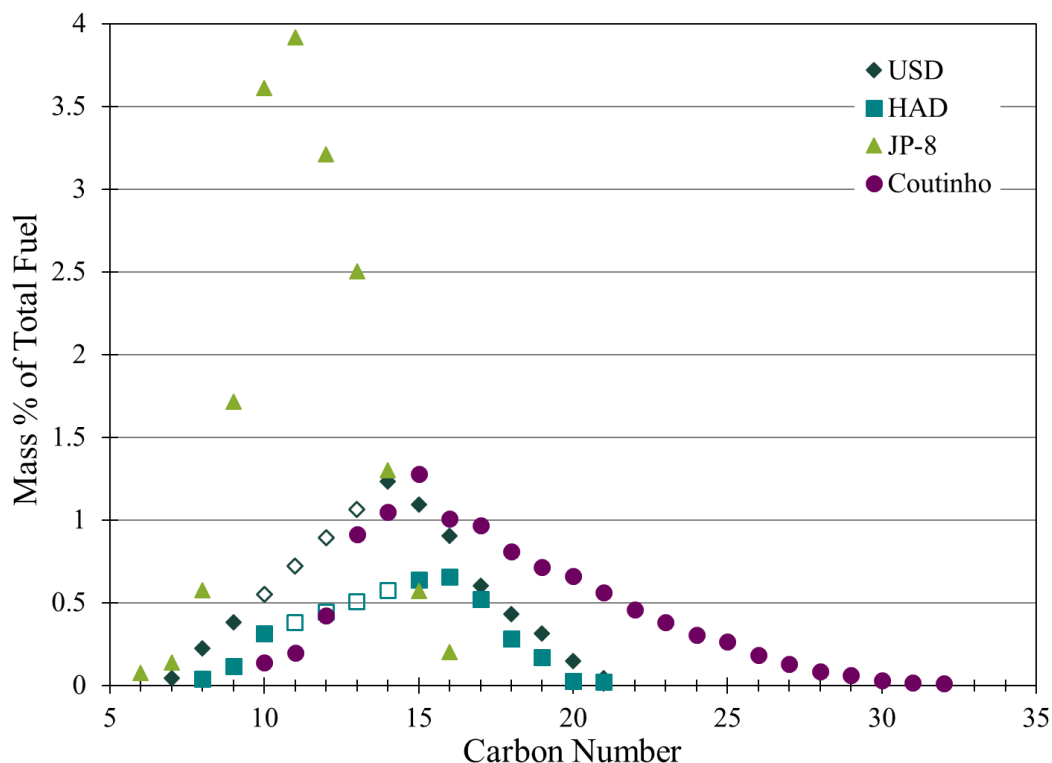


Figure 4.2. Distribution of n-paraffin content in various fuels. Coutinho sample shown for comparison [17]. Open points indicated interpolated values due to being unable to get baseline resolution on individual peaks.

Distilled fuels display a lognormal distribution of n-paraffins [71]. The JP-8 fuel does display the expected lognormal distribution (Figure 4.2), as does the Coutinho fuel [17]. The two diesel fuels, however, have a biased distribution towards the higher molecular weight side of the bell curve. This could be caused by the mixing of multiple distilled batches.

4.2.2.2 HPLC for aromatic content

High performance liquid chromatography (HPLC) was used to quantify the aromatic content for the group A fuels using a similar method to that of Segudovic et al. [72]. This method can only distinguish between mono-, di-, and tri-aromatics. A Shimadzu LC-2010A HT pump system was used with a Shimadzu RIT-10A refractive index detector. The column was a Restek Pinnacle II Cyano 5 μ m 250 x 3.2 mm. N-heptane was used for the mobile phase. Unlike the method of Segudovic et al., there was no backflow. Cyclohexane, o-xylene, 1-

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methylnaphthalene, and anthracene were used to determine the relative response for each group of aromatics, which allowed for the mass fraction of each group to be quantified.

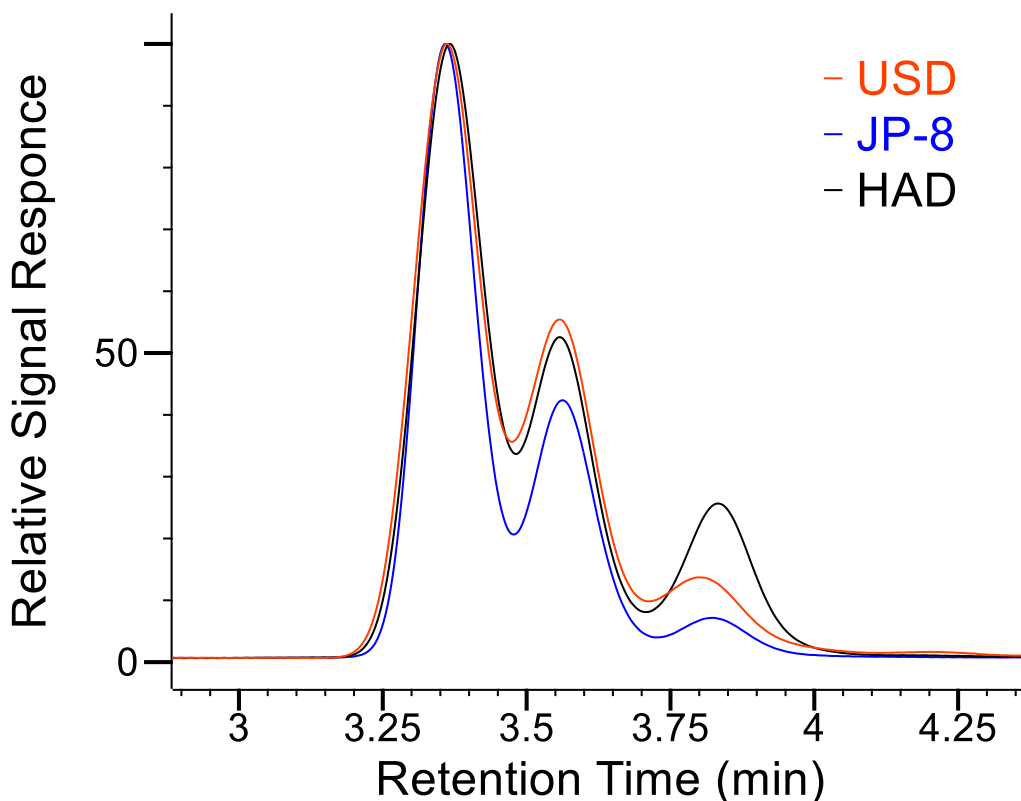


Figure 4.3. Aromatic distribution for the group A fuels.

Four peaks are found through HPLC testing, though the fourth peak is very small and only present for the USD (Figure 4.3). The first peak at about 3.3 min represents all the components without aromatic rings. This peak includes paraffins as well as cyclohexanes. The second peak, at about 3.6 min, represents the mono-aromatics compounds. The second peak at 3.8 min represents the di-aromatic compounds, and the very small peak at 4.2 min is the tri-aromatics.

4.2.2.3 Average molecular weight

The average molecular weight was found by using melting point depression in *p*-xylene for both group A and B fuels. Small concentrations of diesel fuels were added to *p*-xylene, and

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the sample was placed in a constant temperature bath 3-5 °C below the expected cloud point. The temperature of the solution was recorded using a thermocouple data recorder. Before a sample starts to freeze, the temperature drops with a constant rate. Once freezing begins, the slope of the sample temperature curve changes. By plotting lines through each section and finding the intersection point, the temperature of the onset of freezing can be found. The difference between the fuel/*p*-xylene mixture's freezing temperature and that of the pure *p*-xylene relates to the average molecular weight of the added fuel.

Equation (4.1) relates the melting point calculated for the mixture to that of the pure *p*-xylene in order to calculate the mole fraction of *p*-xylene in the mixture. Then, the equation for mole fraction is rearranged in equation (4.2) to use the calculated mole fraction of *p*-xylene to find the corresponding molecular weight of the fuel.

$$\ln[x_{pX}] = -\frac{\Delta H_{pX}^{fus}}{R} \left(\frac{1}{T_{m,mix}} - \frac{1}{T_{m,pX}} \right) \quad (4.1)$$

$$MW_{fuel} = \frac{M_{fuel} MW_{pX}}{M_{pX} \left(\frac{1}{x_{pX}} - 1 \right)} \quad (4.2)$$

where x_{pX} is the mole fraction of *p*-xylene, ΔH_{pX}^{fus} is the heat of fusion of *p*-xylene, R is the ideal gas constant, $T_{m,mix}$ is the melting point of the fuel/*p*-xylene mixture, $T_{m,pX}$ is the melting point of the pure *p*-xylene, MW_{fuel} is the average molecular weight of the fuel, M_{fuel} is the mass of the fuel in the mixture, MW_{pX} is the molecular weight of *p*-xylene, and M_{pX} is the mass of *p*-xylene in the mixture.

Best practices for using this method included allowing the fuel mixture to supercool by no more than 1-2 °C during operation. The sides of the test tube were too smooth to provide many nucleation sites, and sometimes nucleation would need to be induced by sharply tapping

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the test tube or thermocouple. This allowed for a longer linear region during freezing, which in turn made for a more repeatable calculation of the melting temperature.

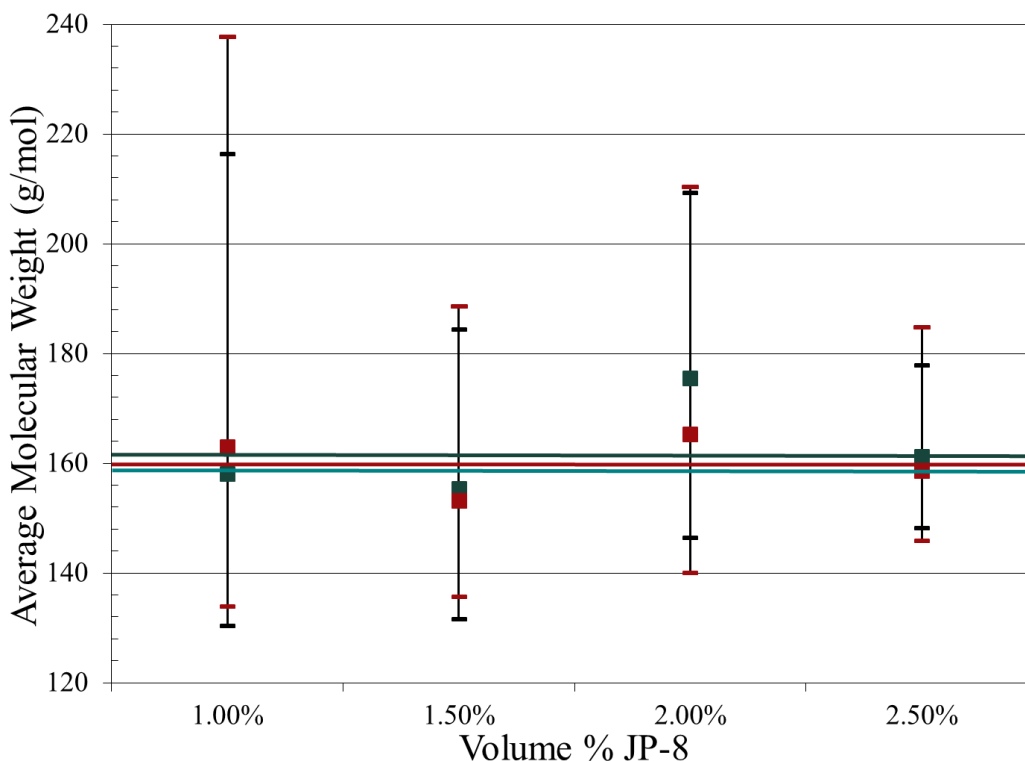


Figure 4.4. Distribution of calculated average molecular weight of JP-8 in *p*-xylene. The red and green symbols represent repeat runs taken a year apart. The red and green lines represent the average of the melting point depression runs, and the blue line represents the average molecular weight found by GCxGC testing.

Figure 4.4 shows a typical distribution of average molecular weights found by melting point depression for JP-8 for two separate runs. The bars represent the maximum and minimum calculated values at each composition, rather than the error. The symbols represent the average at each composition. The horizontal lines represent the average of values given by the symbols of corresponding color. While the distribution is large, the overall average gives a good prediction. When butyl butyrate was tested using this method, the error was 3.13%, and the absolute average error between the GCxGC results (explained in section 4.2.2.4) and the melting point depression

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method is 1.81%. The melting point results are presented with a confidence of ± 20 g/mol (Table 4.4).

Table 4.4. Average molecular weights for all fuels as determined by melting point depression and GCxGC when available. GCxGC testing was not available for the USD or HAD fuels.

Fuel	Average molecular weight (g/mol)	
	Melting Point Depression	GCxGC
JP-8	162.6	159
USD	193.3	-
HAD	191.0	-
IPK	151.0	154
HRJ	170.6	176
SPK2	144.7	143.4
HRJ-8	171.9	172
SPK	163.0	166
HRD	207.8	213.3

4.2.2.4 GCxGC for isoparaffin and naphthenes content

Two dimensional gas chromatography (GCxGC) was performed on the neat fuels at the Air Force Research Laboratory, Fuels and Energy Branch, located at Wright-Patterson Air Force Base in Dayton, OH. The method is discussed in detail in Striebich et al. [73, 74]. The sample is separated in the first dimension by volatility using a non-polar column. Six-second fractions of the initial separation are then directed into a polar column for separation by polarity in the second dimension. A combination of flame ionization and mass spectral detection (FID and MS) is used. This method allows for the separation and quantitation of hydrocarbon functional groups by carbon number, as well as identification of individual components that are present above a certain level. It was found that for the HRJ, HRJ-8, SPK2, and HRD fuels, there were significant amounts of isoparaffins co-eluting with the n-paraffins. For these fuels, GC-MS was employed to determine the n-paraffin content using molecular ion quantitation. The amount each n-paraffin

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was over-predicted by GCxGC-FID was added to the iso-paraffin content of one carbon number larger.

The results for the fuels are presented as stacked bar graphs in Figure 4.5-Figure 4.11. JP-8 displays the expected normal distribution for a distilled fuel. The JP-8 also has a large diversity of components in it, since it is petroleum based. The IPK and SPK2 fuels (Figure 4.6 and Figure 4.8) both have a very narrow distribution. The IPK fuel is almost entirely isoparaffins, while the SPK2 fuel is split between n-paraffins and isoparaffins. The HRJ fuel has a broader distribution than either IPK or SPK2, but it does not have the same bell-curve shape (Figure 4.7). The HRJ-8 fuel has a bimodal distribution, which is very unusual for a fuel (Figure 4.9). The HRJ fuel does not have as pronounced of a bimodal distribution as the HRJ-8, likely because it is a mixture of multiple fuel batches (one of which is the HRJ-8 fuel). The SPK fuel has close to the normal distribution that the JP-8 and other distilled fuels display, but it does not have the same diversity of composition (Figure 4.10). The composition of the HRD fuel is concentrated around C16-C18, which is expected for a fuel made from a plant based oil (Figure 4.11).

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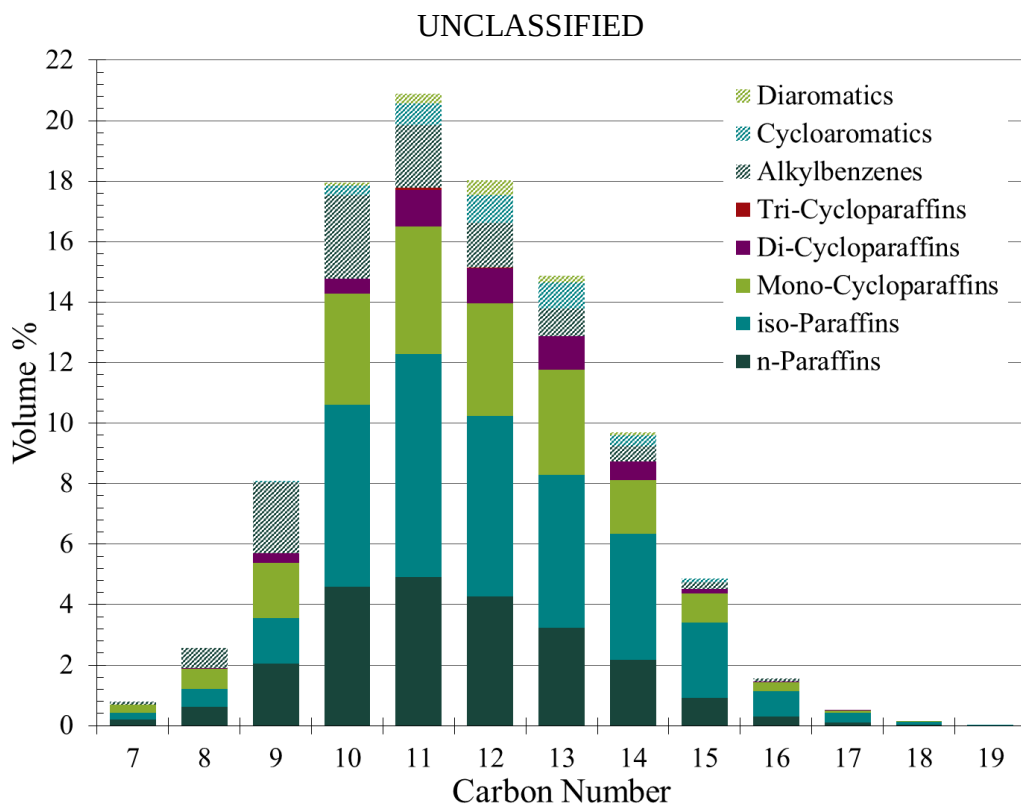


Figure 4.5. Composition of JP-8 broken down by carbon number and functional class.

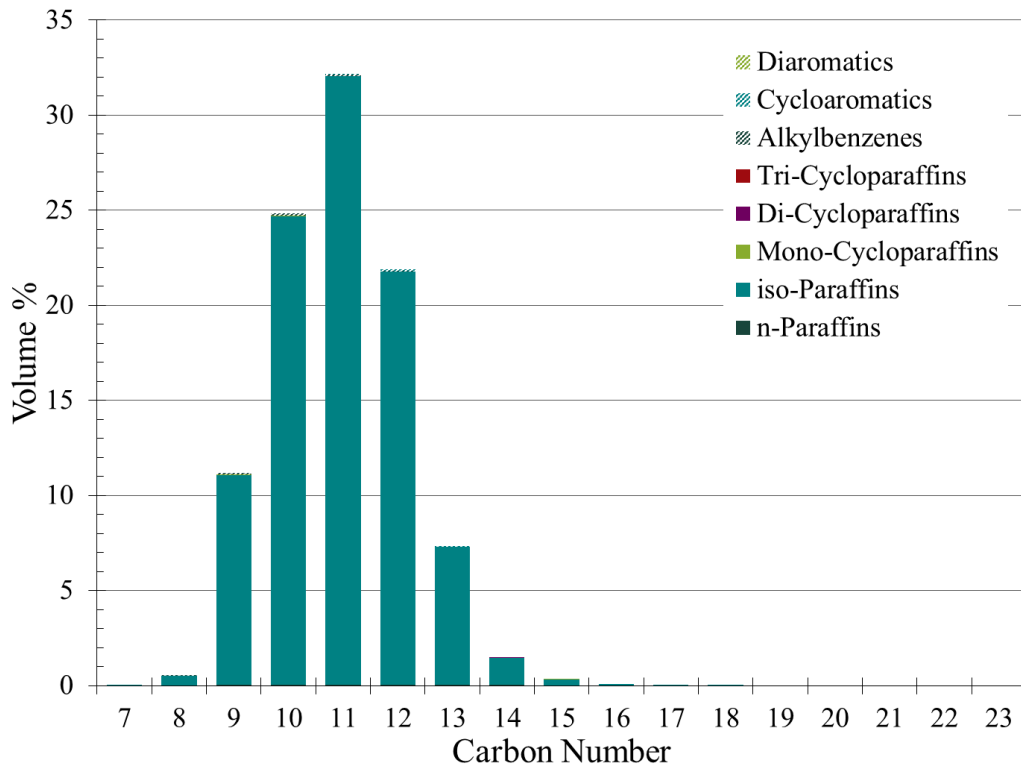


Figure 4.6. Composition of IPK broken down by carbon number and functional class.

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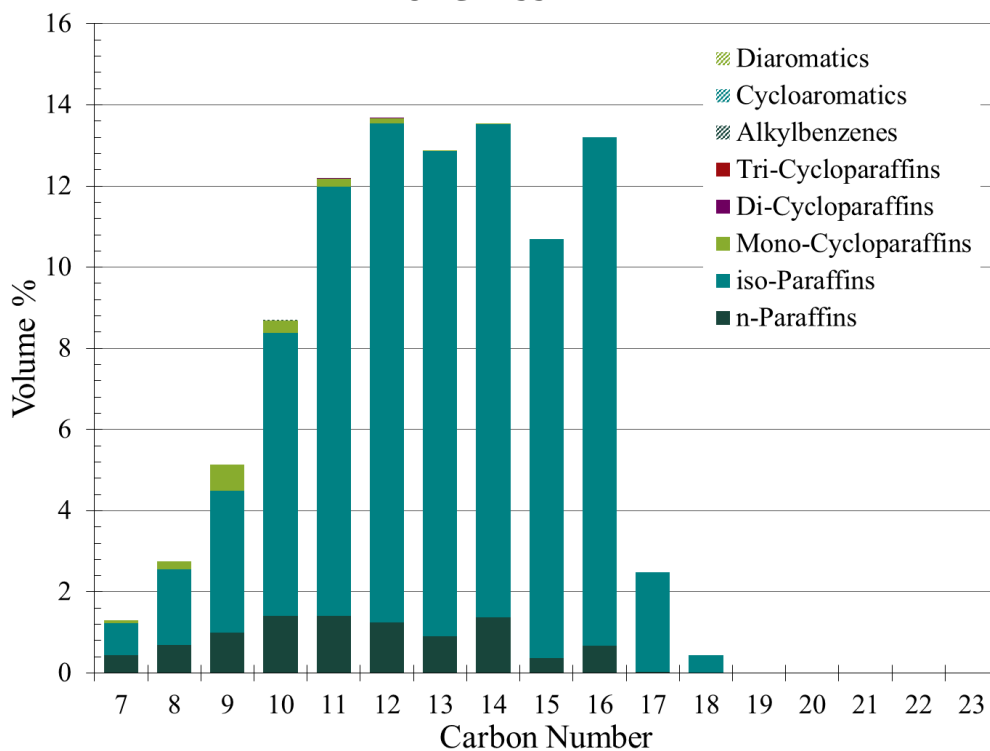


Figure 4.7. Composition of HRJ broken down by carbon number and functional class.

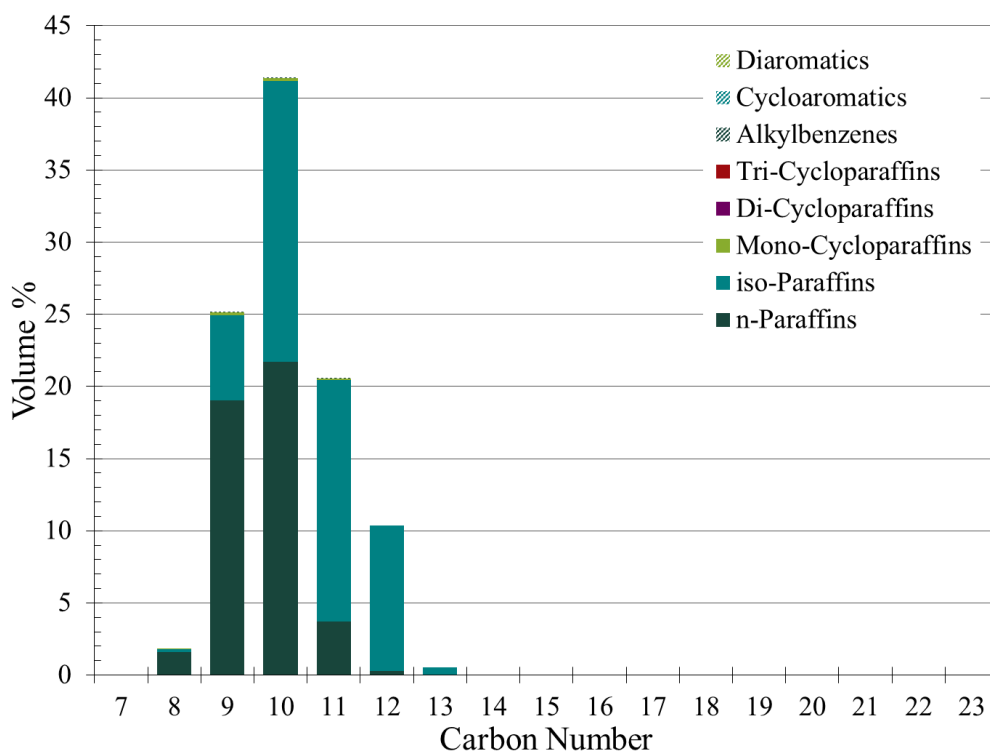


Figure 4.8. Composition of SPK2 broken down by carbon number and functional class.

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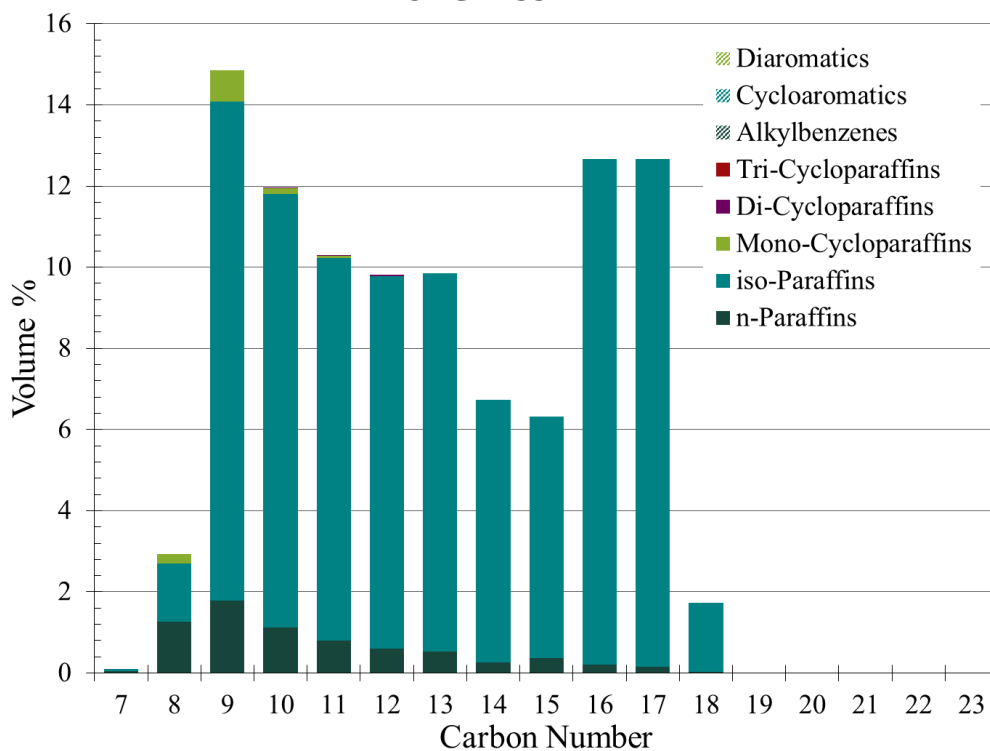


Figure 4.9. Composition of HRJ-8 broken down by carbon number and functional class.

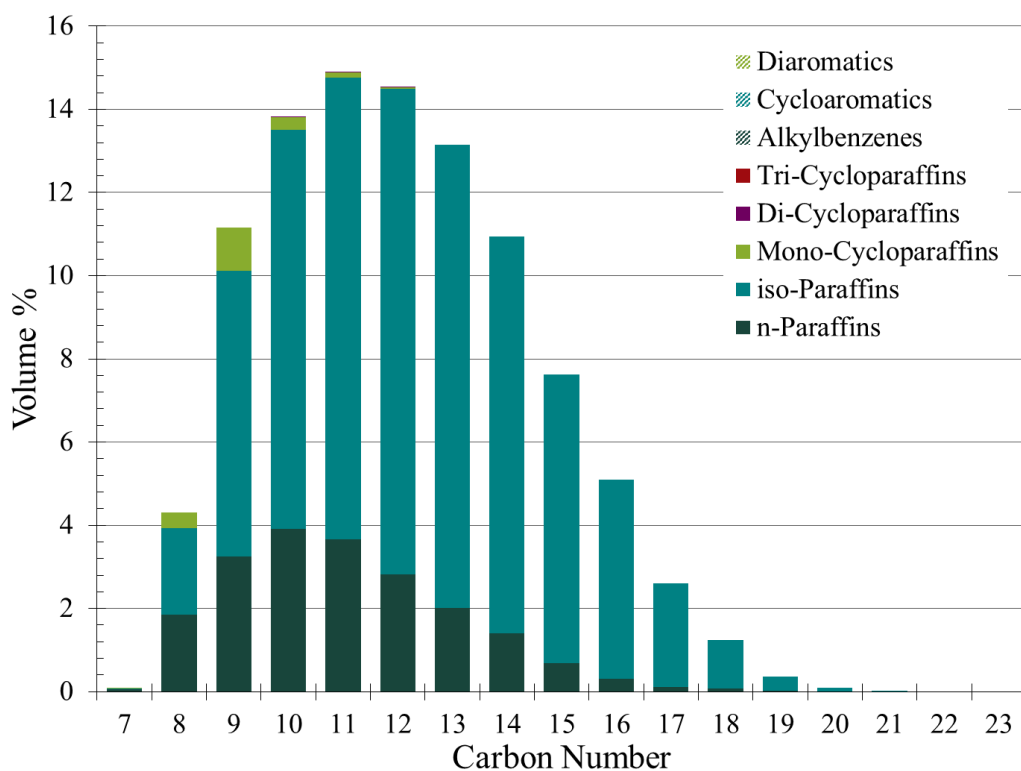


Figure 4.10. Composition of SPK broken down by carbon number and functional class.

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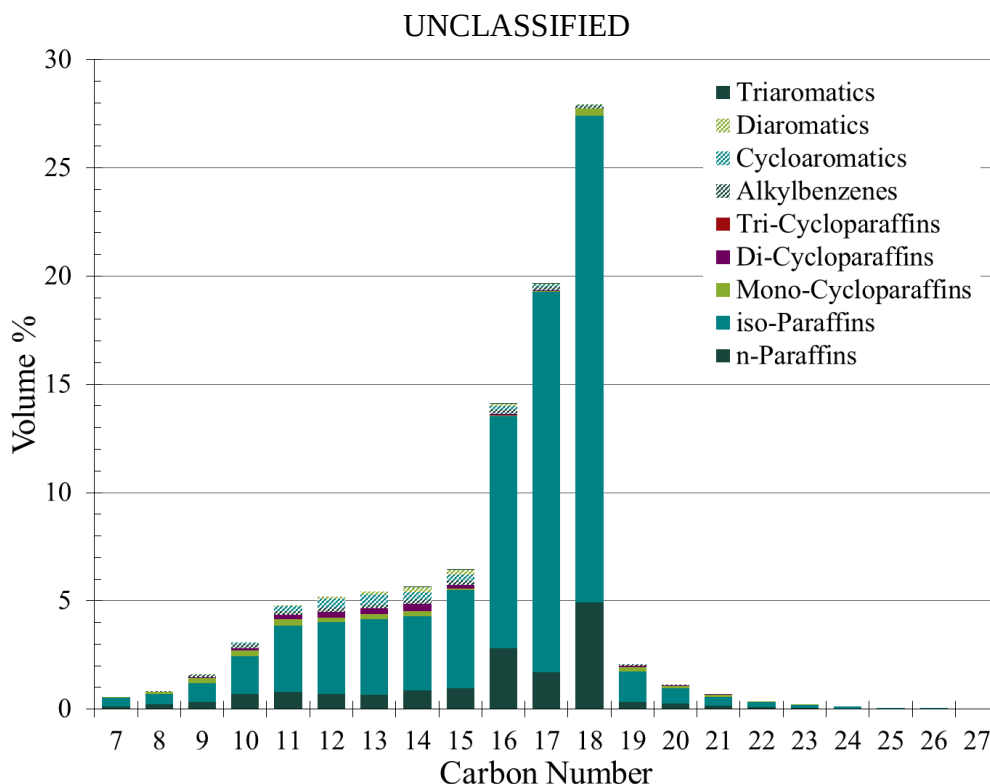


Figure 4.11. Composition of HRD broken down by carbon number and functional class.

4.2.2.5 Cloud and freezing point testing

Cloud point temperatures were found for the group A using the same method as outlined in Chapter 2, section 2.2.2.2. The freezing point of the group B fuels were tested at TARDEC in Warren, MI, following ASTM D7153. The difference between the two methods is that the cloud point is detected when crystals form upon cooling, and the freezing point is detected when the crystals disappear upon warming. The cloud point method can suffer from supercooling effects, while the freezing point method would not.

4.2.2.6 Distillation testing

Distillation curves were collected for the group B fuels and JP-8. Two liter distillations were performed with a method scaled to mimic that of ASTM D86. Two liters of each fuel was placed into a 3 L three neck round bottom flask. Nitrogen was fed through one of the necks of the flask to purge the headspace of oxygen prior to heating. The flow rate of nitrogen was 40

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mL/min, and it was kept at this flow rate throughout distillation to ensure an oxygen-free environment inside the vessel. Thermocouples were placed in the pot liquid and at the intake to the condenser. The flask and distillation head were insulated using fiberglass insulation up to the condenser intake. Both a Liebig and Friedrichs condenser were used in series due to the high vapor flow rate.

Heating was adjusted until the distillation rate was approximately 100 mL per 4-5 min, which corresponds to approximately 4 L/min of vapor flow. This distillation rate corresponds volumetrically to a scaled ASTM D86 distillation rate. Both the vapor and pot temperatures were recorded at each 100 mL distilled. The pot was usually 9-10 °C warmer than the vapor temperature. The vapor temperature corresponds more closely to what the equilibrium boiling temperature of the fuel would be, since the pot is usually superheated, and for this reason the vapor temperatures were used for all distillation curves. The distillation was ended after 95% of the total volume was distilled. The sample that was collected between first boiling and the first 100 mL (5% of the total sample volume) was designated as the 5% sample, the next section from 5%-10% was designated as the 10%, etc. The atmospheric pressure was recorded prior to all runs. This allowed the vapor temperatures to be adjusted using the Sydney Young equation to the correct boiling temperature at standard atmospheric pressure [75, 76]. The uncorrected data for the group B fuels can be found in Appendix C. Two of the fuels were not distilled in this work. The values used for the HAD fuel distillation curve are from Windom et. al [15], and the USD values are from the D86 fuel specification sheet from Ford Motor Company.

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Table 4.5. Distillation vapor temperatures for all fuels. JP-8 through HAD have been adjusted to the normal boiling point using the Sydney Young equation. Note a) HAD temperatures from [15]; b) from D86.

Volume % Distilled	Vapor Temperature (°C)								
	JP-8	IPK	HRJ	SPK2	HRJ-8	SPK	HRD	HAD ^a	USD ^b
0	167.7	162.5	160.9	159.8	147.8	146.7	164.8	209.1	177.8
5	183.8	170.3	184.4	165.2	173.8	176.8	231.0	220.3	197.8
10	187.2	171.5	192.2	165.9	177.6	180.5	243.0	225.6	208.9
15	189.8	172.6	197.8	166.2	181.4	183.9	255.0	229.3	-
20	192.5	173.5	201.8	166.9	185.3	187.1	263.0	233.4	224.4
25	196.1	175.0	207.8	167.5	189.8	191.0	269.1	237.6	-
30	197.8	176.0	211.8	168.2	195.6	194.7	274.1	242.1	236.7
35	200.4	177.4	215.8	168.9	200.4	199.0	279.1	246.8	-
40	202.3	178.8	220.8	169.6	208.4	203.6	283.1	251.8	247.2
45	206.3	180.2	224.8	170.5	215.4	206.6	286.1	256.8	-
50	209.3	181.8	229.8	171.6	222.4	211.6	289.1	262.1	256.7
55	212.3	183.6	232.8	172.5	230.4	216.6	291.1	267.5	-
60	215.3	185.5	237.9	173.8	240.4	221.6	294.1	274.3	266.7
65	219.4	187.6	241.9	174.9	249.4	226.6	296.1	280.8	-
70	223.4	190.0	245.9	176.8	256.4	231.6	298.1	287.0	277.2
75	228.4	192.7	250.9	178.2	263.5	237.6	300.1	293.6	-
80	233.4	195.9	255.9	180.8	270.5	243.6	302.1	301.3	290.6
85	239.4	199.7	259.9	182.6	275.5	251.7	305.1	309.6	-
90	245.4	205.8	264.9	186.2	279.5	260.7	308.1	320.1	311.1
95	256.5	214.8	270.9	191.5	283.5	270.7	314.1	-	332.2
100	-	-	-	-	-	-	-	342.0	349.4
Boiling Range	88.7	52.3	110.0	31.7	135.7	124.0	149.3	132.9	171.7

4.2.3 Models*4.2.3.1 Cloud point model*

A variety of methods have been described in the literature for the determination of cloud point temperature or wax appearance temperature for petroleum based fuels. Two different models were evaluated in this work for the prediction of cloud point temperature. These predictions require the use of surrogates to represent the composition of the fuel. The first assumes that only the component with the warmest melting point will solidify [77, 78]. The second allows a solid solution to form [18, 22, 79].

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If only one surrogate component is allowed to solidify, the equation takes the form:

$$\ln[x_2\gamma_2] = -\frac{\Delta H_2^{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_{m,2}}\right) \quad (4.3)$$

where x_2 is the mole fraction of component 2 in liquid phase, γ_2 is the activity coefficient of component 2 in liquid phase, H_2^{fus} (J/mol) is the heat of fusion of component 2, $T_{m,2}$ (K) is the melting temperature of component 2, and T is the cloud point temperature (K). An activity coefficient model can be used, or the liquid phase can be assumed to be ideal.

A more accurate representation of the solid phase is to allow the solid phase to be a mixture of components:

$$K_i = \frac{x_i^L \gamma_i}{x_i^S} = \exp\left[\frac{\Delta H_i^{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_{m,i}}\right)\right] \quad (4.4)$$

where K_i is the equilibrium ratio of component i between the liquid and solid phases, x_i^S is the mole fraction of i in the solid phase, and x_i^L is the mole fraction of i in the liquid phase. The cloud point temperature is found by iteration: T is changed until the sum of x_i^S is equal to 1. This also allows us to manipulate which classes of components are allowed to precipitate by forcing the mole fraction of the other components to be zero.

In order to evaluate which model and conditions to use for surrogate modeling, five sets of assumptions were evaluated using 6 different fuel surrogates. The first two calculations were done using equation (4.3) and assuming either ideal behavior (designated “Pure 1 Component Solid (Ideal)”), or using the UNIFAC model for the activity coefficient (designated “Pure 1 Component Solid (UNIFAC)”). The remaining three conditions used equation (4.4) with the UNIFAC model, and allow either all components (designated “Solid Solution”), only the alkane components (designated “Solid Solution of Alkanes Only”), or only the aromatic components to

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precipitate (designated “Solid Solution of Aromatics Only”). Each group A fuel is represented by two surrogates from the literature.

4.2.3.2 Cloud point modeling of literature surrogates

For Figure 4.12-Figure 4.14, all predicted cloud point temperatures are represented using their deviation from the experimental cloud point for the fuel. The experimental cloud point is shown as the horizontal line in all figures. The predicted cloud point is shown above or below the bar, and the bar is used to show the deviation relative to the experimental cloud point.

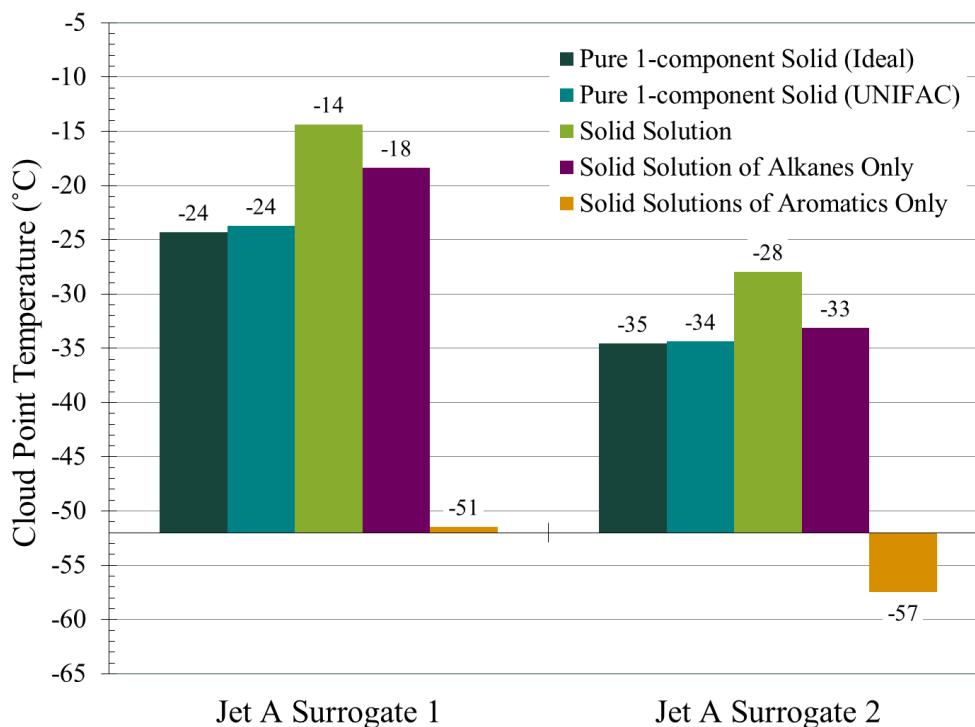


Figure 4.12. Deviations from experimental cloud point temperature for various jet fuel surrogates. Jet A surrogates 1 and 2 from [14].

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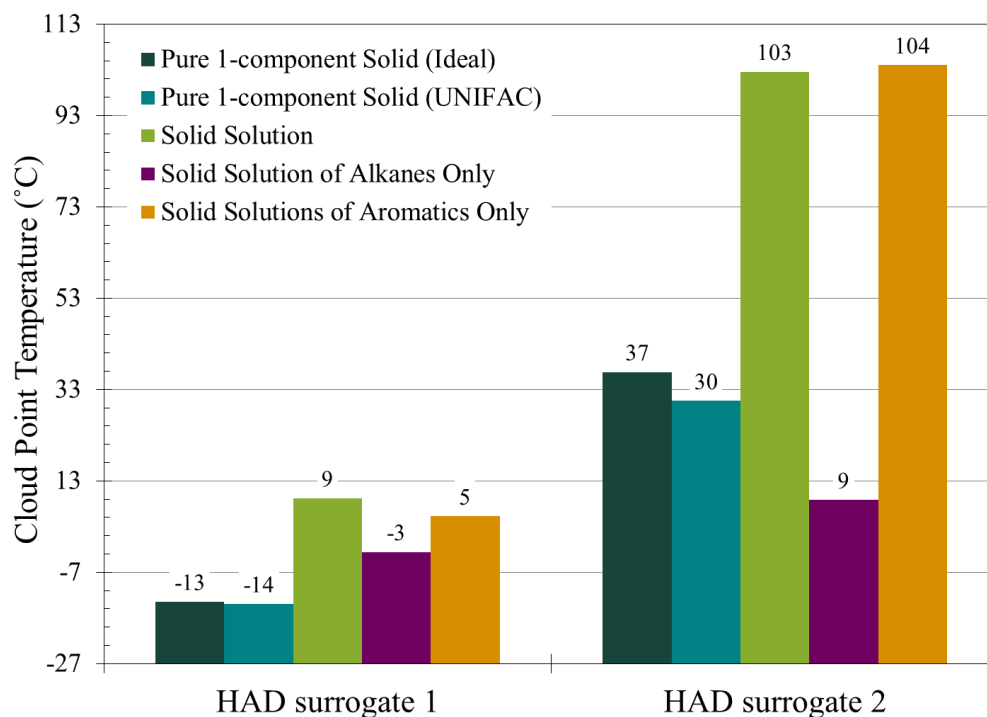


Figure 4.13. Deviations from experimental cloud point temperature for various high aromatic diesel (HAD) fuel surrogates. HAD surrogates 1 and 2 from [15].

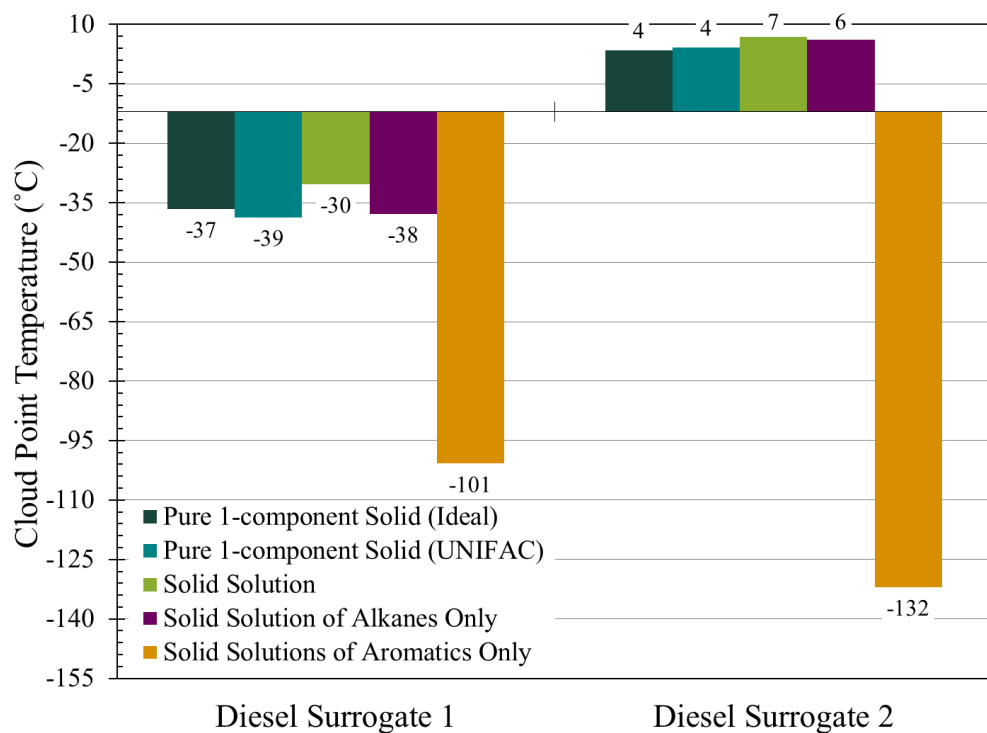


Figure 4.14. Deviations from experimental cloud point temperature for various US diesel (USD) fuel surrogates. Diesel surrogate 1 from [24] and surrogate 2 from [23].

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The calculation can be constrained so that only certain surrogate components are modeled in the precipitate. Since the paraffins have been found to be the main component in the precipitate [17], a solid solution of only n-paraffins was used for the optimization predictions. The study was configured to allow all components to be in the solid phase, or limit it to only certain hydrocarbon classes, such as paraffins or aromatics. Coutinho [17] and Dirand [71] state that the components which come out of solution during an experimental cloud point of a fuel are the paraffins, and that the distribution of paraffins needs to be accurately represented for an accurate cloud point temperature. To simplify optimization, only the paraffins are allowed to precipitate during iterations and a solid solution of alkanes only is assumed. The solid phase is also assumed to be an ideal solution.

4.2.3.3 Distillation curve model

A single-stage batch distillation model was used to model the distillation curve. The bubble point temperature of the mixture is calculated using Raoult's law [69]. A fixed, small volume of liquid is evaporated using the equilibrium vapor phase concentrations at the bubble point temperature (equation (4.5)). To simplify calculations, the K -ratio is used (equation (4.6)), which is a rearrangement of Raoult's law [69]. The new mole fractions in the liquid phase are calculated by subtracting the change in the liquid phase mole fraction (dx_i in equation (4.5)), and are used to calculate the new bubble point temperature. The iterations continue until a component mole fraction in the liquid phase reaches 0.9999, meaning that there is then only one component remaining in the liquid phase.

$$dx_i = (K_i - 1)x_i d(\ln[n^L]) \quad (4.5)$$

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{sat}}{P} \quad (4.6)$$

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here dx_i is the change in liquid phase mole fraction of component i , K_i is the ratio of gas to liquid mole fraction of component i , x_i is the equilibrium liquid phase mole fraction of component i , $d(\ln[n^L])$ is the amount of liquid allowed to evaporate during each iteration step, y_i is the equilibrium gas phase mole fraction of component i , P_i^{sat} is the saturation pressure of component i at the bubble point temperature, and P is the system pressure, which is set to be atmospheric.

ASTM D86 is the accepted standard experimental method for determining the distillation curve of a fuel. However, this method can be inconsistent and the products of distillation are not necessarily at equilibrium during operation [70, 80]. The initial boiling temperature can vary by up to 30 °C depending on how well the heating rate is controlled, and the temperatures are almost always higher than the equilibrium boiling temperature. Because of these inconsistencies, it is difficult to model a D86 distillation using an equilibrium model. By using a larger distillation volume, a stirred distillation flask, and insulating the still head up to the thermocouple, the distillation method used for the group B fuels will give results that are closer to equilibrium temperatures.

4.2.3.4 Cetane number model

The cetane number of each surrogate mixture was calculated using the method of Ghosh and Jaffe [26]. The calculation is done using the cetane number, volume fraction, and β value of each component (equation (4.7)). The β values are fitted parameters which represent the impact that a specific class of fuel component has on the cetane number. For example, n-paraffins have a low β value and isoparaffins have a high β value.

$$CN = \sum_i \frac{v_i \beta_i CN_i}{v_i \beta_i} \quad (4.7)$$

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where CN is the cetane number of the mixture, v_i is the volume fraction of component i , β_i is the blending coefficient of component i , and CN_i is the cetane number of component i .

This method requires a cetane number for each potential surrogate component. Ghosh and Jaffe [26] give cetane numbers for components with different carbon numbers in each functional class. The beta values and cetane numbers for each potential surrogate component are taken directly from this paper, unless cetane values for the specific isomer were specified in the Murphy Compendium [61]. Each surrogate is made up of n-paraffins ($\beta = 0.5212$), isoparaffins ($\beta = 7.3717$), naphthenes ($\beta = 0.0727$), mono-aromatics ($\beta = 3.1967$), and di-aromatics ($\beta = 3.1967$). The cetane method will be discussed in more detail in Chapter 5.

4.2.4 Surrogate optimization

To develop the surrogate for each fuel, the compositional data was used as a basis. The distribution of the paraffins was fixed based on the amount found in the GC-MS for the group A fuels, and the GCxGC for the group B fuels and JP-8. Methyl naphthalene was used for the di-aromatic component for all fuels. The total mass fractions of mono-, di-, and tri-aromatics were fixed to match the compositional analysis, using the HPLC data for the group A fuels and the GCxGC data for the group B fuels. For the group A fuels, the difference between the naphthenes and isoparaffins could not be identified using GC-MS, so the total amount for both groups was found by subtracting the composition of the other classes from 1. The total mass fraction of naphthenes was fixed using the GCxGC data for the group B fuels, and the isoparaffin fraction was set as the balance of the other components. The exact paraffin distributions and di-aromatic mass fractions are presented in Table 4.6, and the remaining mass fractions are presented in Table 4.7 for all fuel surrogates. Then, components within each class were selected, and the properties of the surrogate were calculated as outlined in section 4.2.3. The boiling curve, cloud

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point temperature, average molecular weight, and cetane number of the neat fuel were used to optimize the composition of each component within the overall constraint on each class.

Table 4.6. Weight fractions for the fixed components of the proposed surrogates for all fuels, split by type of testing.

n-Paraffin Carbon Number	GC-MS / HPLC			GCxGC						
	JP-8	HAD	USD	JP-8	IPK	HRJ	SPK2	HRJ-8	SPK	HRD
C6	0.0008	-	-	-	-	-	-	-	-	-
C7	0.0014	-	0.0004	0.0017	0.0000	0.0040	0.0003	0.0004	0.0005	0.0010
C8	0.0058	0.0004	0.0023	0.0056	0.0001	0.0064	0.0151	0.0118	0.0162	0.0020
C9	0.0172	0.0012	0.0038	0.0188	0.0006	0.0095	0.1875	0.0171	0.0266	0.0031
C10	0.0361	0.0031	0.0055	0.0426	0.0006	0.0137	0.2171	0.0110	0.0313	0.0065
C11	0.0392	0.0038	0.0072	0.0463	0.0006	0.0138	0.0375	0.0079	0.0284	0.0074
C12	0.0321	0.0044	0.0089	0.0407	0.0005	0.0124	0.0031	0.0060	0.0214	0.0065
C13	0.0250	0.0051	0.0106	0.0312	0.0005	0.0092	0.0001	0.0054	0.0141	0.0063
C14	0.0130	0.0057	0.0123	0.0212	0.0003	0.0140	-	0.0026	0.0082	0.0083
C15	0.0057	0.0064	0.0110	0.0090	0.0002	0.0038	-	0.0038	0.0036	0.0095
C16	0.0020	0.0066	0.0090	0.0031	0.0001	0.0070	-	0.0022	0.0014	0.0278
C17	-	0.0052	0.0060	0.0011	-	0.0003	-	0.0016	0.0005	0.0171
C18	-	0.0028	0.0043	0.0003	-	-	-	0.0002	0.0001	0.0490
C19	-	0.0017	0.0032	-	-	-	-	-	-	0.0034
C20	-	0.0003	0.0015	-	-	-	-	-	-	0.0024
C21	-	0.0002	0.0005	-	-	-	-	-	-	0.0014
C22	-	-	-	-	-	-	-	-	-	0.0009
C23	-	-	-	-	-	-	-	-	-	0.0005
C24	-	-	-	-	-	-	-	-	-	0.0003
C25	-	-	-	-	-	-	-	-	-	0.0002
C26	-	-	-	-	-	-	-	-	-	0.0001
Subtotal weight fraction paraffins	0.1784	0.0866	0.0469	0.2218	0.0035	0.0942	0.4609	0.0700	0.1524	0.1538
Weight fraction di- aromatics	0.0120	0.0590	0.0350	0.0158	0.0002	0.0002	0.0001	0.0001	0.0001	0.0107

Table 4.7. Total weight fractions for the remaining functional classes in the surrogates. For the Group A fuels, the naphthenic and isoparaffin components were treated as one class.

	GC-MS / HPLC			GCxGC						
	JP-8	HAD	USD	JP-8	IPK	HRJ	SPK2	HRJ-8	SPK	HRD
Mono-Aromatic	0.148	0.223	0.237	0.1229	0.0044	0.0004	0.0006	0.0002	0.0002	0.0225
Naphthenic	0.6616	0.6712	0.6434	0.2152	0.0013	0.0171	0.0064	0.0137	0.0207	0.0439
Isoparaffin				0.4243	0.9904	0.8881	0.5320	0.9160	0.8265	0.7691

A database of potential surrogate components was developed. For each component, the tabulated properties were: melting point temperature, freezing temperature, liquid density at 25

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°C, heat of fusion, UNIFAC groups, vapor pressure equation coefficients, cetane numbers, and β values. The vapor pressure equation is the same one used in the DIPPR database [54]. For all potential components, the DIPPR database [54] and the NIST Webbook [53] were used to find the required properties, with the exception of cetane number and β values, which were found as discussed in section 4.2.3.4. A table of all the potential surrogate components and select properties can be found in Appendix D.

Surrogates were developed using the Matlab function “fgoalattain” to adjust composition while constraining the weight fractions in each functional class to minimize a composite objective function including the cetane number, distillation curve, cloud point, and average molecular weight. Each optimization used an initial composition based on component freezing temperatures and boiling temperatures. Multiple initial guesses were given during the course of optimization to rule out local minima, as well as to help select the optimum components. Each property that was being used as a metric for the optimization was also given a weight. The cloud point temperature and distillation curve objective functions were weighted with a value of 100, while the cetane number and average molecular weight were assigned a weight of 10.

The errors for each property were calculated using the square of the difference between the calculated property and the desired property, with the exception of the distillation curve. For the distillation curve, an error was calculated at each experimental point using a point in the calculated curve with the same volume distilled. The square of the differences at each point in the experimental curve was calculated and summed, then divided by the total number of points. These errors were set as the values of a vector and the minimization of the values was the objective function for fgoalattain.

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4.3 Results and Discussion

The optimized surrogates had differing degrees of ability to correctly predict both low and high temperature properties. Two JP-8 surrogates have been proposed. The first uses the GC-MS and HPLC data to define the paraffin and aromatic content, and allowed the program adjust the naphthenic and isoparaffinic components directly. This was the method used for the group A fuels as well. The second JP-8 surrogate uses the GCxGC information to fix the total content of all groups, like the group B fuels. A summary of the surrogates, their predictions, and percent errors are shown in Table 4.8. The errors in cloud point prediction temperature are represented as error in the absolute temperature measurement (K), while the values are shown in degrees Celsius.

Table 4.8. Summary of surrogate predictions and errors.

Fuel	Number of Adjusted Components	Predicted Cloud Point (°C)	% Error	Predicted Cetane Number	% Error	Surrogate Ave. Mol. Weight	% Error
JP-8							
GC-MS / HPLC	4	-35.76	7.42%	44.40	-3.01%	156.92	-3.47%
HAD	7	-23.90	1.32%	44.16	0.37%	187.84	-1.65%
USD	6	-17.30	-0.83%	44.16	7.71%	190.14	-1.63%
JP-8 GCxGC	6	-30.14	9.96%	47.73	4.25%	161.47	-0.67%
IPK	6	-46.48	16.24%	37.73	19.44%	152.40	0.93%
HRJ	9	-32.67	7.45%	50.45	-13.00%	170.11	-0.29%
SPK2	5	-47.95	2.59%	48.07	-17.28%	140.45	-2.94%
HRJ-8	9	-40.23	6.16%	50.01	-12.08%	168.58	-1.96%
SPK	9	-38.15	9.76%	50.93	-15.19%	170.67	4.71%
HRD	6	-1.30	3.44%	57.37	-11.26%	220.12	5.94%

The predicted cetane numbers have a low percent error for the petroleum based group A fuels, with errors less than 7%, while the alternative fuels have errors of up to 19.5%. The larger errors with the alternative fuels are attributed to the high isoparaffin content. The scatter of

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isoparaffin cetane numbers and the shortcomings of the Ghosh and Jaffe method create large uncertainties, and the issues will be addressed further in Chapter 5.

All surrogates do a good job of matching the average molecular weight, with errors of less than 5%. For a typical fuel, an error of about 8% represents a change in composition by one carbon number. The exception is the HRD surrogate. The HRD surrogate has larger errors due to the DIPPR database not containing branched isoparaffins in the boiling range required to fit the distillation curve.

The cloud point temperatures are predicted within 8% error for the group A fuels and 16.5% error for the group B fuels. The two JP-8 surrogates developed here differ in the distribution of the paraffin content (Table 4.6) and the limits set by the greater resolution obtained by the GCxGC testing. The cloud point temperature prediction is significantly dependent on the paraffin content and distribution. Because the GCxGC testing detects almost 5 wt% more paraffins than the GC-MS, the cloud point predicted for the surrogates differs by 5.5 °C. Part of the differences between the two methods could be due to the valley-to-valley integration employed by the GC-MS method. The GCxGC testing projects the peaks to a theoretical baseline, which has been shown to over predict the mass of paraffins in the fuel [22]. This was corrected in part by using GC-MS, and for the corrected fuels the error is lower than 7.5%. While the JP-8 GC-MS surrogate still over-predicts the cloud point by approximately 17 °C, this is still an improvement over the literature surrogates by about 6 °C, and the distillation curves for the proposed surrogates are as good as the literature surrogates [14].

The distillation curves for all the predicted fuel surrogates are shown in Figure 4.15- Figure 4.24. The surrogates which give the best fits are the HAD, both JP-8s, IPK, and SPK fuels.

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In some cases, like the USD, HRJ, and SPK2, the general trend of prediction is correct, but the values are shifted by 5-20 °C. This shift is caused by the optimization model adding more of a compound to help match the cetane number or average molecular weight. The two JP-8 surrogates have slightly different predicted distillation curves. The GC-MS surrogate generally under predicts the boiling temperature by about 3 °C, while the GCxGC surrogate over predicts by about 5 °C during the latter half of distillation. The differences between the two surrogates are primarily due to the fact that the GCxGC testing can determine the difference between the isoparaffin and naphthenic components, while the GC-MS testing cannot. This results in different restrictions of the components that can be used in the surrogates, and how much of each component that can be used.

The HRD, HRJ, and HRJ-8 fuels have particularly poor predictions. The bimodal distribution of the HRJ-8 fuel makes it harder to predict a distillation curve with two plateaus. In addition, the database does not include isoparaffins that boil between 250-350 °C, which compromises the ability to create high boiling surrogates comprised of high isoparaffin content. The only alkane component in the current DIPPR database that boils between 250-350 °C is a naphthenic compound. Because the GCxGC testing shows the HRD, HRJ, and HRJ-8 fuels are at least 70% isoparaffins, a surrogate built from the database cannot represent the high temperature portion of the distillation curve correctly. The initial boiling point is usually over predicted by 15-20 °C.

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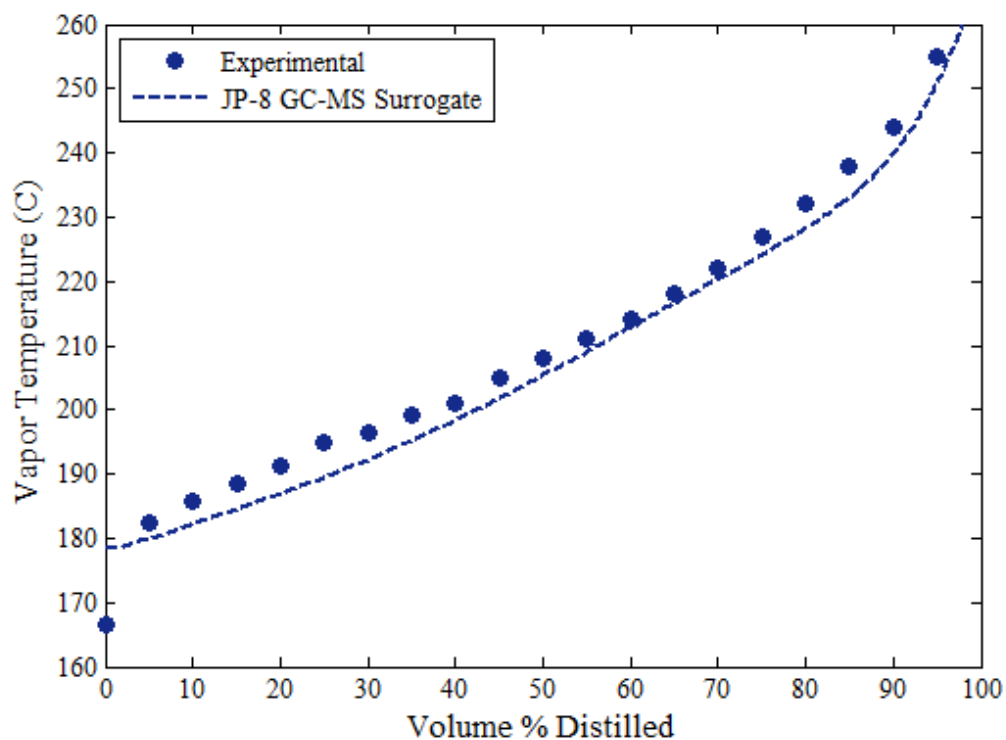


Figure 4.15. Experimental and predicted distillation curve for the JP-8 fuel and proposed surrogate developed using the GC-MS and HPLC data.

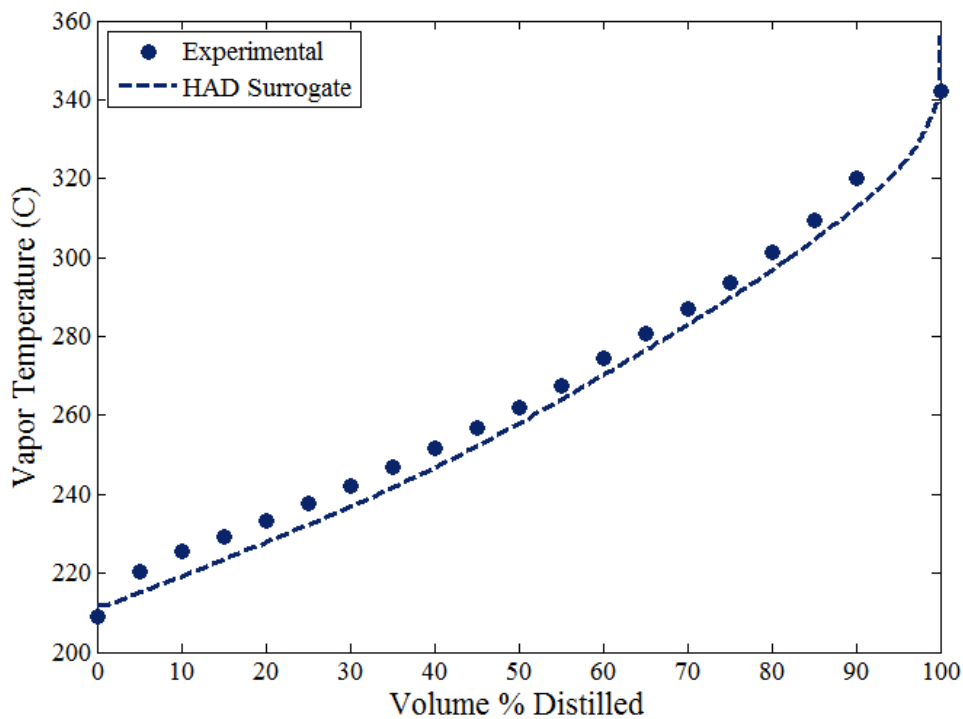


Figure 4.16. Experimental and predicted distillation curve for the HAD fuel and proposed surrogate.

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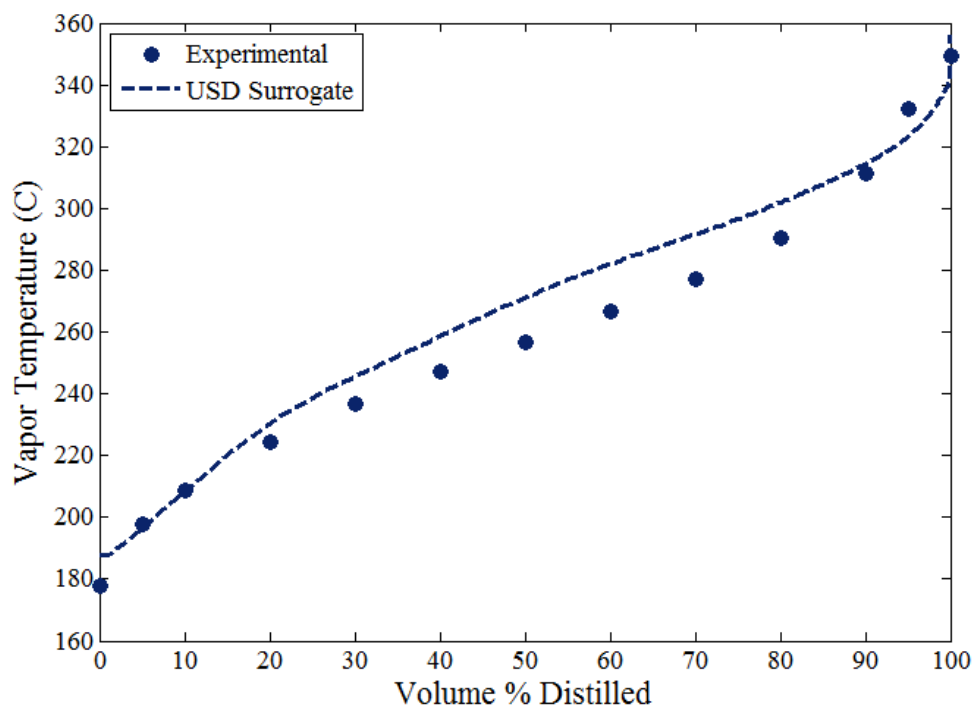


Figure 4.17. Experimental and predicted distillation curve for the USD fuel and proposed surrogate.

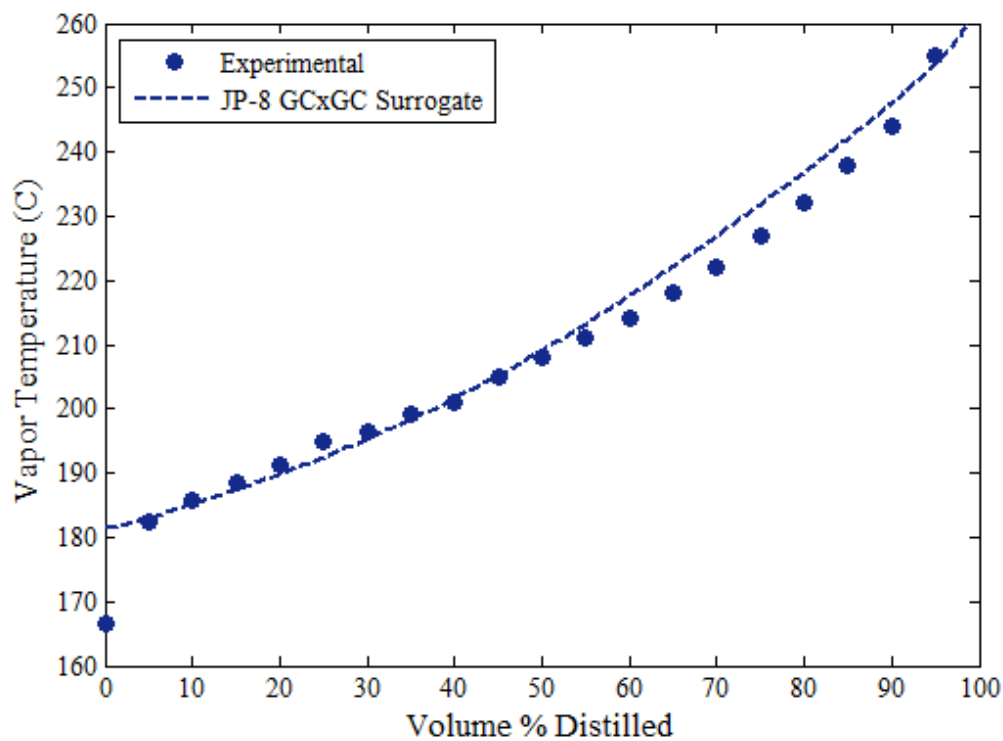


Figure 4.18. Experimental and predicted distillation curve for the JP-8 fuel and proposed surrogate developed using the GCxGC data.

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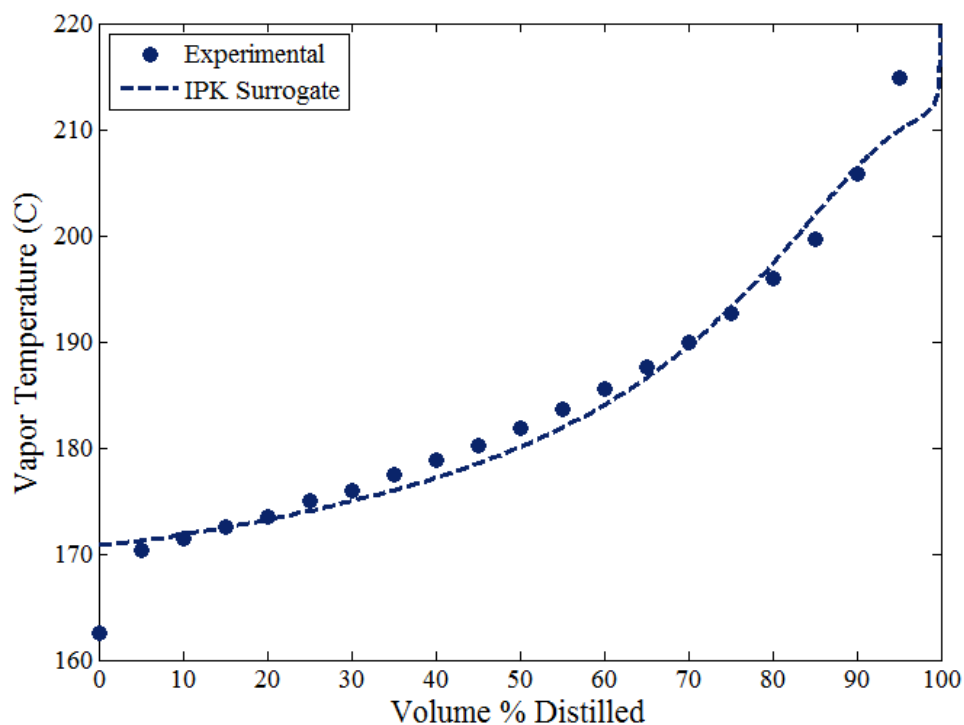


Figure 4.19. Experimental and predicted distillation curve for the IPK fuel and proposed surrogate.

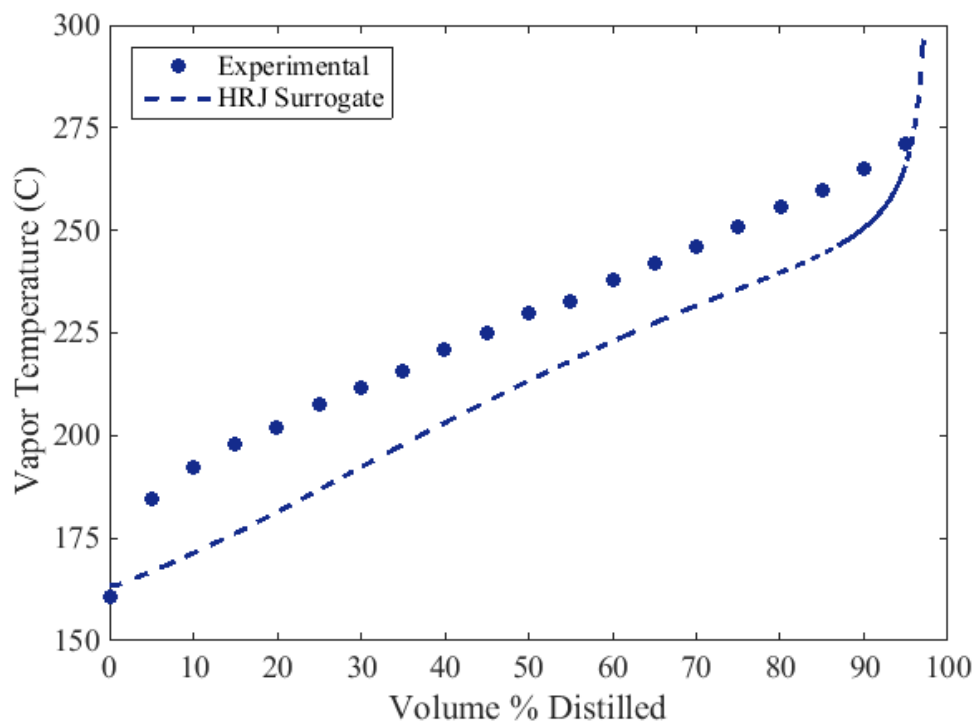


Figure 4.20. Experimental and predicted distillation curve for the HRJ fuel and proposed surrogate.

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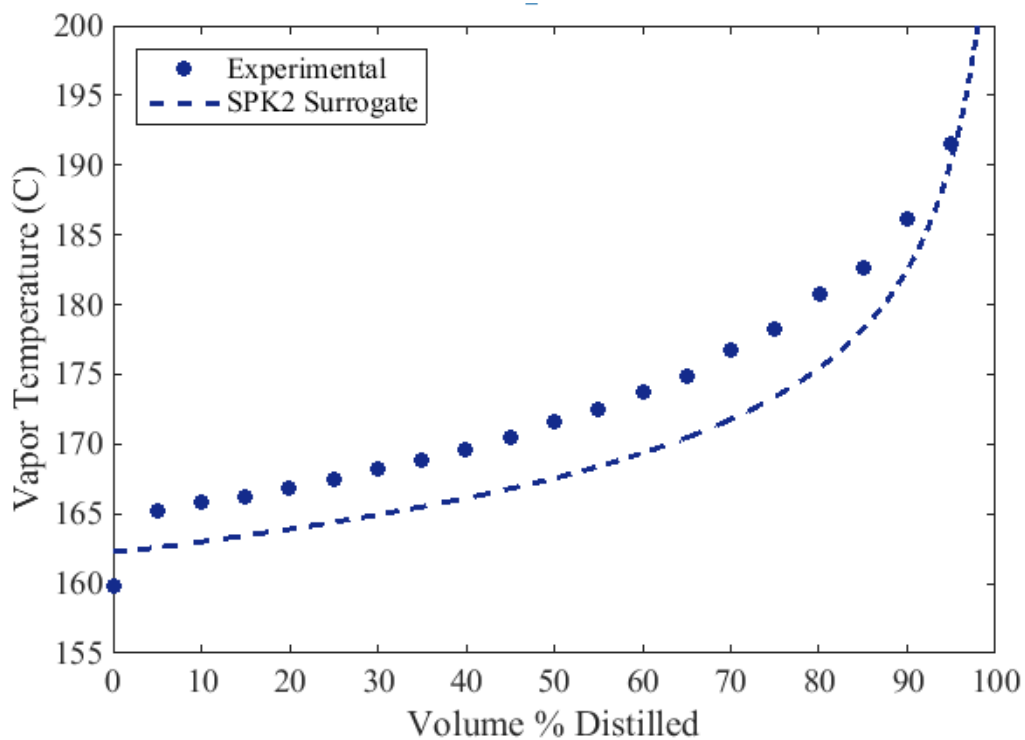


Figure 4.21. Experimental and predicted distillation curve for the SPK2 fuel and proposed surrogate.

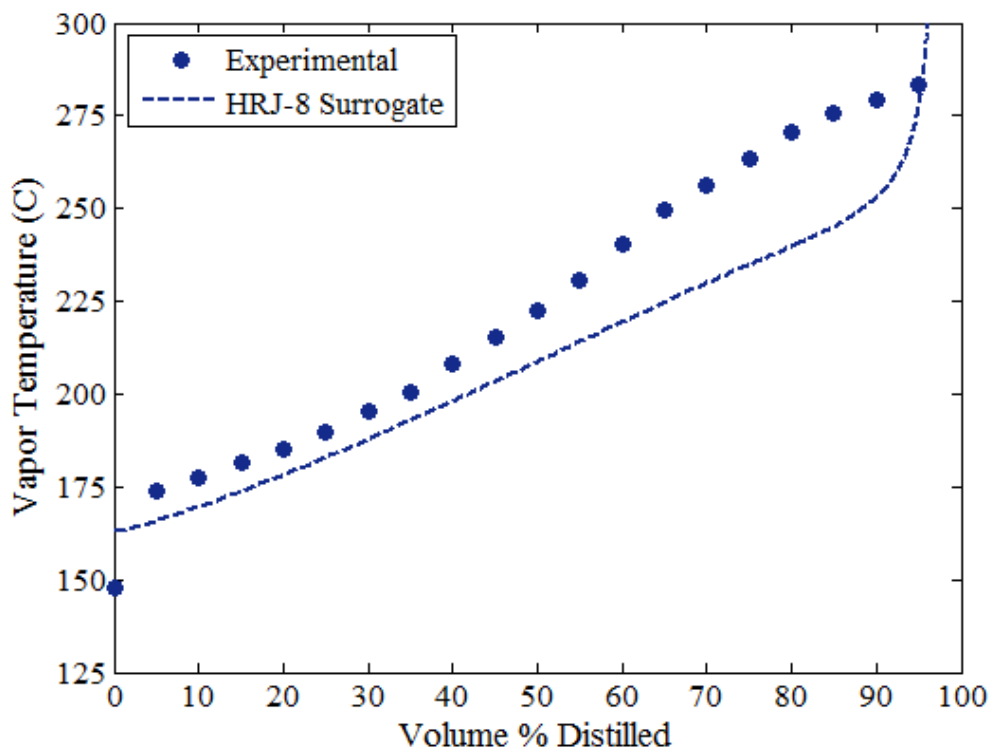


Figure 4.22. Experimental and predicted distillation curve for the HRJ-8 fuel and proposed surrogate.

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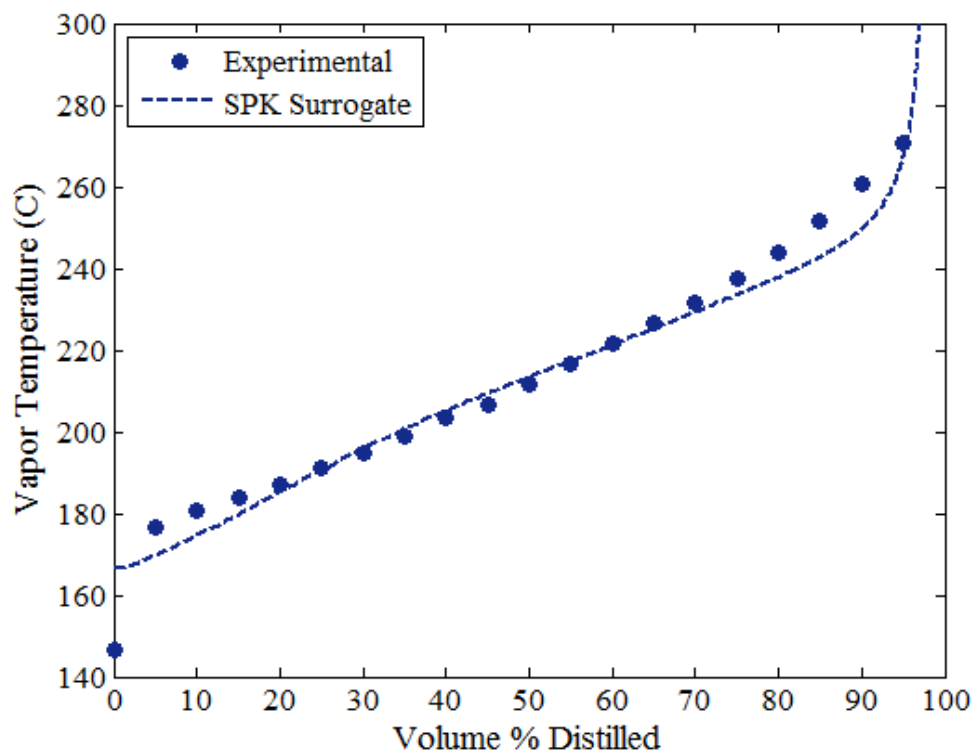


Figure 4.23. Experimental and predicted distillation curve for the SPK fuel and proposed surrogate.

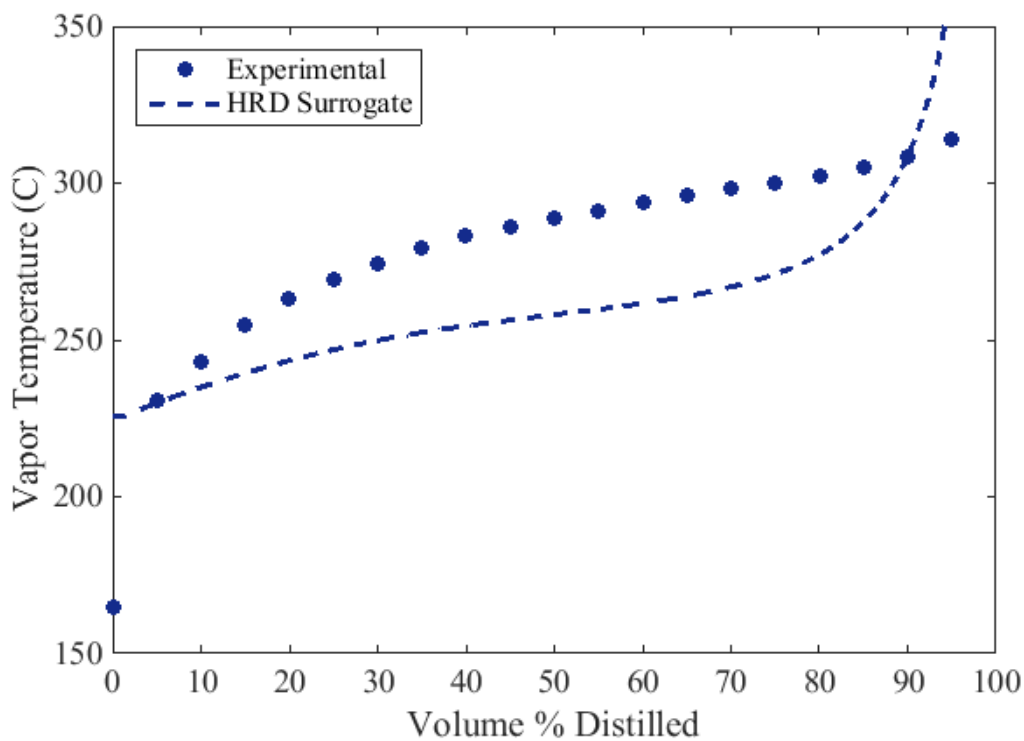


Figure 4.24. Experimental and predicted distillation curve for the HRD fuel and proposed surrogate.

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Detailed surrogate composition information is presented in Table 4.9-Table 4.18. Each table outlines the individual components in each surrogate. An interesting trend that can be noted by looking at the Group B surrogates is that increasing the number of potential components does not increase the model accuracy.

Table 4.9. Adjusted components for the proposed JP-8 surrogate developed using the GC-MS and HPLC data.

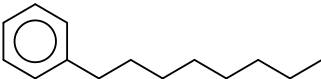
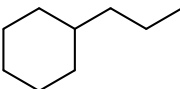
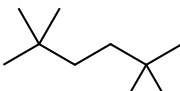
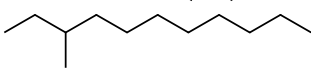
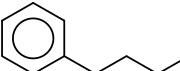
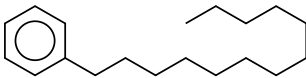
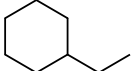
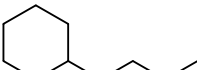
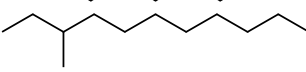
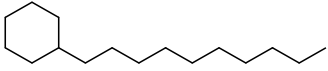
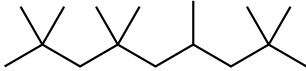
Name	Structure	Melting Temperature (°C)	Boiling Temperature (°C)	Mass Fraction in Surrogate
n-Octylbenzene		-36.00	264.55	0.1480
n-Propylcyclohexane		-74.73	181.13	0.1945
2,2,5,5-Tetramethylhexane		-12.60	137.61	0.0776
3-Methylundecane		-58.00	210.95	0.3896

Table 4.10. Adjusted components for the proposed HAD surrogate.

Name	Structure	Melting Temperature (°C)	Boiling Temperature (°C)	Mass Fraction in Surrogate
n-Butylbenzene		-87.85	183.46	0.1143
n-Tridecylbenzene		10.00	341.43	0.1087
Ethylcyclohexane		-111.31	131.95	0.0225
n-Butylcyclohexane		-74.73	181.13	0.0572
3-Methylundecane		-58.00	210.95	0.1166
n-Decylcyclohexane		-1.73	297.75	0.2366
2,2,4,4,6,8,8-Heptamethylnonane		-110.15	246.50	0.2382

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Table 4.11. Adjusted components for the proposed USD surrogate.

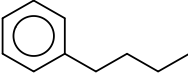
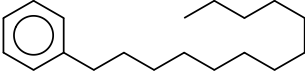
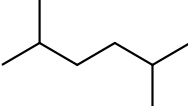
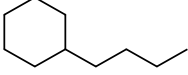
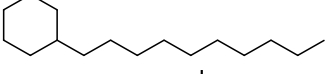
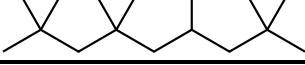
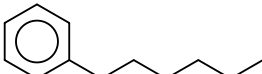
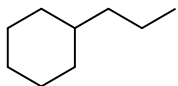
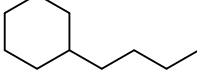
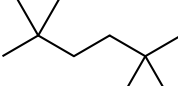
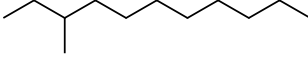
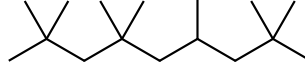
Name	Structure	Melting Temperature (°C)	Boiling Temperature (°C)	Mass Fraction in Surrogate
n-Butylbenzene		-87.85	183.46	0.11672
n-Tridecylbenzene		10	341.43	0.12028
2,5-Dimethylhexane		-91.15	109.26	0.05842
n-Butylcyclohexane		-74.73	181.131	0.046535
n-Decylcyclohexane		-1.73	297.75	0.28896
2,2,4,4,6,8,8-Heptamethylnonane		-110.15	246.5	0.24946

Table 4.12. Adjusted components for the proposed JP-8 surrogate developed using the GCxGC data.

Name	Structure	Melting Temperature (°C)	Boiling Temperature (°C)	Mass Fraction in Surrogate
n-Hexylbenzene		-61.15	226.26	0.1229
n-Propylcyclohexane		-111.31	131.95	0.1355
n-Butylcyclohexane		-74.73	181.131	0.1366
2,2,5,5-Tetramethylhexane		-12.60	137.61	0.0601
3-Methylundecane		-58.00	210.95	0.1537
2,2,4,4,6,8,8-Heptamethylnonane		-110.15	246.5	0.1537

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Table 4.13. Adjusted components for the proposed IPK surrogate.

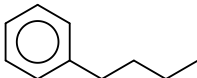
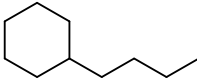
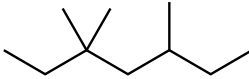
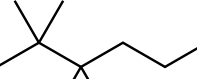
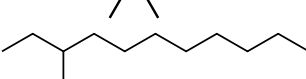
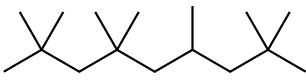
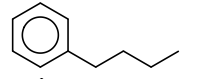
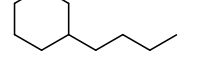
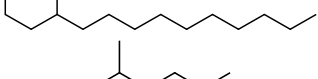
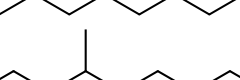
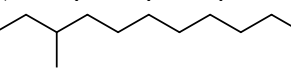
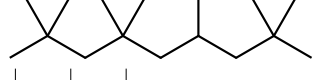
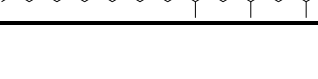
Name	Structure	Melting Temperature (°C)	Boiling Temperature (°C)	Mass Fraction in Surrogate
n-Butylbenzene		-87.85	183.46	0.0044
n-Butylcyclohexane		-74.73	181.13	0.0013
3,3,5-Trimethylheptane		-108.15	155.83	0.2618
2,2,3,3-Tetramethylhexane		-54.00	160.46	0.3298
3-Methylundecane		-58.00	210.95	0.3957
2,2,4,4,6,8,8-Heptamethylnonane		-110.15	246.50	0.0031

Table 4.14. Adjusted components for the proposed HRJ surrogate.

Name	Structure	Melting Temperature (°C)	Boiling Temperature (°C)	Mass Fraction in Surrogate
n-Butylbenzene		-87.85	183.46	0.0004
n-Butylcyclohexane		-74.73	181.13	0.0086
n-Decylcyclohexane		-1.73	297.75	0.0086
2,5-Dimethylhexane		-91.15	109.26	0.0786
4-Methyloctane		-113.20	142.59	0.0786
4-Methylnonane		-98.70	165.85	0.1572
3-Methylundecane		-58.00	210.95	0.1965
2,2,4,4,6,8,8-Heptamethylnonane		-110.15	246.50	0.3537
Squalane		-38.00	447.00	0.0236

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Table 4.15. Adjusted components for the proposed SPK2 surrogate.

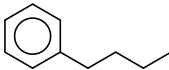
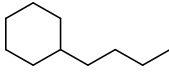
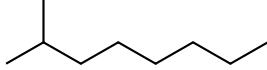
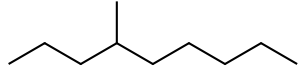
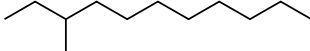
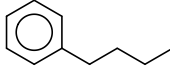
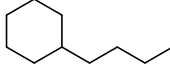
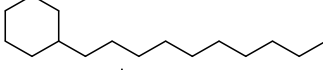
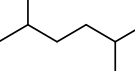
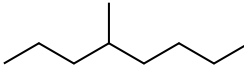
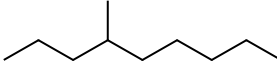
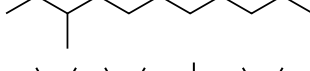
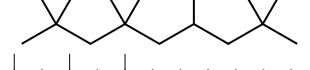
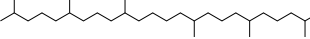
Name	Structure	Melting Temperature (°C)	Boiling Temperature (°C)	Mass Fraction in Surrogate
n-Butylbenzene		-87.85	183.46	0.0006
n-Butylcyclohexane		-74.73	181.13	0.0064
2-Methyloctane		-80.10	143.45	0.0859
4-Methylnonane		-98.70	165.85	0.3435
3-Methylundecane		-58.00	210.95	0.1026

Table 4.16. Adjusted components for the proposed HRJ-8 surrogate.

Name	Structure	Melting Temperature (°C)	Boiling Temperature (°C)	Mass Fraction in Surrogate
n-Butylbenzene		-87.85	183.46	0. 0179
n-Butylcyclohexane		-74.73	181.13	0. 0069
n-Decylcyclohexane		-1.73	297.75	0. 0069
2,5-Dimethylhexane		-91.15	109.26	0. 084
4-Methyloctane		-113.20	142.59	0. 084
4-Methylnonane		-98.70	165.85	0. 1681
3-Methylundecane		-58.00	210.95	0. 2101
2,2,4,4,6,8,8-Heptamethylnonane		-110.15	246.50	0. 3361
Squalane		-38.00	447.00	0. 0336

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Table 4.17. Adjusted components for the proposed SPK surrogate.

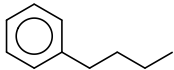
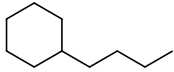
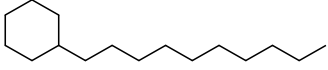
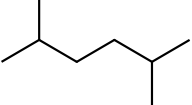
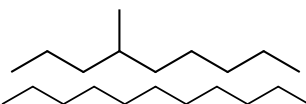
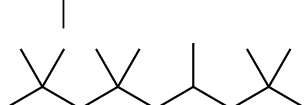
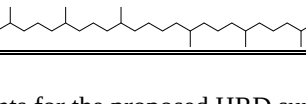
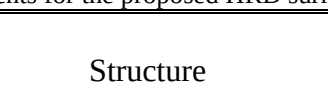
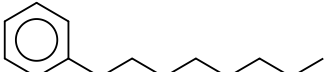
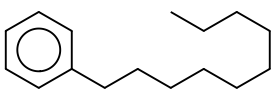
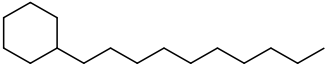
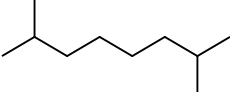
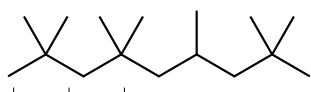
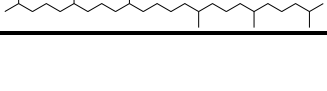
Name	Structure	Melting Temperature (°C)	Boiling Temperature (°C)	Mass Fraction in Surrogate
n-Butylbenzene		-87.85	183.46	0.0002
n-Butylcyclohexane		-74.73	181.13	0.0103
n-Decylcyclohexane		-1.73	297.75	0.0104
2,5-Dimethylhexane		-91.15	109.26	0.0844
4-Methylnonane		-98.70	165.85	0.1684
3-Methylundecane		-58.00	210.95	0.2109
2,2,4,4,6,8,8-Heptamethylnonane		-110.15	246.50	0.3375
Squalane		-38.00	447.00	0.0253

Table 4.18. Adjusted components for the proposed HRD surrogate.

Name	Structure	Melting Temperature (°C)	Boiling Temperature (°C)	Mass Fraction in Surrogate
n-Octylbenzene		-61.15	226.26	0.0059
n-Decylbenzene		-14.38	298.04	0.0166
n-Decylcyclohexane		-1.73	297.75	0.0439
2,7-Dimethyloctane		-54.00	160.02	0.0576
2,2,4,4,6,8,8-Heptamethylnonane		-110.15	246.50	0.6603
Squalane		-38.00	447.00	0.0512

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4.4 Conclusions

Ten different fuel surrogates were developed to fit both traditional petroleum fuels and a variety of alternative fuels. All surrogates used 10 or less adjusted components. Paraffins were constrained to match experimental compositions. Two different surrogates were developed for the JP-8 fuel based on two different sets of composition information. The difference in the paraffin distributions between the GC-MS and GCxGC predictions causes a difference of 5 °C in the cloud point prediction temperatures, with the GC-MS prediction being much closer to the experimental value. The JP-8 surrogates represent an improvement of 6 °C over the literature Jet A surrogates at predicting the cloud point temperature, and predict the distillation curve equally well [14]. The USD and HAD fuel surrogates predict all properties within 10% for the cetane number, average molecular weight, and cloud point temperature, and show an improvement of 15 and 20 °C respectively over the literature surrogates cloud points [15, 23, 24], while modeling the distillation curves simultaneously.

The alternative fuel surrogates for IPK and SPK predict the distillation curves within 5 °C and cloud point temperatures within 16%. The SPK2 surrogate predicts the cloud point temperature with 12% error and gets the general shape of the distillation curve correct, but shifted by 3-5 °C. The HRD, HRJ and HRJ-8 fuels were difficult to represent with surrogates. These higher boiling fuels were unable to be fitted due to a lack of high molecular weight isoparaffin components in the database. It is likely that a lack of diversity in the set of potential surrogate components hindered optimization for the higher boiling fuels.

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CHAPTER 5

Prediction of Cetane Number for Fuels and Fuel Mixtures

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5.1 Introduction

The cetane number of a fuel is an important metric for the evaluation of diesel fuels. The cetane number is a measure of the ignition delay in a compression-ignition engine. It is a property that is usually evaluated for jet fuels, but since jet engines do not rely on autoignition there is no minimum or maximum value for the fuel specification. However, the one fuel for the battlefield program [33-35, 81] calls for the use of JP-8 fuel in all military vehicles, including tanks and trucks. Because cetane number is not a specification for jet fuel, different batches of JP-8 as well as biofuels from different sources can have largely different cetane numbers, while still being within spec for all other properties. Knowledge of blend behavior is thus important in the field.

Cetane number prediction is challenging. Ignition delay depends on fuel structural, thermodynamic, and transport properties, because the process involves droplet breakup dependent on surface tension, vaporization, mixing, and the free radical process of combustion. Common cetane number predictive correlations use other fuel properties [82]. These can include aniline point [83-87], API gravity [83-86], density [83, 85], distillation curve [32, 83-86], and viscosity [83-87]. The majority of these equations are empirical relations, with fitted parameters. They work well for other petroleum based fuels from outside the training set. However, when alternative fuels with different compositions or biofuels with oxygenated components are used, the empirical relationships can fail [25, 88].

Quantitative structure-property relationship (QSPR) methods have also been used to relate the structure of fuel compounds to the compound cetane number [89-92]. The QSPR method relates the different structural elements of individual molecules to a selected property. This can be done using either basic structural information about the molecule [89], or using

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NMR spectra to relate peaks to the desired property [90]. This method works very well for n-alkanes, but has the same amount of scatter as other methods for branched compounds. It has also only been applied to potential fuel compounds, and not to fuel surrogates or actual fuel mixtures.

An alternative to comparative property prediction is to use spectroscopy to predict cetane numbers. Nuclear magnetic resonance (NMR) spectroscopy has been used to relate the ratio of aromatic and paraffin carbons to the cetane number [88]. Other groups have used carbon NMR to relate the density of the CH₂ and CH₃ groups to the cetane number [31]. The DeFries method works well for n-paraffin cetane number prediction, but has a large amount of scatter for isoparaffin prediction. Being able to relate the cetane number to common fuel components allows for the model to be applied to multiple fuel types.

Chemometric methods can be used to relate the IR spectra to cetane number [27-30, 89, 93-95]. Chemometrics is defined by using data analysis methods to extract results from large volumes of data. In the case of cetane number, the peaks in the spectra are correlated to the cetane number using various types of regression. This work focuses on using the partial least squares (PLS) method of regression. In PLS regression, the absorbance at each wavelength or wavenumber is linearly related to the cetane number or other fuel property [89, 94, 95]. This differs from principle component analysis (PCA) which finds links and correlations between sets of data [96, 97]. In PLS, a vector of linear coefficients are developed, which can then be used to predict cetane numbers for fuels that weren't used to create the coefficients.

In this chapter, two different methods for predicting cetane number are evaluated. The first method takes a strictly composition-based approach to predicting cetane number. Two dimensional gas chromatography (GCxGC) testing is used to analyze the fuel in terms of each

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molecular class (paraffin, isoparaffin, naphthenes, aromatic, ect.) by carbon number. The composition of each class is then used to find the volume average carbon number for each class, and a pseudocomponent of that carbon number is used to represent the individual molecular class. Then, the method of Ghosh and Jaffe [26] is used to predict the cetane number for the fuel based on the pseudocomponents. Because of the form of the cetane formula, the pseudocomponent method used here is mathematically equivalent to including each surrogate component because each class shares the same blending number.

The second method for cetane prediction uses partial least squares (PLS) regression to relate the cetane number to the infrared spectra of the fuel [27-30, 93]. Both near-infrared (NIR) and Fourier Transform infrared (FTIR) spectra were used to create separate regressions. NIR and FTIR were selected for this work due to their greater portability than NMR. Neat fuels and the distillation fraction samples were used as a training set, and mixtures of the fuels were used as the testing set. A chemometric algorithm was developed that can be rapidly applied to predict cetane number based on spectroscopy.

5.2 Materials and Methods

5.2.1 Materials

5.2.1.1 Fuels

The seven fuels evaluated here are previously described in Chapter 4, section 4.2.1. This chapter focuses on the jet fuels: the six group B alternative fuels plus JP-8. Two different techniques were used to develop a wider variety of cetane numbers from the test set. The fuels were distilled, and the T10, T50, and T90 fractions were tested, which resulted in different compositions and cetane numbers for each fraction. The second technique analyzed blends of

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15%, 35%, 50%, 65% and 85% by volume of each alternative fuel in JP-8. Derived cetane numbers for each distillation fraction and blend were measured by TARDEC in Warren, MI.

5.2.1.2 Pure compounds

Six pure isoparaffin compounds were used for validation of the PLS model. These compounds were: 2-methylpentane, 3-methylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 2,2,4-trimethylpentane, and 2,2,4,4,6,8,8-heptamethylnonane. The compounds were selected because the specific isomer had a cetane number reported in the Murphy Compendium of Cetane Numbers [35], and were available from Sigma Aldrich. The cetane numbers and testing methods for the selected compounds are recorded in Table 5.1.

Table 5.1. Branched compounds used for comparison, with their cetane numbers and the method used to find the cetane number. Cetane numbers and measurement methods from the Murphy Compendium [35].

Compound	Measurement Method	Cetane Range (If multiple values given)	Cetane number used for benchmarking
2-Methylpentane	Blend or Correlated from Octane number	23-34	33
3-Methylpentane	Blend		30
2,3-Dimethylpentane	IQT		21
2,4-Dimethylpentane	CFR Engine		29
2,2,4-Trimethylpentane	Blend	12-17.5	14
2,2,4,4,6,8,8- Heptamethylnonane	Direct		15

5.2.2 Experimental Methods

5.2.2.1 Distillation

The distillation method is discussed in detail in Chapter 4, section 4.2.2.6. A two liter sample was distilled using a scaled up method similar to ASTM D86. One-hundred mL samples were collected, and the temperature was recorded after each sample collection. The sample referred to as T10 corresponds to the mixture of the 10% and 15% volume distilled samples, T50 corresponds to the mixture of the 45% and 50%, and T90 to the mixture of 85% and 90%.

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5.2.2.2 Derived Cetane Number

Tests for derived cetane number were performed at TARDEC in Warren, Michigan. An ignition quality tester (IQT) from Advanced Engine Technologies (AET) was used. ASTM D6890 was followed for all tests (Table 5.2). The cetane numbers for all fuels are shown in Figure 5.1, and are linear with composition in JP-8.

Table 5.2. Derived cetane numbers for all neat fuels, distillation fractions, and fuel mixtures.

	JP-8	IPK	HRJ	SPK2	HRJ-8	SPK	HRD
Neat Fuel	45.78	31.59	57.99	58.11	56.88	60.05	64.65
Distillation Fraction T10	41.95	31.2	53.11	57.30	49.88	52.96	55.08
Distillation Fraction T50	44.45	30.82	57.87	57.80	55.84	57.38	67.59
Distillation Fraction T90	49.91	30.77	64.53	58.38	64.89	63.83	73.90
15:85 JP-8:Fuel Mixture	-	33.35	55.88	56.21	54.96	56.36	62.16
35:65 JP-8:Fuel Mixture	-	36.66	54.00	54.07	52.70	53.98	58.04
50:50 JP-8:Fuel Mixture	-	39.22	52.13	51.73	51.05	52.52	55.62
65:35 JP-8:Fuel Mixture	-	41.52	50.02	50.01	49.53	49.62	52.97
85:15 JP-8:Fuel Mixture	-	43.77	48.01	47.68	47.76	47.99	48.97

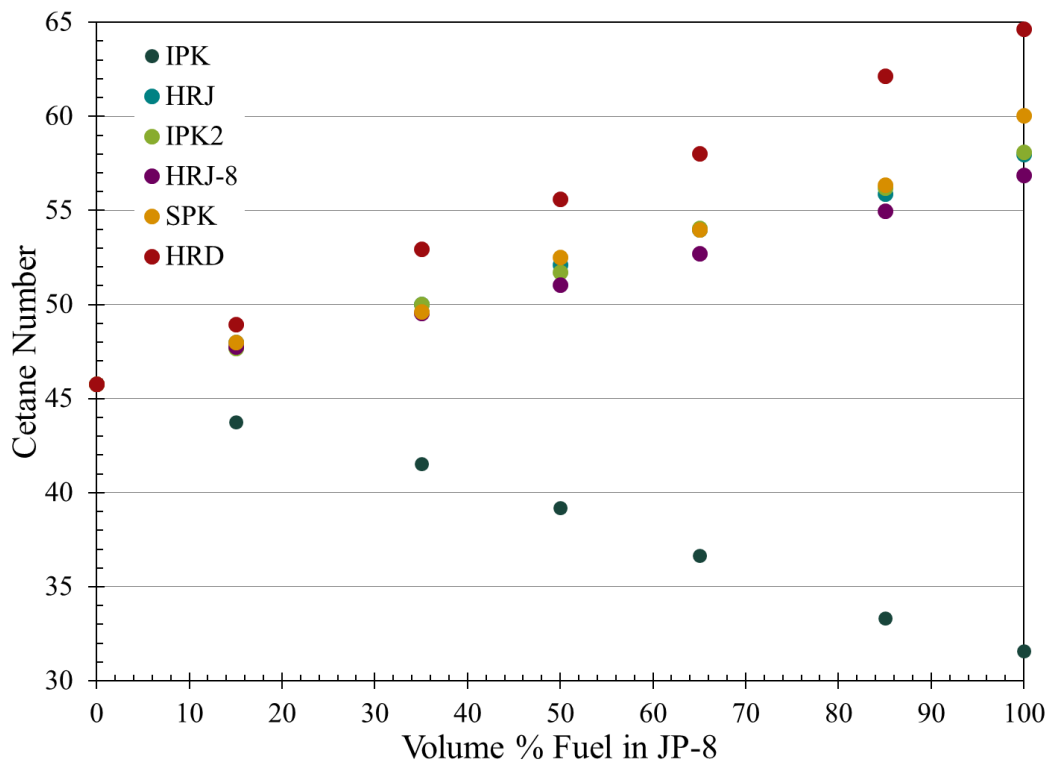


Figure 5.1. Cetane numbers for all alternative fuels in mixtures with JP-8.

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5.2.2.3 Two Dimensional Gas Chromatography

The GCxGC method is discussed in detail in Chapter 4, section 4.2.2.4. The GCxGC results were used to select the simple pseudocomponents for cetane number prediction.

5.2.2.4 Near-Infrared Spectroscopy (NIR)

NIR spectroscopy was used on all fuels, distillation fractions, and fuel mixtures. A Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer was used. Light absorbance was measured from 880–1580 nm in 2 nm intervals. The slit width was set to 5.00 nm with a gain of 1 and an integration time of 0.68 s. The baseline was assessed at both normal transmittance and zero transmittance. A quartz cuvette was used with a path length of 1 cm, and a blank cuvette was used as the reference. Simpson [93] was used for all NIR peak identification discussed in this section. The NIR spectra for the neat fuels are presented in Figure 5.2-Figure 5.5. Figure 5.2 shows the entire region, while Figure 5.3-Figure 5.5 focus in on the third overtone, second combination overtone, and first combination overtone respectively. There is a double peak in the range of 880–980 nm, as well as a broad peak from 980–1100 nm. The double peak at 880–980 nm represents the ratio of CH₃ to CH₂ groups. The peak at 980–1100 nm has not been identified.

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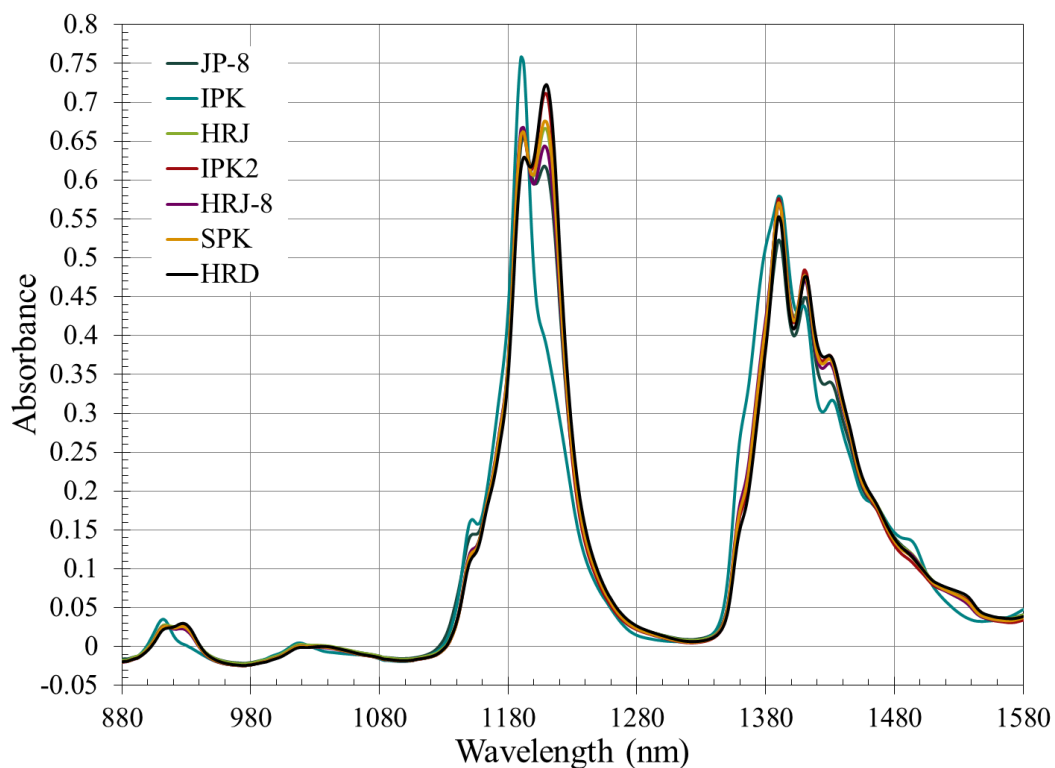


Figure 5.2. NIR spectra for all neat fuels.

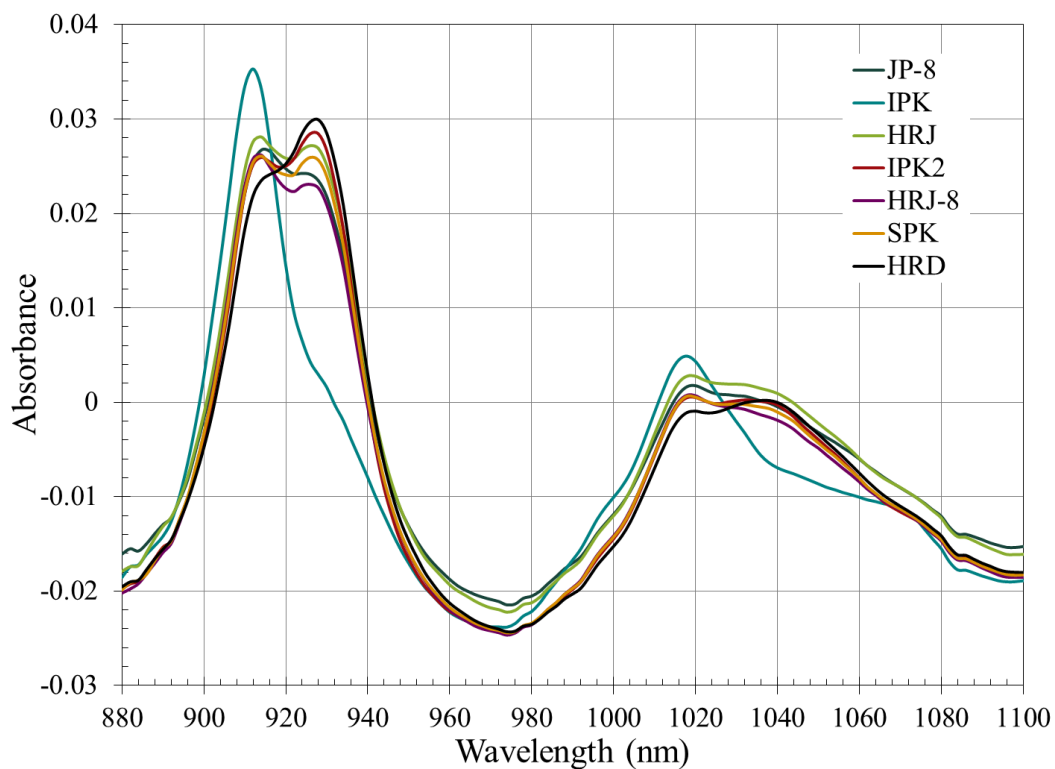


Figure 5.3. NIR spectra of the neat fuels, with focus on the third overtone region.

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Figure 5.4 shows a triplet peak from 1120–1280 nm. The shoulder at 1150–1160 nm is likely the aromatic CH group. The peak at 1160–1200 nm is likely caused by the paraffin CH₃ group, and the 1200–1240 nm peak the paraffin CH₂ group.

Figure 5.5 shows the final overtone section, with a triplet peak with a shoulder. It is unclear what contributes to the shoulder at 1340–1380 nm. The peak at 1380–1400 nm is most likely the CH₃ group, the peak from 1400–1420 nm the CH₂ group, and the peak at 1420–1460 nm the paraffin CH group.

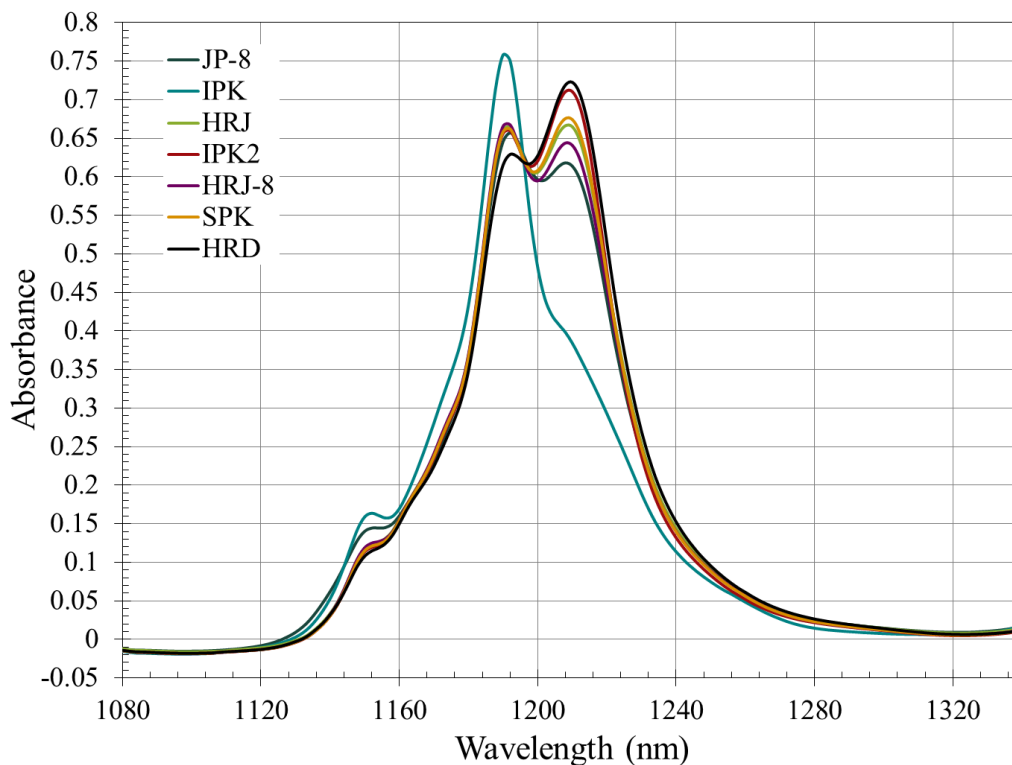


Figure 5.4. NIR spectra of the neat fuels, with focus on the second combination overtone region.

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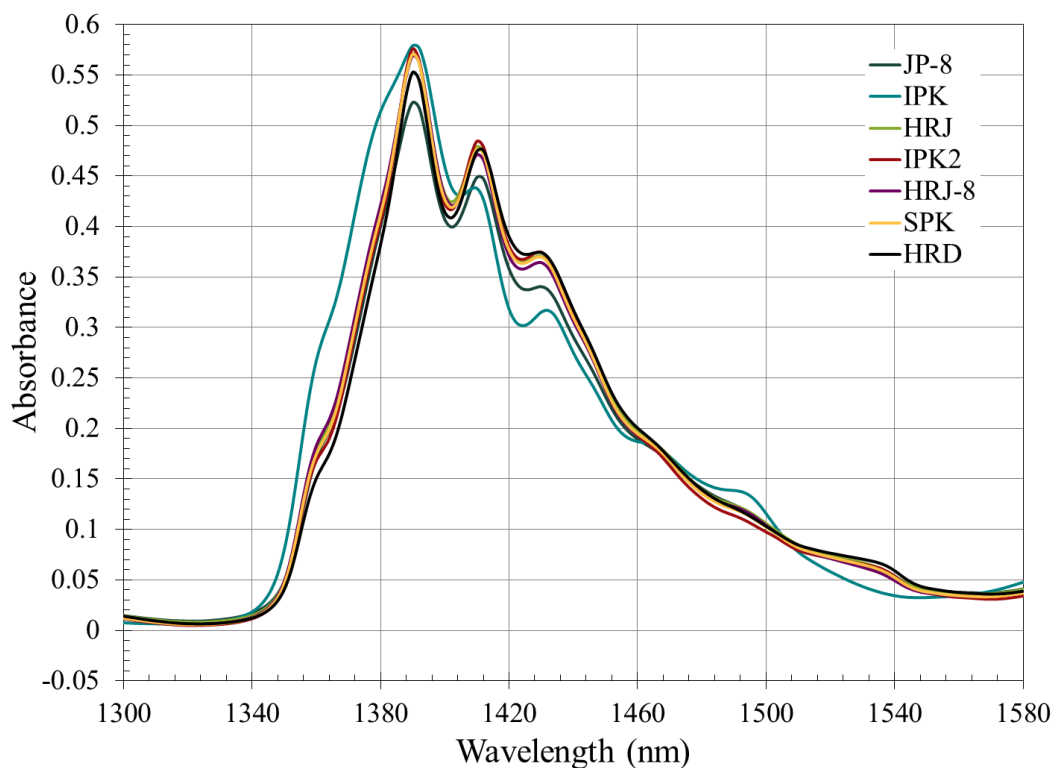


Figure 5.5. NIR spectra of the neat fuels, with focus on the first combination overtone region.

A few examples for the distillation fraction spectra and mixture spectra are shown here. The spectra for all fuels and mixtures can be found in Appendix E. The distillation fractions of IPK show very little difference in absorbance relative to the neat fuel (Figure 5.6). The IPK fuel has a narrower mass distribution than the other fuels. Because of this, the distillation fractions have a smaller differences in composition than other fuels, and also very little difference in derived cetane numbers as shown in Table 5.2. The HRJ-8 fuel has a bimodal distribution of molecular weight components, spread out over a larger range than the IPK fuel. Consequently, the distillation fractions exhibit a larger difference in spectra (Figure 5.7). For all fuels, the more diverse the fuel composition, the larger the difference between the T10 and the T90 spectra.

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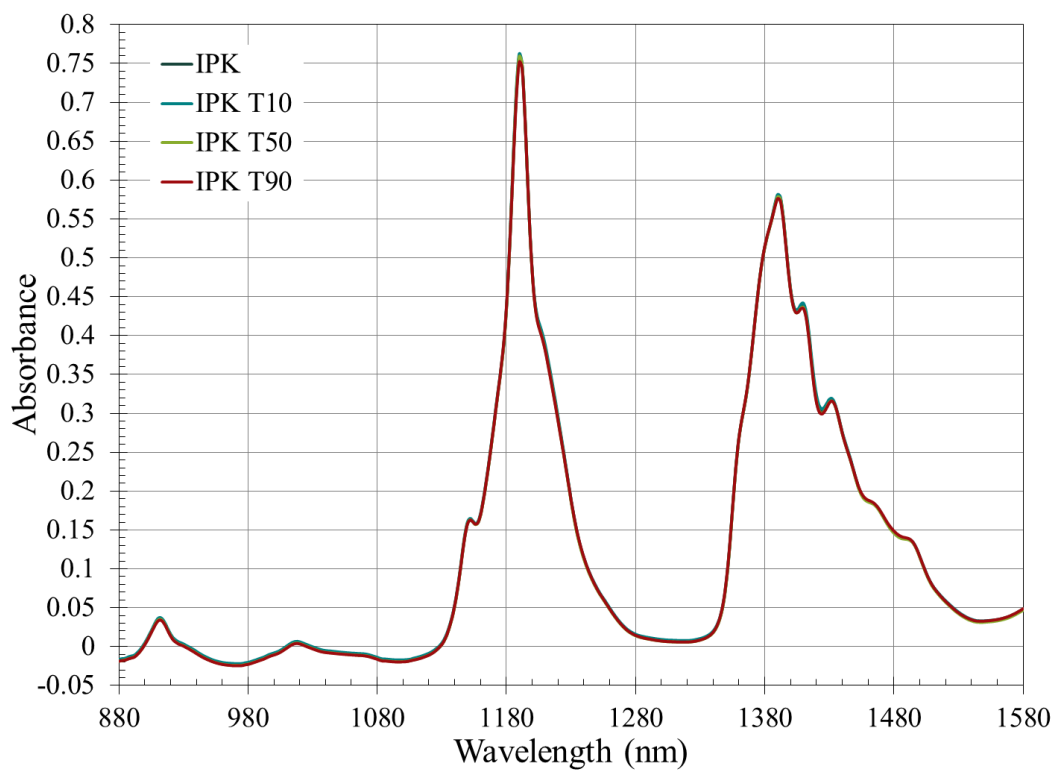


Figure 5.6. NIR spectra for neat IPK and its distillation fractions. Differences between spectra a difficult to see.

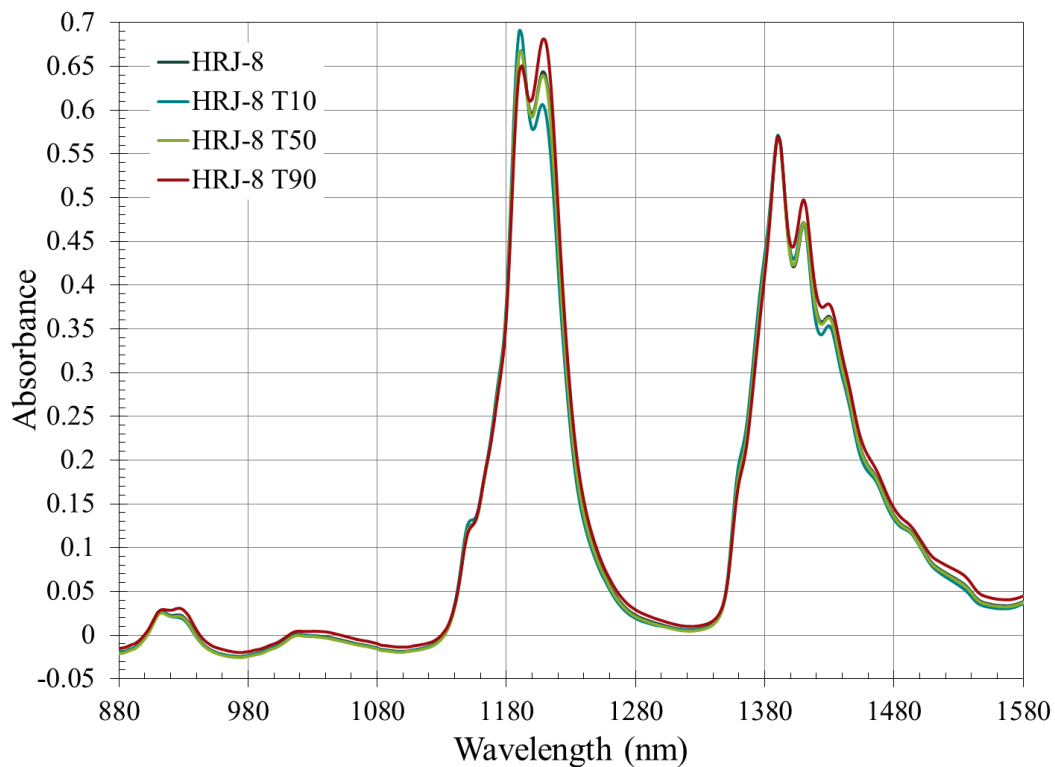


Figure 5.7. NIR spectra for neat HRJ-8 and its distillation fractions.

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The IPK and the JP-8 fuels have largely different compositions, so the spectra of the blends in Figure 5.8 show a strong composition dependence. The largest changes are in the 1200–1240 nm peak, and the shoulder at 1380 nm. The HRD and JP-8 are closer together in composition and the spectral differences between the mixtures can mainly be seen in the 1200–1240 nm peak and the triplet peak at 1340–1460 nm (Figure 5.9).

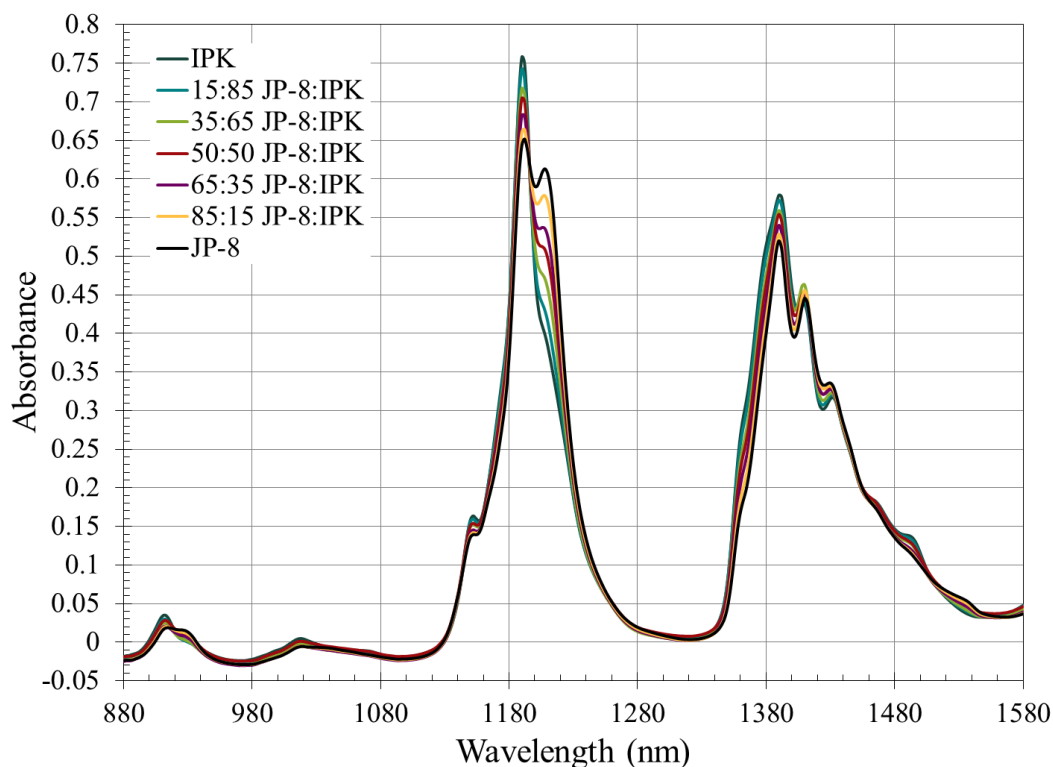


Figure 5.8. NIR spectra for mixtures of JP-8 and IPK.

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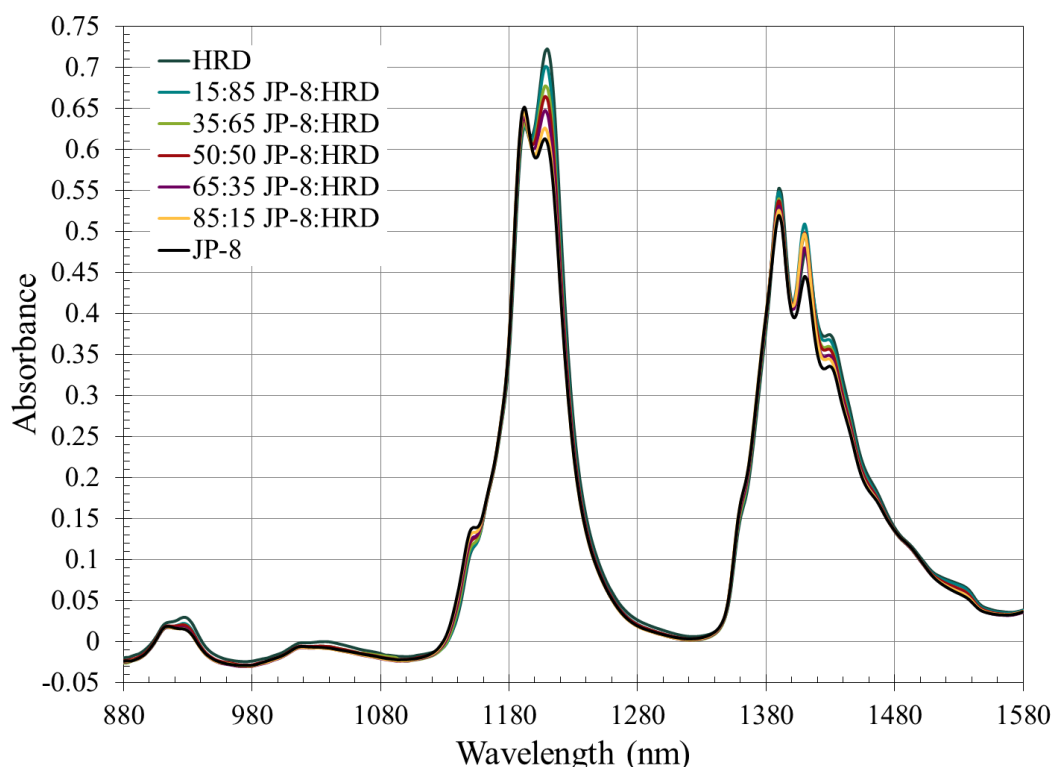


Figure 5.9. NIR spectra for mixtures of JP-8 and HRD.

5.2.2.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was performed on all fuels, distillation fractions, and fuel mixtures. A Perkin Elmer Spectrum One FTIR spectrometer was used with a universal ATR sampling unit. 2-3 drops of each sample were placed on the ATR plate, and a Teflon lined plastic vial cap was placed over the sample to reduce evaporation during scans. Four scans were taken from $4000\text{--}650\text{ cm}^{-1}$ and an ATR correction was applied. Absorbance values were reported at each wavenumber. The spectra for the neat fuels are presented in Figure 5.10-Figure 5.13. The FTIR peak identification in this section comes from Socrates [98], as well as comparison with known compounds through NIST Webbook [53]. The full range is shown in Figure 5.10, and Figure 5.11-Figure 5.13 show the three main peak absorbance regions. Figure 5.11 shows a close up view of the aromatic

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region, Figure 5.12 shows a view of the carbon-carbon stretch region, and Figure 5.13 shows the carbon-hydrogen stretch region.

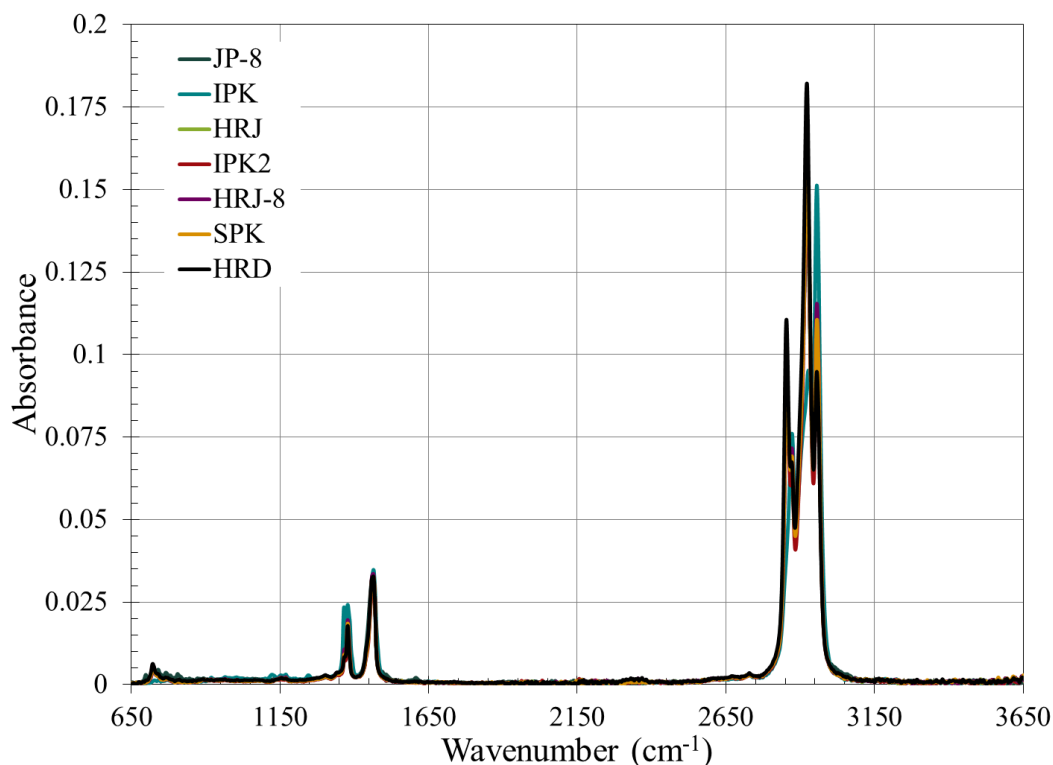


Figure 5.10. FTIR spectra for all neat fuels.

The first region is from 650–950 cm^{-1} and has a quintuple or double peak, depending on the fuel (Figure 5.11). This region shows the out of plane bending for the aromatic ring. The number of peaks reflects the substitution pattern of the aromatic rings. Most of the fuels are mono-substituted, with a peak at about 725 cm^{-1} and a small shoulder at 745 cm^{-1} . The exception is JP-8, which has a quintuple peak in this region. It is possible this is a sextuplet or more split peak, but the signal-to-noise ratio in this region makes it hard to distinguish the peaks from the background noise.

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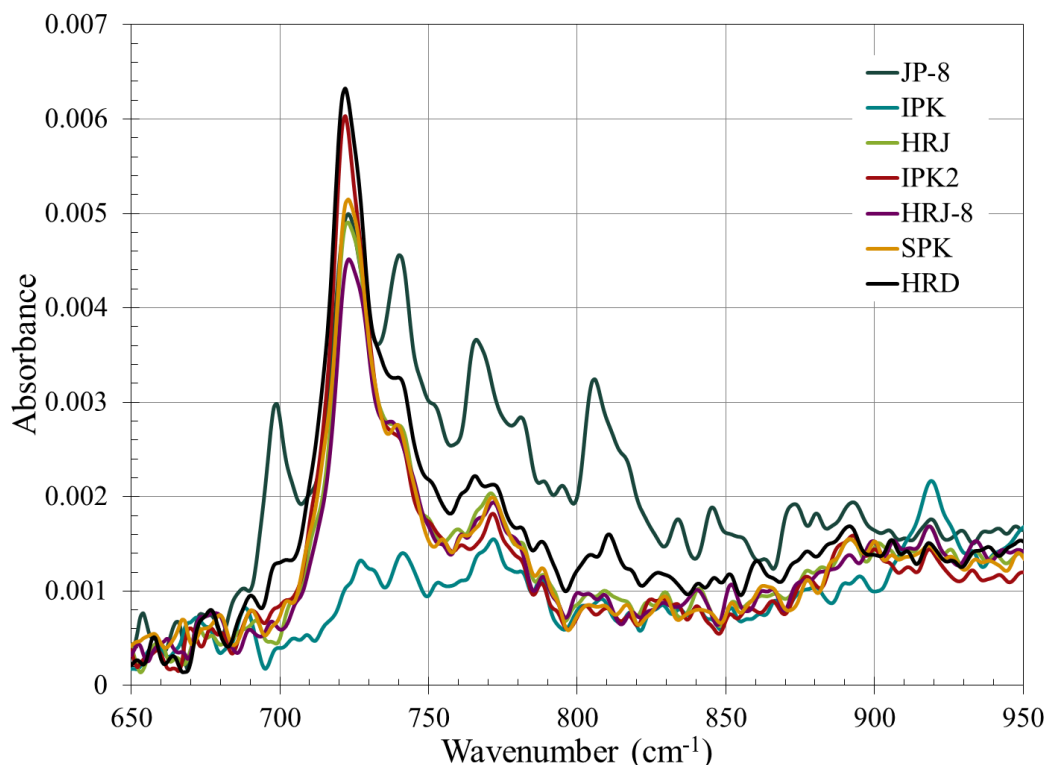


Figure 5.11. FTIR spectra for all neat fuels, with a focus on the aromatic out of plane bending region.

Figure 5.12 shows the carbon-carbon stretch region. There are two peaks in this region, a double peak from 1350–1400 cm^{-1} , and what might be a non-resolved double peak at 1425–1500 cm^{-1} . For most fuels except the IPK, the double peak at 1350–1400 cm^{-1} appears more as a single peak with a shoulder. Since the IPK likely has a much higher ratio of multi-branched to mono-branched isoparaffins than the other fuels, the peak at 1350–1400 cm^{-1} most likely represents the side chain carbon stretch. The peak from 1425–1500 cm^{-1} likely represents the stretching of the backbone carbon chain. Some of the fuels show the peak “leaning” to one side or the other of the main peak. This “lean” might reflect the position of the side chains on the paraffin backbone.

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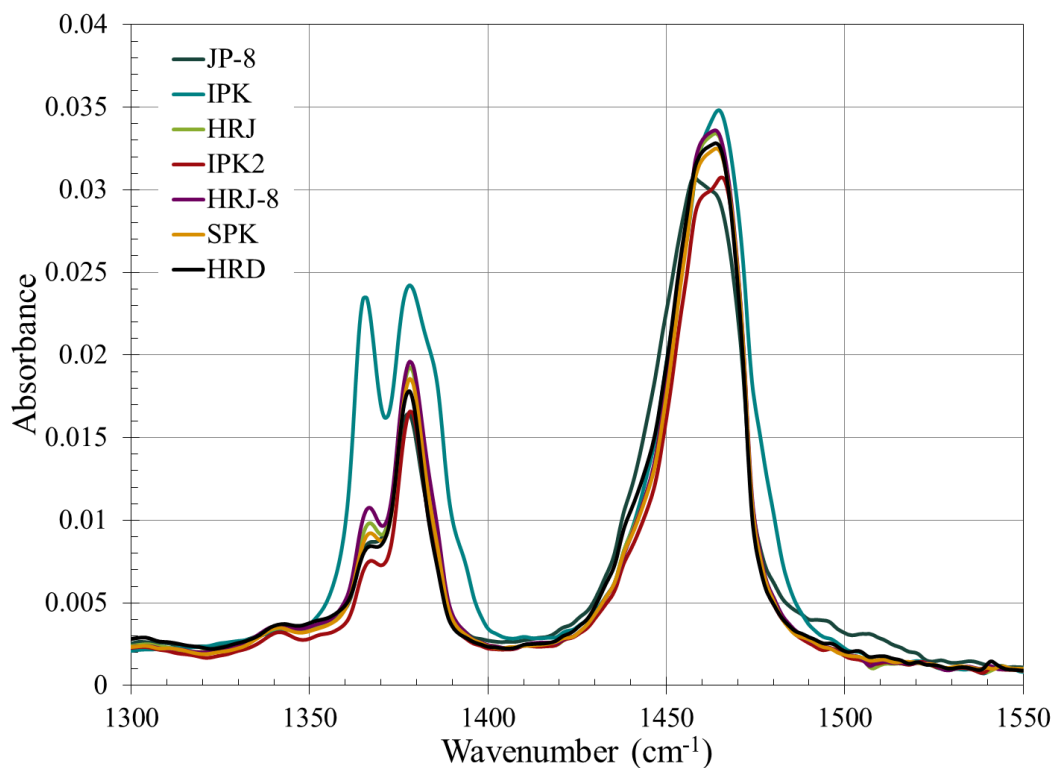


Figure 5.12. FTIR spectra for all neat fuels, with a focus on the carbon-carbon stretch region.

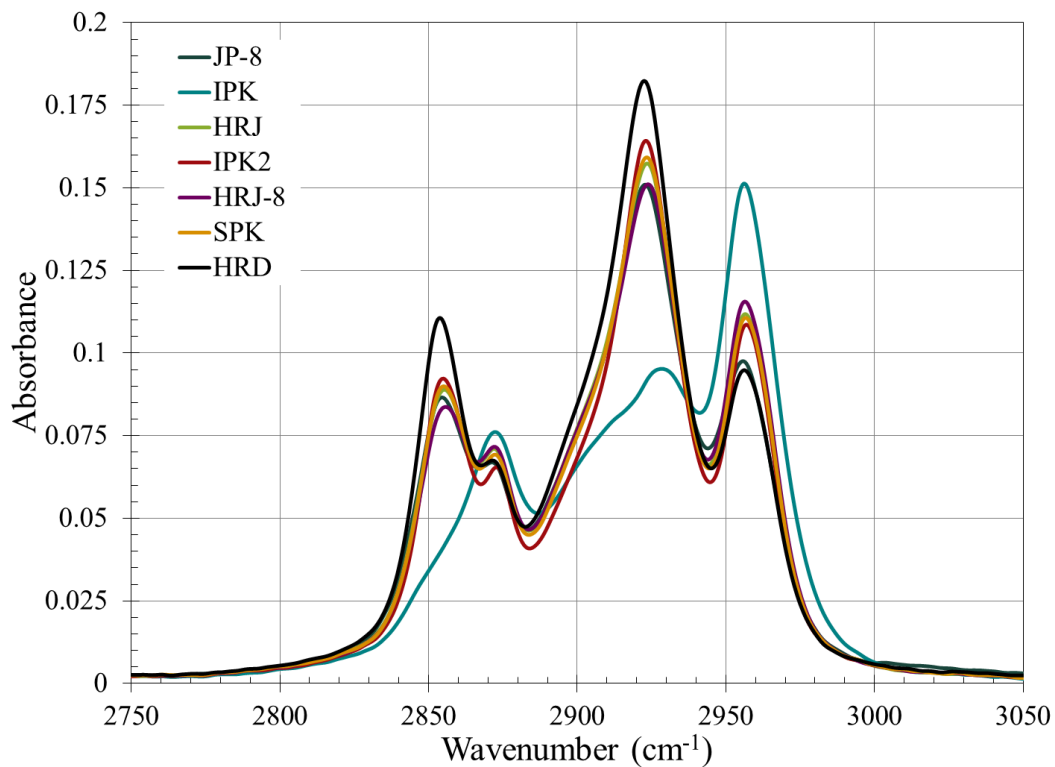


Figure 5.13. FTIR spectra for all neat fuels, with a focus on the carbon-hydrogen stretch region.

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Figure 5.13 shows a close up view of the carbon-hydrogen stretching region. There is a quadruplet peak from 2825–3000 cm^{-1} . This region contains the stretches for all the carbon-hydrogen bonds, including the CH_3 , CH_2 , and CH groups in paraffins, isoparaffins, and aromatic side chains.

The FTIR spectra for distillation fractions and mixtures of select fuels are presented in Figure 5.14-Figure 5.17. Figures for all fuel distillation fractions and mixtures can be found in Appendix E. As with the NIR spectra, the more diverse the composition of the neat fuel, the more differences there are in the distillation fraction and mixture spectra. However, the peaks in the FTIR spectra are sharper than the NIR spectra, and the FTIR differences are primarily in peak height and more difficult to discern with the eye than the NIR differences.

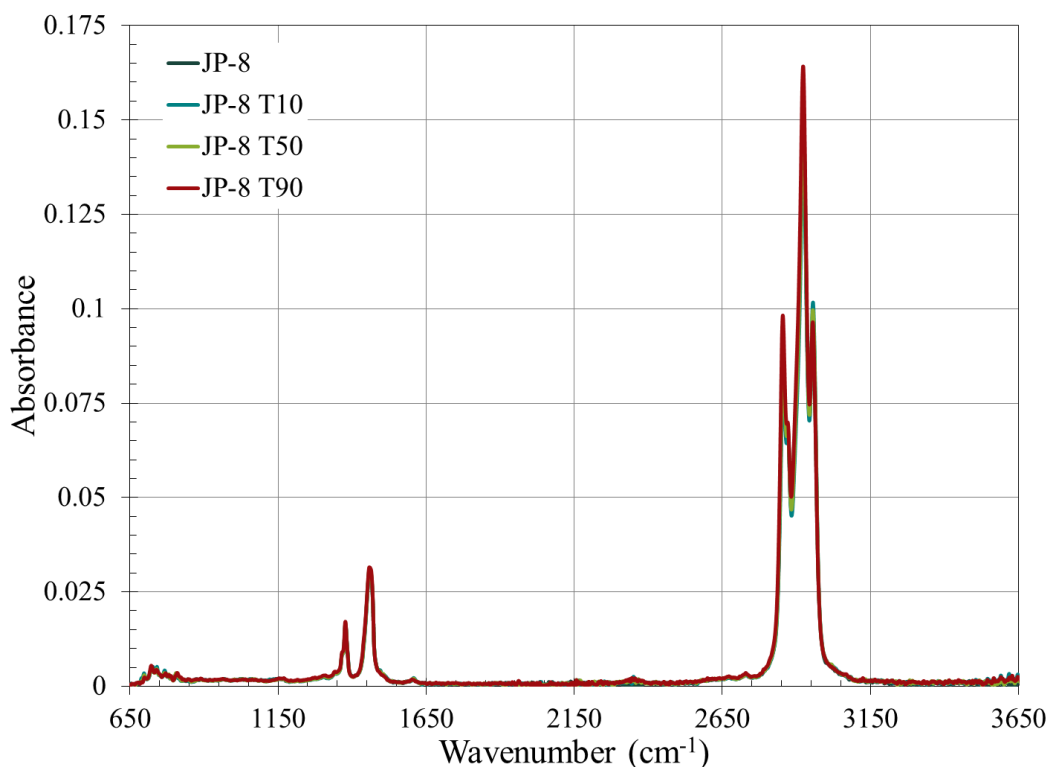


Figure 5.14. FTIR spectra for neat JP-8 and its distillation fractions.

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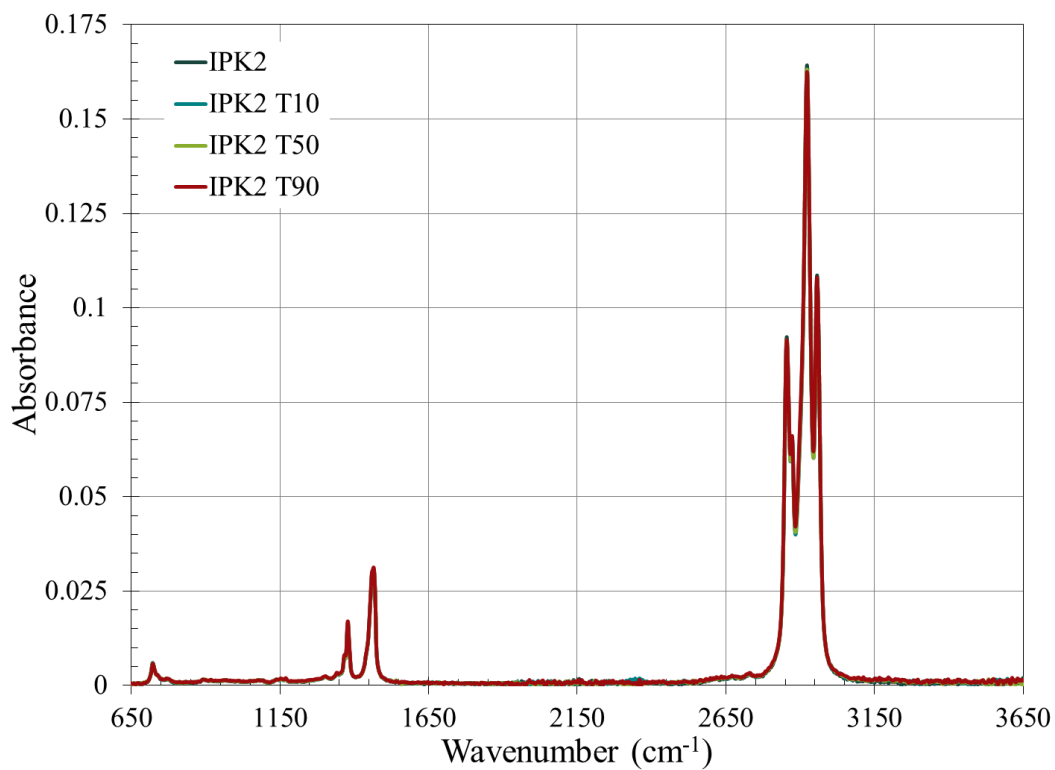


Figure 5.15. FTIR spectra for neat SPK2 and its distillation fractions.

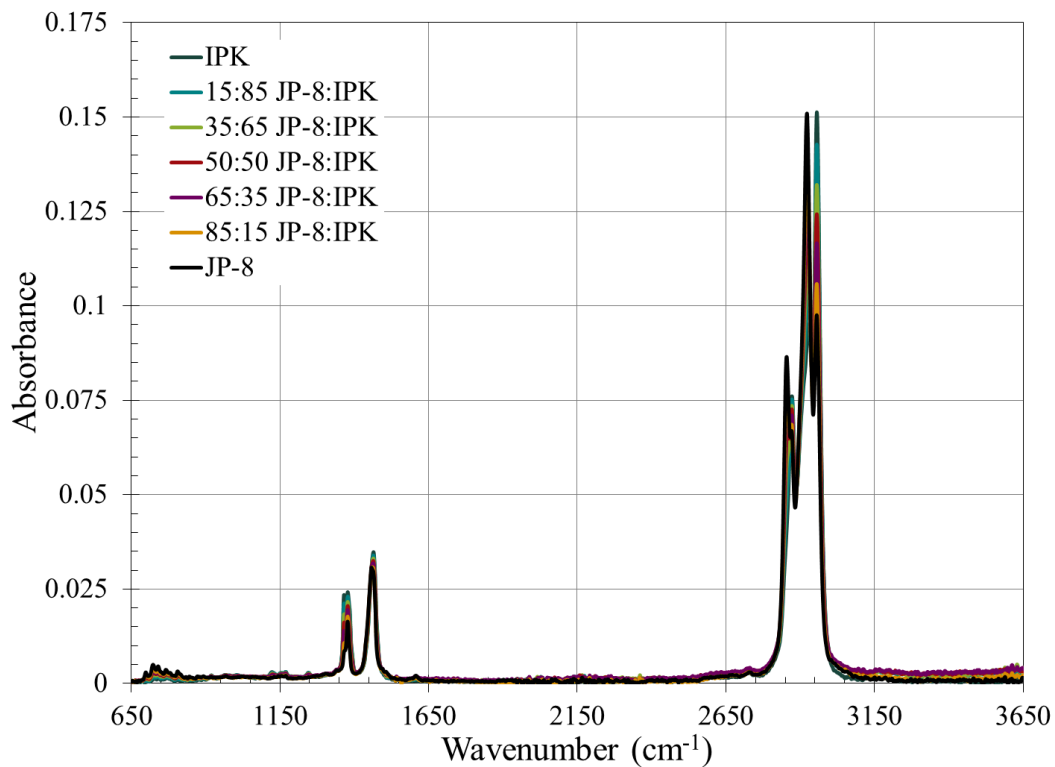


Figure 5.16. FTIR spectra for mixtures of JP-8 and IPK.

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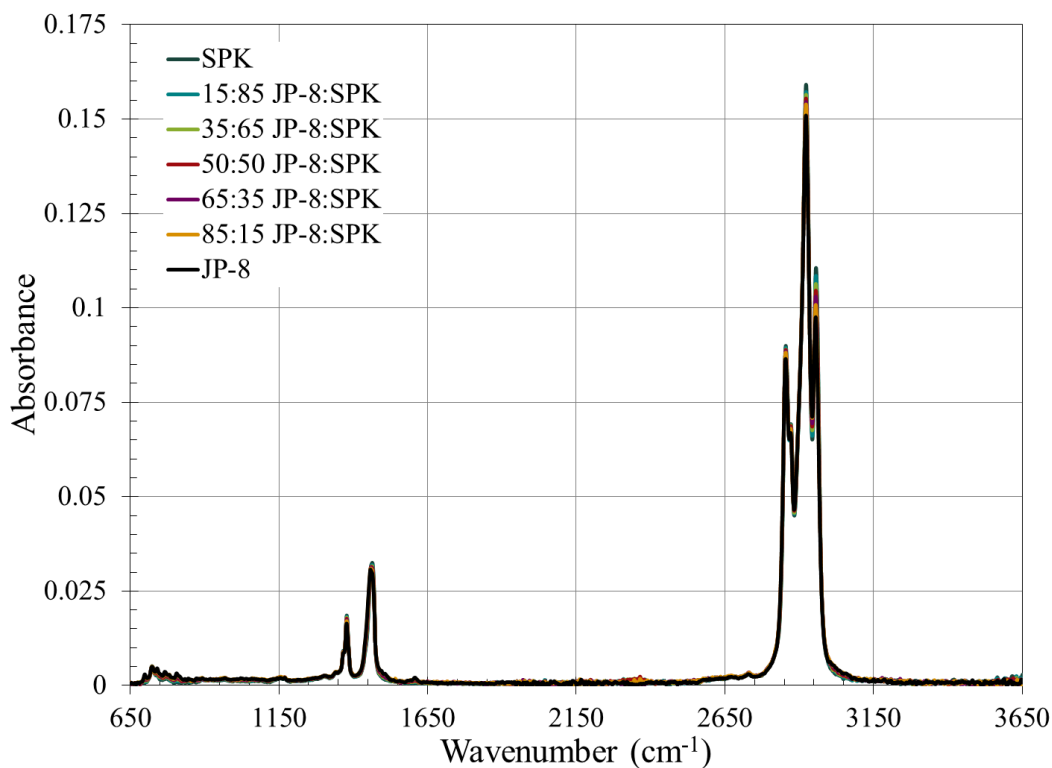


Figure 5.17. FTIR spectra for mixtures of JP-8 and SPK.

5.2.3 Calculation Methods

5.2.3.1 Cetane Number by Molecular Class via the method of Ghosh and Jaffe

Cetane numbers of fuel mixtures were estimated by the method of Ghosh and Jaffe [26]. This model relates the volume fraction, v_i , pure component cetane number CN_i , and an adjustable parameter, β_i , to the mixture cetane number, CN . The general form of this equation is:

$$CN = \frac{\sum_i v_i \beta_i CN_i}{\sum_i v_i \beta_i} \quad (5.1)$$

Equation (5.1) permits the lumping of fuel classes into a single pseudocomponent. This can both simplify the individual fuel surrogates, and also allow a mixture of two fuels to be represented as a binary mixture of two pseudocomponents. The strategy is justified by the form of Equation 5.1 and explained here. The pseudocomponent model is valid if the

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pseudocomponent β value, β_x , is defined as the volume average of the surrogate component β s such that:

$$v_x = \sum v_i \quad (5.2)$$

$$\beta_x = \sum \frac{v_i}{v_x} \beta_i \quad (5.3)$$

$$CN_x = \sum_i \frac{\frac{v_i}{v_x} \beta_i CN_i}{\beta_x} \quad (5.4)$$

where v_x is the volume fraction of the summed components assuming excess volume is zero. The Ghosh and Jaffe method is consistent with equations (5.2), (5.3), and (5.4) as proven in Appendix F, where pure component β s and cetane numbers are also tabulated.

According to equations (5.1) through (5.4), all components sharing a common β value can be lumped as a single pseudocomponent using algebraic association. For example, because all paraffins have the same β , the paraffin portion of the fuel surrogate can be represented by one representative paraffin pseudocomponent calculated by the volume fraction weighted cetane number.

The cetane number for compounds other than n-paraffins can depend on the isomerization of the compounds, and there can be multiple components with the same carbon number and class that have significantly different cetane numbers. For this reason, the pseudocomponents used for these surrogates have cetane numbers that are purely based on the carbon number. This work makes a distinction between mono-isoparaffins (single-branched) and multi-isoparaffins (multi-branched) for the determination of the surrogate cetane number because the cetane number tends to decrease with branching for a given carbon number. A mono-isoparaffin has one tertiary carbon, and a multi-isoparaffin has multiple tertiary or quaternary carbons, but even this distinction does not result in clear trends. Cetane numbers for various

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compounds from the Murphy Compendium of Experimental Cetane Number Data [61] are plotted against their carbon numbers in Figure 5.18. The isoparaffin cetane numbers scatter significantly, with an overall trend of increasing with carbon number. Selecting an exact cetane number for a given carbon number is impossible because cetane numbers for a given carbon number can vary by nearly 40 cetane numbers. The Ghosh and Jaffe paper has a discrepancy between the cetane numbers listed for their mono- and multi-isoparaffins in the table and those shown on their figures.

Because a fuel is a composite of many branched compounds, some averaging is justified. An arbitrary line was placed through both the mono- and multi-isoparaffins, as well as an average line between the two. For the fuel surrogates presented here, either the plotted line for the mono-isoparaffins are used, or a 50-50 mixture of the mono-iso- and multi-isoparaffins are used, depending on what gives the best fit for the neat fuel. Thus, the neat fuel cetane numbers were correlated instead of predicted. Blends were then predicted based on the fitted neat fuel cetane numbers.

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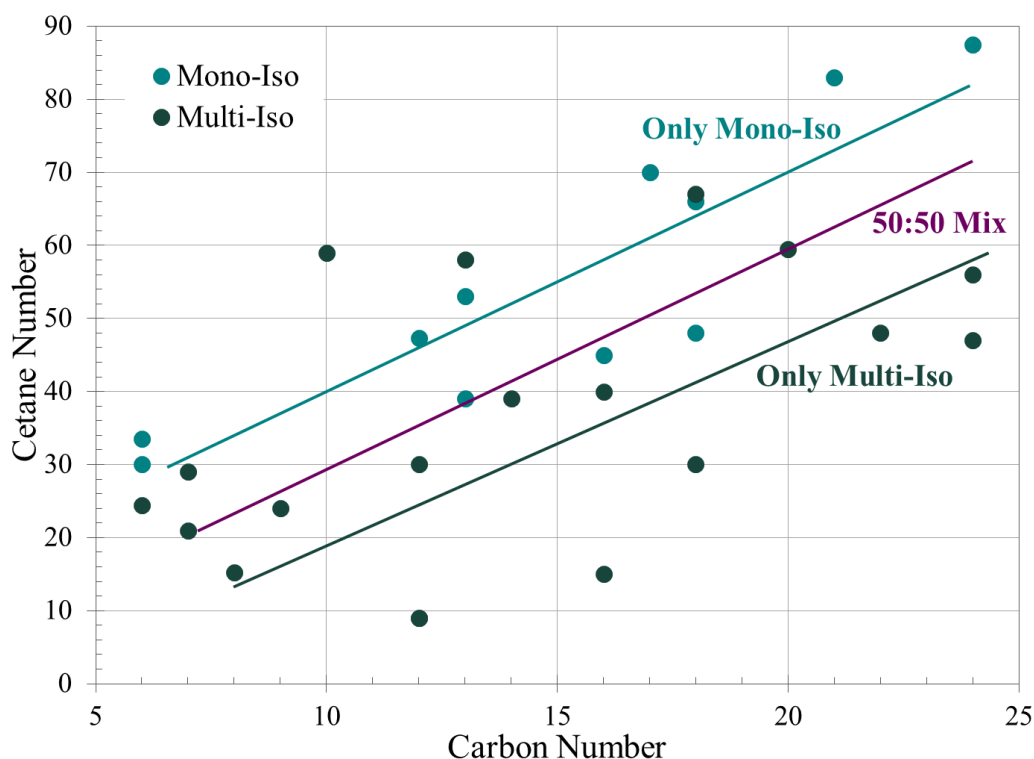


Figure 5.18. Plot of mono- and multi-isoparaffins, with representative lines for the values used in the cetane number prediction.

The cetane number that is used to represent each lump could either be calculated using a volume average of the cetane numbers of the individual paraffin components, or the average carbon number can be calculated using the volume fractions, and that carbon number component can represent the lump. For the isoparaffin lump, because a linear approximation is used, the two methods give the same representative cetane number. For the paraffin lump, changing the method resulted in a 0.02-0.2% change in the prediction of the neat fuel cetane number, depending on the total paraffin content of the fuel. Because these changes were negligible, the simpler method of using the volume average carbon number was used for the pseudocomponent selection.

An overall fuel pseudocomponent is then built from pseudocomponents for each of the 7 molecular classes: n-paraffins, isoparaffins, monocycloparaffins, dicycloparaffins, mononuclear

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aromatics, polynuclear aromatics, and monocycloaromatics. The method is algebraically consistent with writing the sum for each component using equation (5.1), but provides a simple way to represent the fuel as a single component when fuels are blended assuming excess volume is zero.

5.2.3.2 Cetane Number Using Partial Least Squares Regression

Experimental cetane values were correlated with NIR and FTIR spectra using Partial Least Squares (PLS) regression. To provide wide dissemination of the resulting correlation, the program R was used to do the regression [99]. R was selected because it is an open source program that can be downloaded and run on any computer, and has a PLS regression package built into the program. Code was written for R to process and regress the data in a consistent manner, and is presented in Appendix G. The cetane number and absorbance for each sample was fed to the program, and the data was broken up into a training set and a testing set. The training set was regressed to develop the regression coefficients, and those coefficients were used to calculate the cetane numbers for the data not used in the development of the coefficients. This allows the model to be tested with fuels that were not directly used in the regression. The neat fuels and distillation fractions were used as the training set, and the blends were used as the predicted (testing) set. A section of the code permits the removal of baseline sections if desired.

An important factor in the regressions is the number of regression components. Within the PLS regression, the term “components” refers to the number of times that the error is re-regressed. The R statistical package “pls” combines these regression components into one set of regression coefficients. The coefficients are then multiplied against the absorbance values at each wavelength or wavenumber and summed to give the predicted cetane number. The resulting equation looks like:

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$$CN_{predicted} = \sum_n b_n A_n + C \quad (5.5)$$

where $CN_{predicted}$ is the predicted cetane number, n is the number of wavelengths or wavenumbers at which there is a measured absorbance, b_n is the regressed coefficient at the n^{th} wavelength or wavenumber, and A_n is the absorbance at the n^{th} wavelength or wavenumber, C is the intercept.

The data was mean centered during processing. Mean centering of the data allows for the intercept C to be calculated. Mean centering is performed on the training and testing sets separately. To mean center the data, the absorbance at each wavelength is averaged, then the average is subtracted from the absorbance of each sample at that wavelength. The experimental cetane numbers are mean centered as well. The intercept is calculated using the values from the training set, where the experimental cetane numbers are known. This allows the model to be extended to datasets that were not used in the training set. The intercept is calculated using the average values for the cetane number and the absorbance at each wavelength such that:

$$C = CN_{train,mean} - \sum_n b_n A_{train,mean,n} \quad (5.6)$$

where $CN_{train,mean}$ is the average of the cetane numbers in the training set, and $A_{train,mean,n}$ is the average of the absorbance values of the training set at the n^{th} wavelength or wavenumber. For each type of spectroscopy, the testing set used the same coefficients and intercepts developed from the training set.

5.3 Results and Discussion

5.3.1 Ghosh and Jaffe Method

The predicted cetane numbers are compared to the experimental data in Figure 5.19- Figure 5.24. In these figures, the experimental data is presented as points with error bars for the

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experimental error, and the predicted cetane numbers are presented as curves. The curves are named based on the assumption that was made about the branching of the isoparaffin pseudocomponent that was used. In Figure 5.19, the selected isoparaffin component for both the JP-8 and IPK fuels are adjusted simultaneously. For Figure 5.20-Figure 5.24, the optimum JP-8 surrogate was used, and only the isoparaffin component of the alternative fuel was adjusted. The cetane numbers used for both groups are presented in Appendix F.

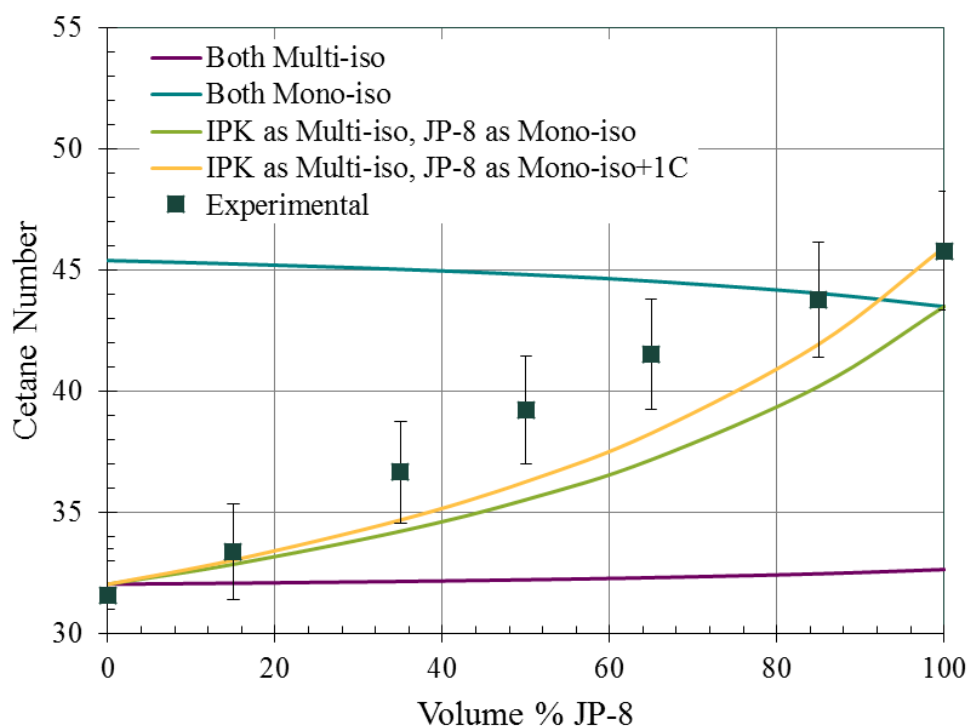


Figure 5.19. Predictions of the cetane number of mixtures of JP-8 and IPK compared to experimental results. Both the JP-8 and IPK fuels are varied to find the correct isoparaffin content and carbon number.

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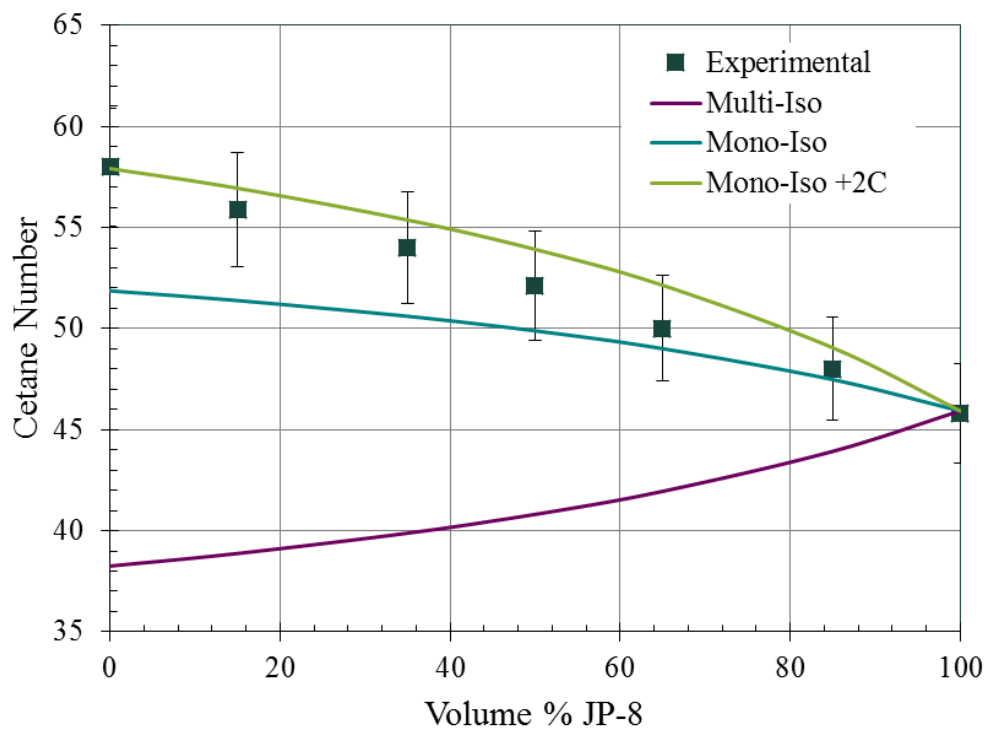


Figure 5.20. Predictions of the cetane number of mixtures of JP-8 and HRJ compared to experimental results.

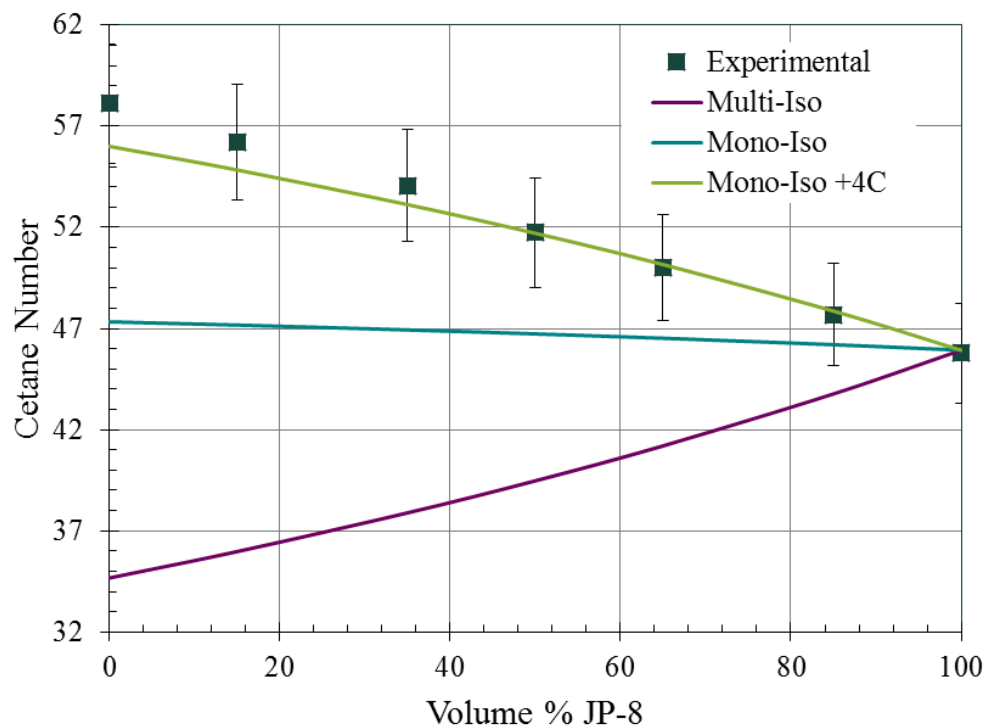


Figure 5.21. Predictions of the cetane number of mixtures of JP-8 and SPK2 compared to experimental results.

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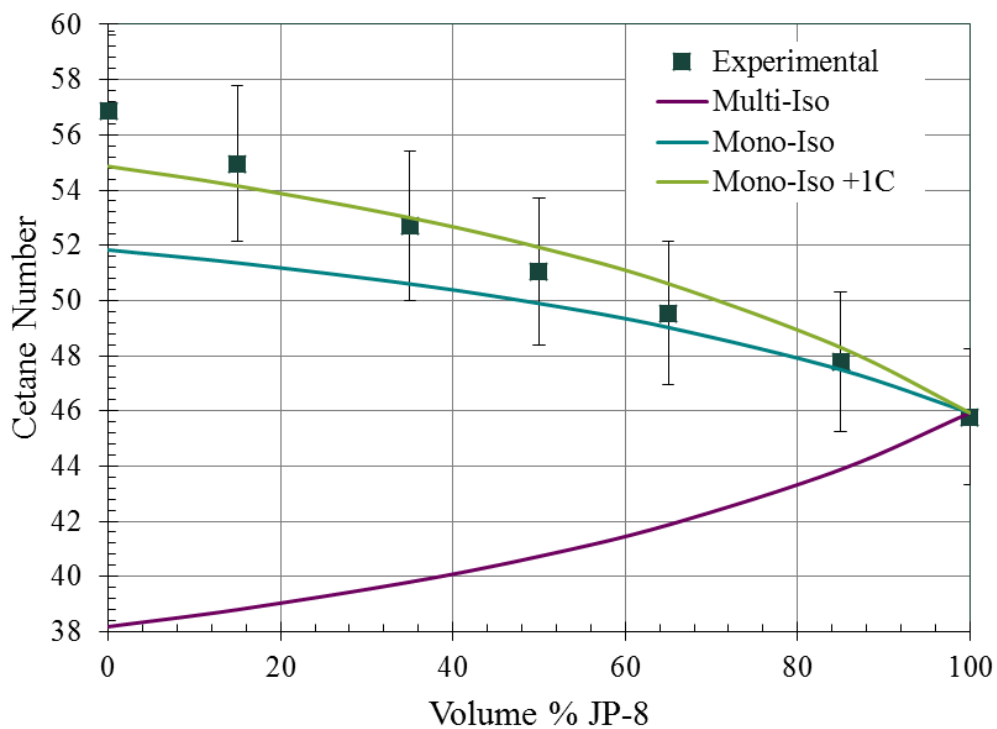


Figure 5.22. Predictions of the cetane number of mixtures of JP-8 and HRJ-8 compared to experimental results.

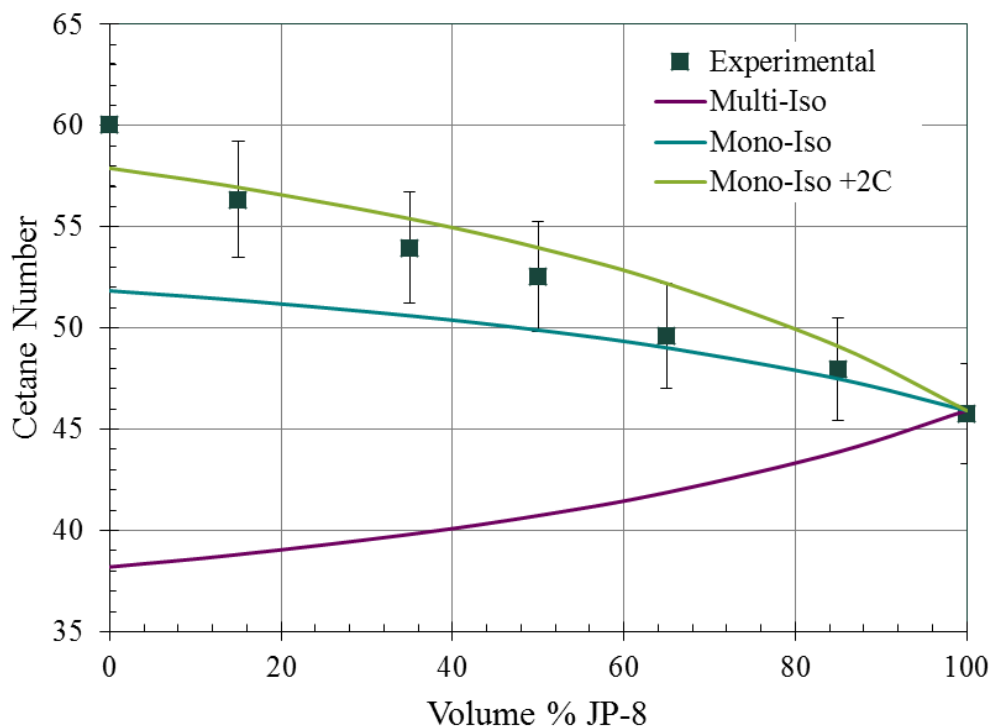


Figure 5.23. Predictions of the cetane number of mixtures of JP-8 and SPK compared to experimental results.

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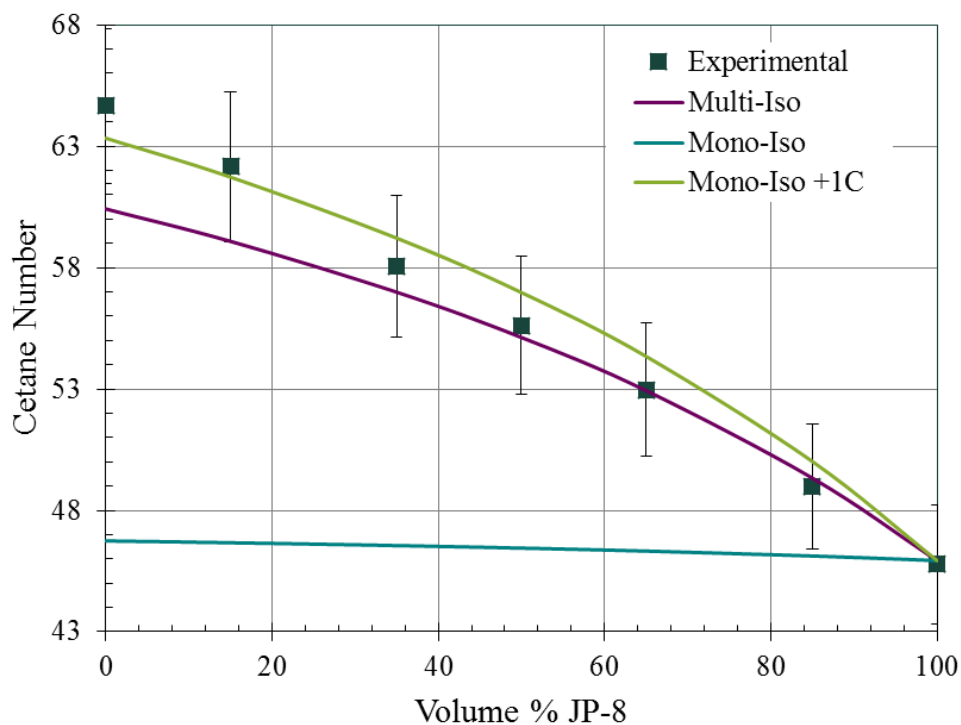


Figure 5.24. Predictions of the cetane number of mixtures of JP-8 and HRD compared to experimental results.

In some cases, the composition of the neat alternative fuel needed to be adjusted to get a better fit. This is noted by, for example, “+2C”, which indicates that a compound is selected for the surrogate that two carbons larger than the average determined by the GCxGC testing. The initial surrogates and the concentrations of each functional class are presented in Table 5.3 and Table 5.4.

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Table 5.3. Surrogate concentrations and components as determined by averaging the GCxGC results (JP-8, IPK, HRJ, and SPK2).

Class	JP-8		IPK		HRJ		SPK2	
	Carbon Number	Vol %	Carbon Number	Vol %	Carbon Number	Vol %	Carbon Number	Vol %
n-Paraffin	12	23.44	11	0.36	12	12.46	10	44.1
Iso-Paraffin	12	34.65	11	98.97	13	85.87	11	55.25
Mono-Cyclohexane	12	20.99	10	0.11	10	1.53	10	0.52
Di-Cyclohexane	12	5.07	14	0.04	12	0	10	0.05
Alkylbenzene	11	11.09	10	0.38	10	0.04	10	0.05
Diaromatic	12	1.24	12	0.02	12	0.01	10	0
Cycloaromatic	12	3.29	10	0.12	10	0.02	10	0

Table 5.4. Surrogate concentrations and components as determined by averaging the GCxGC results (HRJ-8, SPK, and HRD)

Class	HRJ-8		SPK		HRD	
	Carbon Number	Vol %	Carbon Number	Vol %	Carbon Number	Vol %
n-Paraffin	12	10.67	11	10.67	16	19.78
Iso-Paraffin	13	88.01	13	88.01	16	74.05
Mono-Cyclohexane	9	1.21	9	1.21	14	2.66
Di-Cyclohexane	11	0.08	12	0.08	13	1.49
Alkylbenzene	10	0	10	0	14	2.03
Diaromatic	10	0	10	0	14	2.03
Cycloaromatic	10	0	10	0	13	0.85

For all fuels except the IPK fuel, the mono-isoparaffin numbers give better pseudocomponent results than the multi-isoparaffins. For all fuels, the method is able to model the cetane number of the neat fuels within experimental error, once an isoparaffin component with a higher carbon number is substituted for the neat fuels. The adjustment however, compromises the intention of providing a predictive method. For all fuels except the IPK (Figure 5.19), the adjusted carbon number pseudocomponents can predict the cetane number across all mixture concentrations to within experimental error as well. Because there is high uncertainty in

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the correct values to use for the pure component cetane numbers, the effect of a shift of one or two carbon numbers in the surrogate compositions was explored. The only fuel that needs a shift of more than two carbon numbers is the SPK2 fuel (Figure 5.21).

The model always predicts curvature not present in the experiments. Representation of curvature was intended by the model authors, but the fuels considered in this work do not exhibit curvature. The curvature occurs when beta values for the components are different. Curvature is dependent on the difference in β values for the pseudocomponents. The larger the difference between the two pseudocomponent β values, the larger the curvature. A possible cause of the curvature is incorrect beta values for the isoparaffins. The fuels in this study had a much higher isoparaffin content than most petroleum fuels, and thus may be quite different than refinery fuels used to develop the β values. The GCxGC results shown in Chapter 4, section 4.2.2.4, show a distinct difference in the diversity of components represented in alternative fuels versus petroleum fuels. Because of these large composition differences, it is possible that re-regressing the beta values with more alternative fuels would result in a better prediction for the alternative fuels.

The surrogates presented here have significantly less error than the surrogates developed in Chapter 4. The error in the cetane number for those surrogates was approximately 20%, while the neat fuels here have <4% error for the final surrogates. However, the surrogates developed here have highly inaccurate cloud point temperatures and distillation curves. These surrogates work well for the prediction of neat fuel cetane number, and the cetane number of blends, but do not extend to any additional fuel properties.

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5.3.2 NIR and FTIR Predictions

5.3.2.1 Fuel Prediction

The results of the PLS regressions are shown in Figure 5.25-Figure 5.28. In the case of the NIR results, reducing the number of regression components from 25 to seven results in an increase for the training set error from 0.00027% to 1.0% (Table 5.5). However, the reduction improves the prediction in the testing set from 7.3% error to 0.96% (Table 5.5). This is due to the regression coefficients becoming overly specific to the training set when too many regression components are used. The improvement in the training set prediction outweighs the small increase in error for the training set.

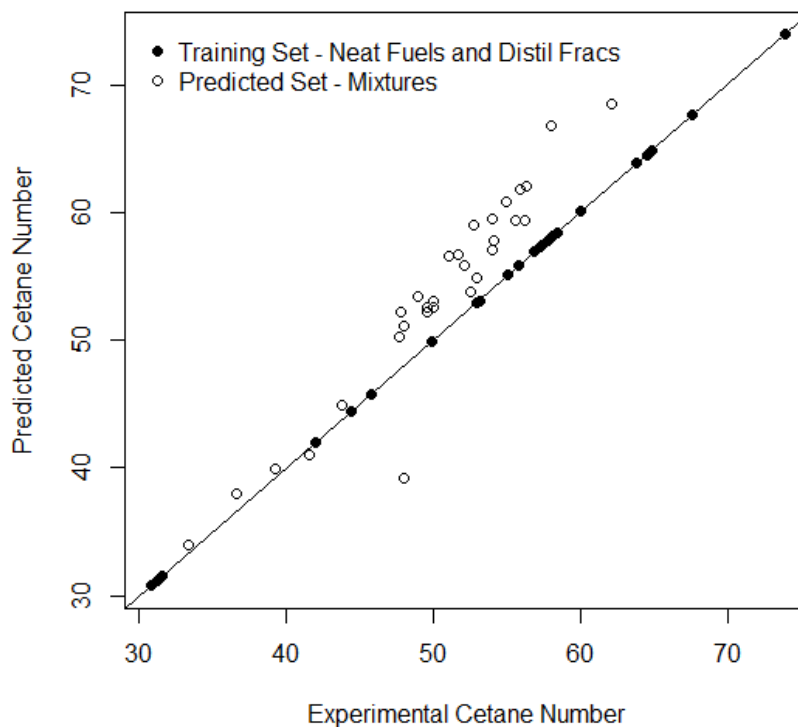


Figure 5.25. Predicted vs experimental cetane number for all fuels, distillation fractions, and mixtures. Prediction done using the NIR data and 25 regression components.

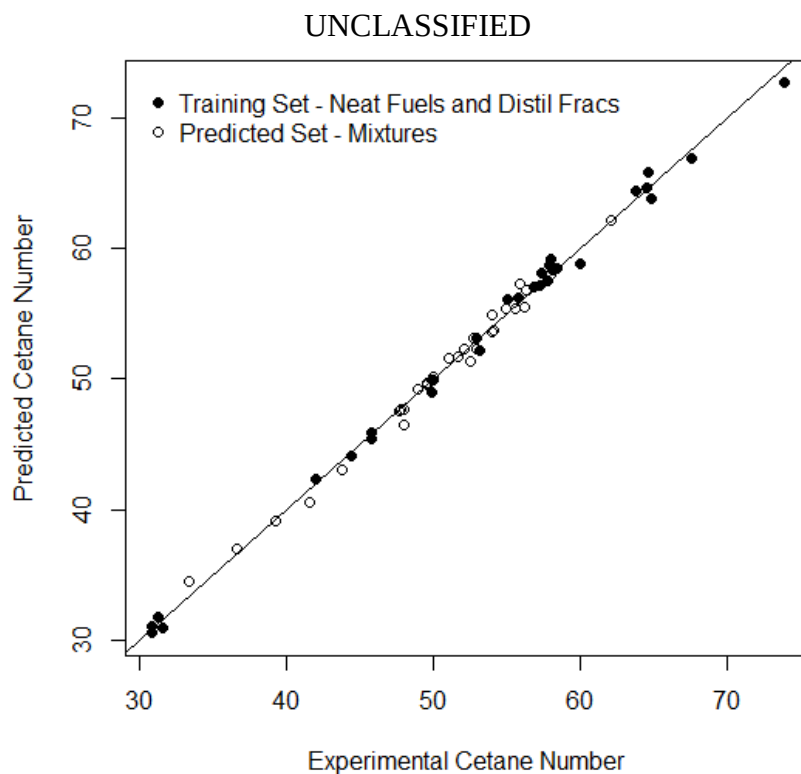


Figure 5.26. Predicted vs experimental cetane number for all fuels, distillation fractions, and mixtures. Prediction done using the NIR data and seven regression components.

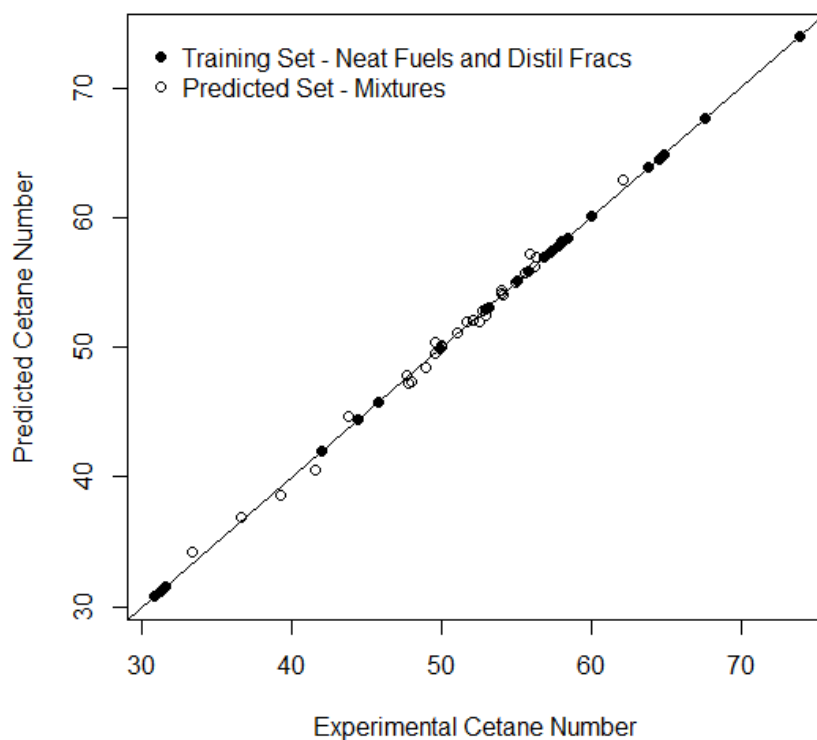


Figure 5.27. Predicted vs experimental cetane number for all fuels, distillation fractions, and mixtures. Prediction done using the FTIR data and 26 regression components.

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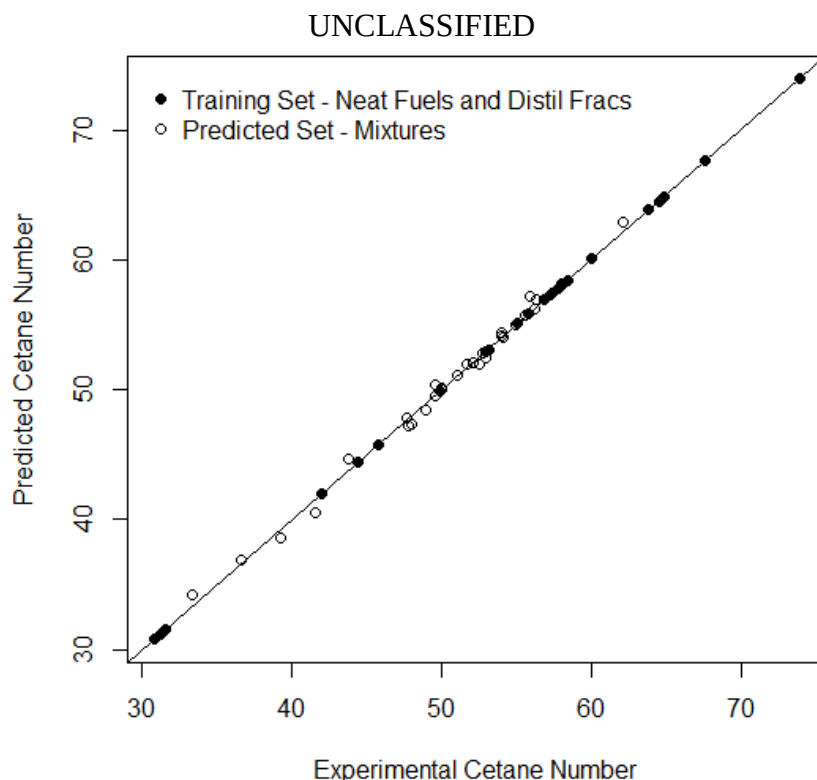


Figure 5.28. Predicted vs experimental cetane number for all fuels, distillation fractions, and mixtures. Prediction done using the FTIR data and seven regression components.

For the FTIR data, both the training and testing set errors are larger for seven regression components compared to 25 but the correlation is still within the experimental uncertainty of the measurements, which is typically $\pm 2\text{-}3\%$ of the cetane number. The training set error goes from essentially 0% to 0.55%, and the testing set error increases by an almost negligible amount (0.078%, Table 5.5). This is a small increase in error, (Figure 5.27 and Figure 5.28). The larger amount of noise in the baseline of the FTIR data could explain this increase. Another explanation for the increase of error in the testing set could be that there are not enough data sets in the training set, to allow for a decrease in regression components.

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Table 5.5 Average absolute error for the prediction of cetane number using NIR and FTIR data, with varying regression conditions. The testing set and training set are evaluated separately.

Spectra Type	Number of Regression Components	Data Set	Average Absolute % Error
NIR	25	Training set	0.00027%
		Testing set	7.3%
	7	Training set	1.0%
		Testing set	0.96%
FTIR	26	Training set	8.3E-13%
		Testing set	0.85%
	7	Training set	0.55%
		Testing set	0.92%

The regression coefficients for the NIR regression with seven regression components and both FTIR regressions are plotted against the spectra in Figure 5.29-Figure 5.30. The NIR coefficients appear to relate directly to the spectra peaks, while the FTIR coefficients don't appear to relate to the spectra. If the weights (coefficients multiplied by absorbance) are inspected instead (Figure 5.31 and Figure 5.32), both the NIR and FTIR coefficient peaks line up well with the spectral peaks. Fodor [27, 29] and DeFries [31] both discuss removal of the baseline, but determine it has no effect on the result beyond decreasing computing time. They do not, however, report the relationship between the regression coefficients and peaks. While the weighted coefficients have a good agreement with the peaks, there are also areas with higher weights in the background region. For this reason, portions of the NIR and FTIR baselines were manually removed, and the data was re-regressed evaluate the effect on cetane prediction.

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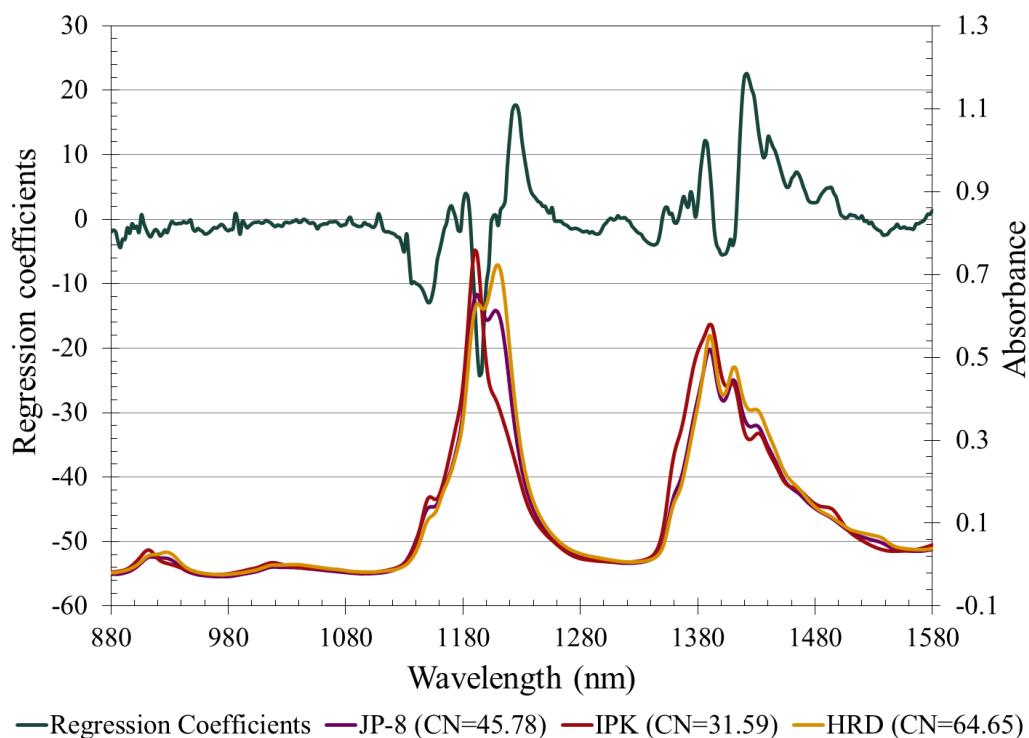


Figure 5.29. Regression coefficients plotted against the NIR spectra for the JP-8, IPK, and HRD fuels for the regression using 7 components.

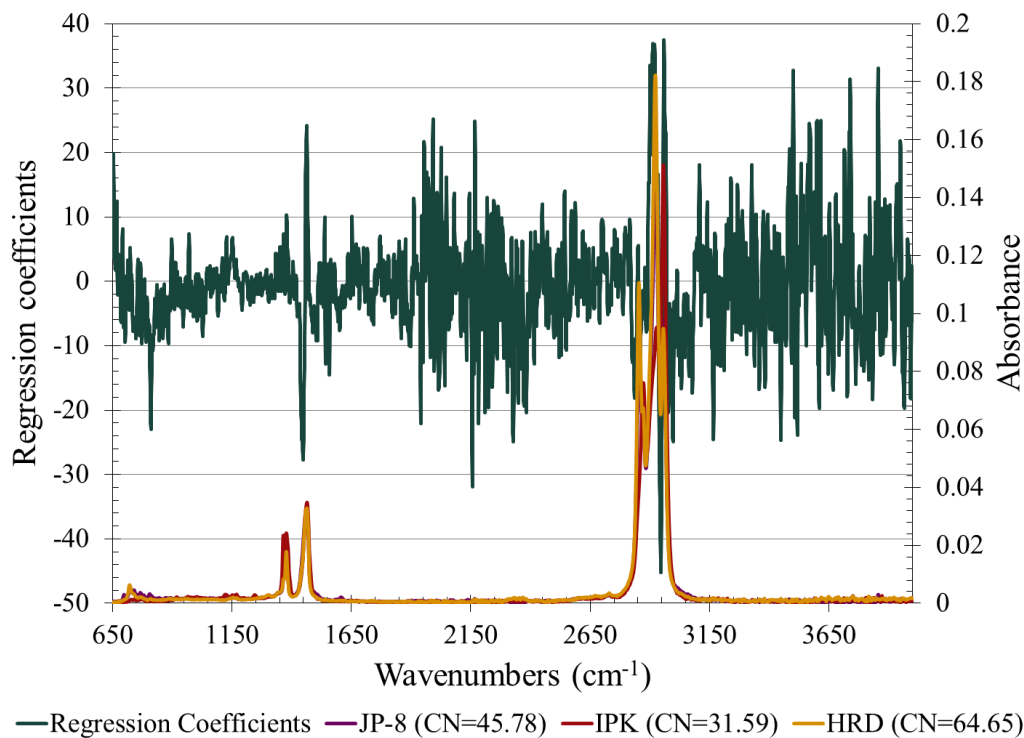


Figure 5.30. Regression coefficients plotted against the FTIR spectra for the JP-8, IPK, and HRD fuels for the regression using 26 components.

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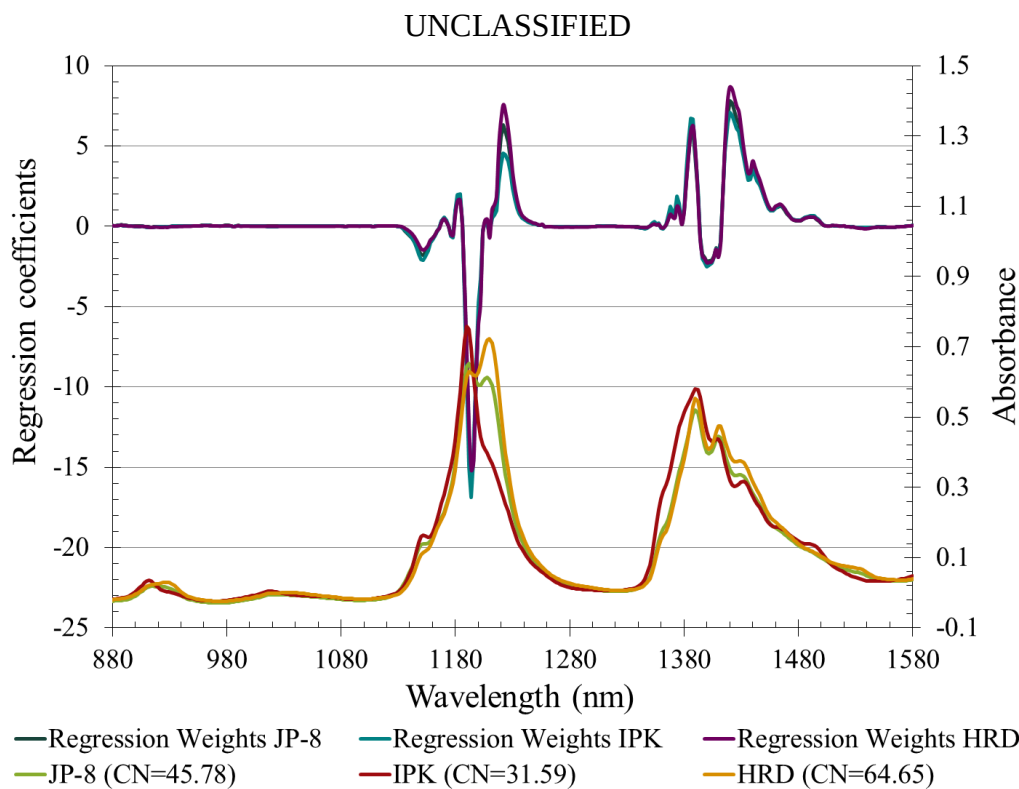


Figure 5.31. Regression weights plotted against the NIR spectra for the JP-8, IPK, and HRD fuels for the regression using 7 components.

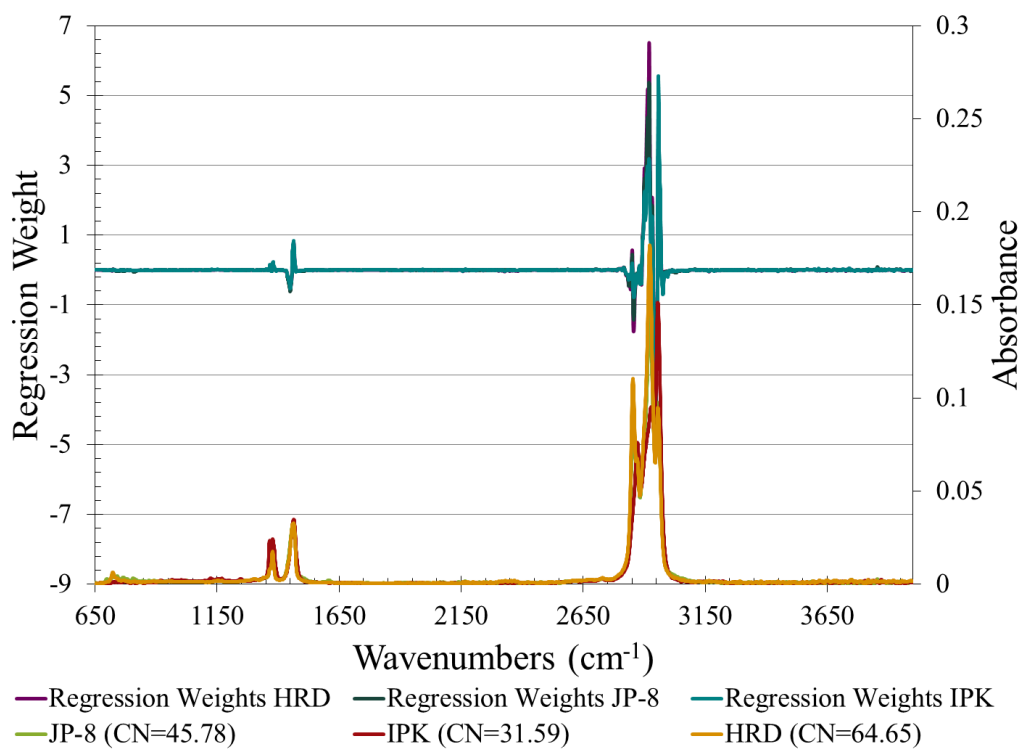


Figure 5.32. Regression weights plotted against the FTIR spectra for the JP-8, IPK, and HRD fuels for the regression using 26 components.

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Visual inspection was used to remove sections of the baseline for the data sets. The NIR sets use the data in the range of 1100-1680nm, and the FTIR data uses the ranges of 650-900cm⁻¹, 1340-1520cm⁻¹, 2800-3000cm⁻¹. Removing the baseline results in increased errors for all training sets except the seven component NIR set, both FTIR testing sets and the NIR testing set using seven regression components (Table 5.6). In the two cases where the baseline removal improves the error, the improvement is by less than 0.1%.

Table 5.6. Average absolute error for the prediction of cetane number using NIR and FTIR data, with varying regression conditions and the baseline removed. The testing set and training set are evaluated separately.

Spectra Type	Number of Regression Components	Data Set	Average Absolute % Error
NIR	25	Training set	0.00025%
		Testing set	6.4%
	7	Training set	1.0%
		Testing set	1.4%
FTIR	26	Training set	1.2E-9%
		Testing set	1.4%
	7	Training set	0.73%
		Testing set	1.1%

The NIR weights did not changed dramatically; while the absolute values were changed, the positions and the peaks which were emphasized did not (Figure 5.33). Even with the baseline removed, the FTIR weights were still noisy (Figure 5.34). The removal of the baseline did increase the absolute values of the weights, and helped to separate the aromatic region from the baseline. But, because the errors were increased overall, the removal of the baseline only helped to decrease processing time, not model accuracy. The coefficients and intercepts for all PLS regressions with 7 components can be found in Appendix G.

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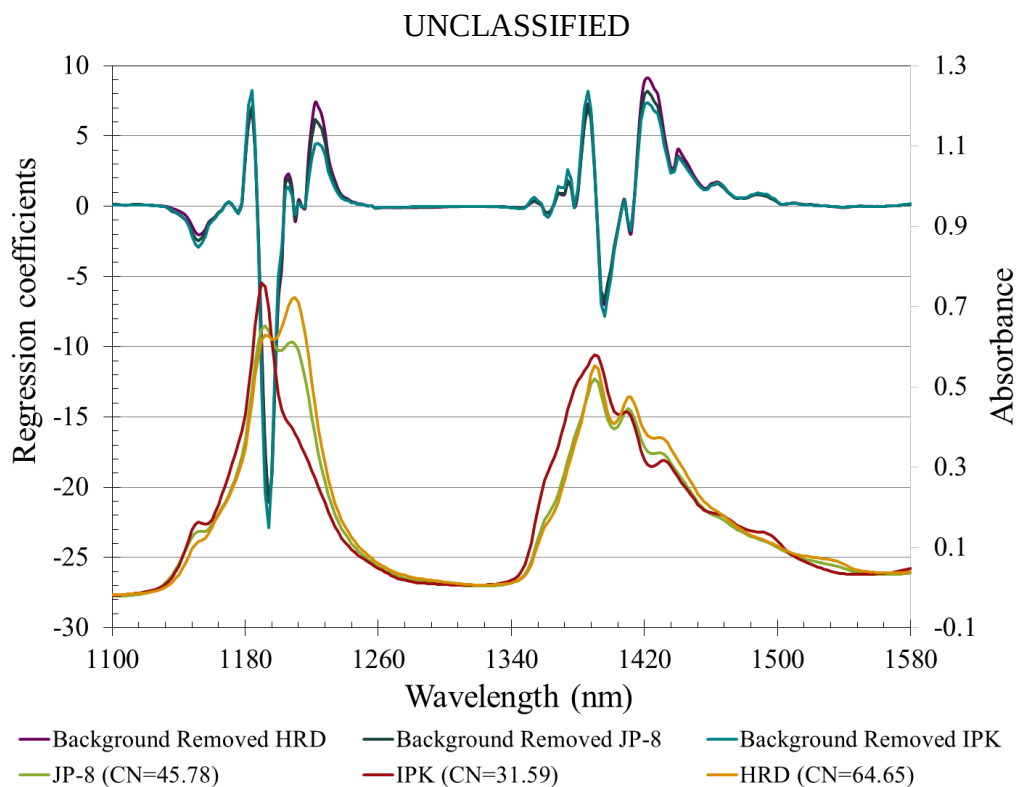


Figure 5.33. Regression weights plotted against the NIR spectra of JP-8, IPK, and HRD fuels with the baseline removed.

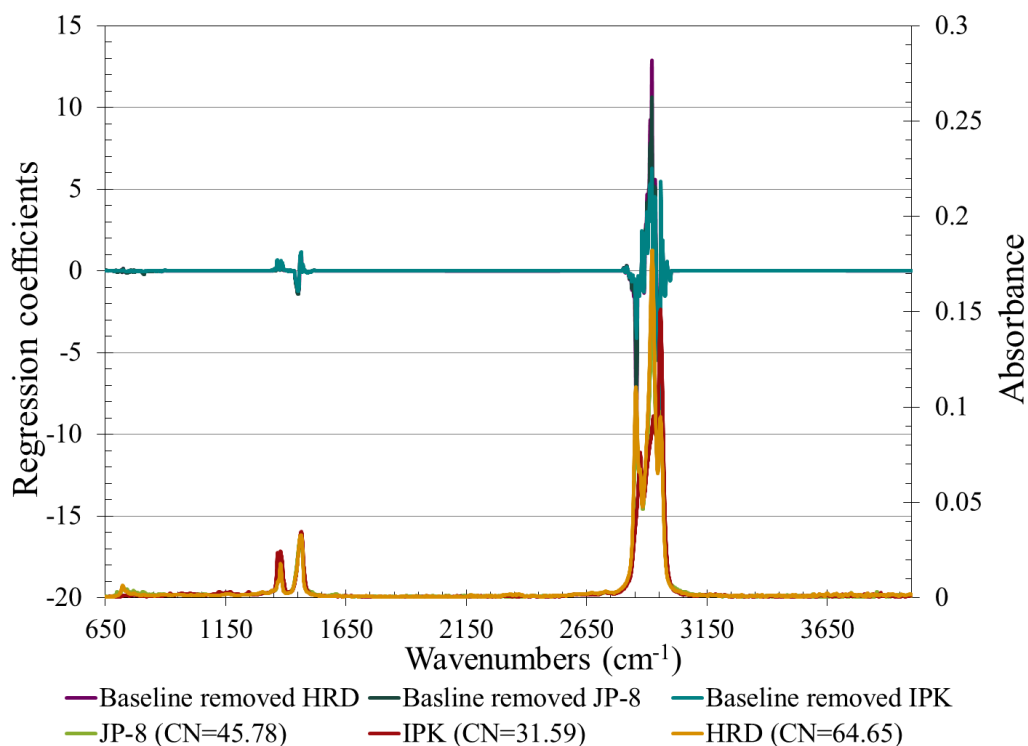


Figure 5.34. Regression weights plotted against the FTIR spectra for the JP-8, IPK, and HRD fuels for the regression using 7 components, with the baseline removed during regression.

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5.3.2.2 Model Validation Using Pure Components

To check the accuracy of the NIR and FTIR models in prediction the cetane number of fuels or compounds outside of the fuel set, six pure isoparaffin components were tested. These six compounds, which were detailed in Table 5.1, were tested with both the NIR and FTIR methods, and the spectra were predicted using the same coefficients as developed during previous regressions. The average absolute errors are shown in Table 5.7. The average error of the compounds is very high for all models, with no regression method giving an average error lower than 33%

Table 5.7. Errors for the regression of various branched compounds using the neat fuels and distillation fractions as the training set.

Spectra Type	Number of Regression Components	Background Sections Removed	Average Absolute % Error
NIR	25	No	112%
		Yes	141%
	7	No	34%
		Yes	40%
FTIR	26	No	41%
		Yes	33%
	7	No	45%
		Yes	61%

The individual predictions are shown along with the training set in Figure 5.35. Three of the compounds are predicted well, while the other three compounds are predicted poorly. 2,2,4,4,6,8,8-Heptamethylnonane (CN = 15) is predicted almost exactly. This compound is used as a calibration standard in the cetane number testing method, so it is a set value. The experimental value for 2,4-dimethylpentane (CN = 29) was found using direct measurement, and it is predicted within experimental error. 2-Methylpentane (CN = 33) was also predicted within experimental error.

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Part of the error for the poor predictions could come from the literature value. For both 2,2,4-trimethylpentane (CN = 14) and 3-methylpentane (CN = 30), the reported cetane number is from the experimental testing of a blend, and the pure cetane number is extrapolated from the blending data (Table 5.1). The extrapolation of a neat compound's cetane number from blending data can be unpredictable, depending on the curvature or lack of curvature displayed, so it is possible that the reported cetane value is incorrect. For 2,3-dimethylpentane (CN = 21), the Murphy Compendium states the value is from an IQT test, but gives no information about the purity of the sample, or a literature reference.

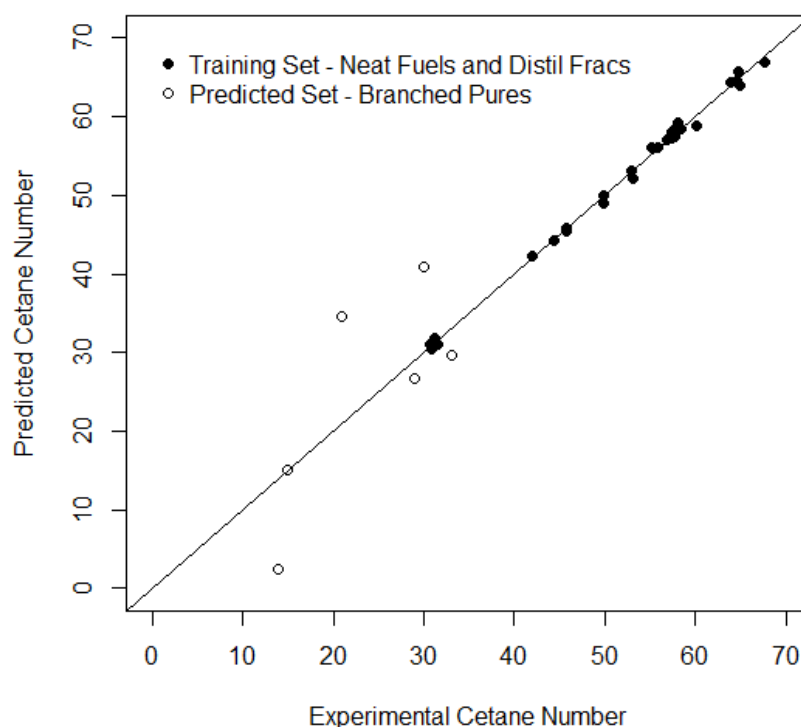


Figure 5.35. Predicted vs experimental cetane numbers of various branched compounds regressed using the neat fuels and distillation fractions as the training set.

5.4 Conclusions

Six different alternative fuels were examined in mixtures with JP-8 to evaluate methods for predicting their cetane numbers. The mixture cetane numbers were found experimentally to

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be linear with composition. The neat fuels were also distilled to create a larger training set for the IR prediction methods.

Two different methods of predicting the cetane number of mixtures were examined. The first used the method of Ghosh and Jaffe. GCxGC data were averaged to develop a surrogate composition, which was in turn used to create a pseudocomponent for the neat fuel. The pseudocomponent was then used to predict the cetane number of mixtures. If the carbon number of the isoparaffins was increased, the model could represent the paraffin number to within experimental error for all neat fuels, and all fuel mixtures except for the JP-8:IPK mixture. The Ghosh and Jaffe method did not work well for the fuels with high isoparaffin content because the model predicts incorrect curvatures. It is likely that the prediction would improve if the beta values were to be re-regressed with a more diverse range of fuels. This kind of re-regression requires a very large data set, and the data set for this study was too limited for good optimization.

The second method used partial least squares regression to relate the NIR or FTIR spectra to the cetane number of the fuel mixture. The FTIR spectra give a smaller overall error for the training sets than the NIR spectra. However, the FTIR regressions do not improve when the number of regression components is decreased. When the baseline was removed, the error increased for all data sets except for the NIR regression with 25 components, while still remaining within the experimental uncertainty. The NIR spectra gave coefficients and weights that were more correlated to the spectral peaks than the FTIR regression weights. While the FTIR regression gives an average error of 0.42%, and the NIR one of 1.0%, the NIR coefficients are more clearly related to the spectra. The NIR regression is the best cetane model out of those evaluated for these fuels. The models were evaluated using six pure isoparaffins with data from

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the literature. The three isoparaffins were predicted well, including heptamethylnonane, which is used as the calibration standard for cetane number testing.

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CHAPTER 6

Isothermal Compressibility of Fuels and Fuel Mixtures

6.1 Introduction

The compressibility of a fuel affects its behavior during the injection. As the fuel is subjected to high pressures during injection, the compressibility determines how much the volume will change. This can affect the mass injected, and is related to the optimum injection timing [100, 101]. In addition, biofuels can have a substantially different (usually lower) compressibility than petroleum fuels [101, 102]. Prediction of compressibility for different fuels based on a representative surrogate composition will allow the engine operation to be optimized. Prediction of fuel compressibility using surrogate compositions is unexplored in the literature.

The adiabatic compressibility is more relevant than the isothermal compressibility because the compression process is so fast that there is little time for heat transfer. In general adiabatic and isothermal compressibility are defined as:

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S \quad (6.1)$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (6.2)$$

where κ_S is adiabatic compressibility, P is pressure, V is the molar volume, S is entropy, κ_T is the isothermal compressibility, and T is temperature. The adiabatic compressibility is related to the isothermal compressibility and heat capacity as shown by Tyrer [103] and Liebenberg, Mills, and Bronson [104]:

$$\kappa_T - \kappa_S = \frac{TV\alpha_P^2}{C_P} \quad (6.3)$$

where C_P is the constant pressure heat capacity, C_V is the constant volume heat capacity, T is the temperature, and α_P is the thermal expansion coefficient. For calculation of the adiabatic compressibility, this equation requires accurate isothermal compressibility, thermal expansion coefficient, and heat capacity. Experimental data for either fuel components or the fuels

themselves are usually available for all of these properties. Kleppa [105] gives a similar equation to (6.3) with a slightly different form. However, it requires iteration on κ_T .

It is impractical to measure adiabatic compressibility directly using P-V-T experiments, and difficult to measure isothermal compressibility accurately. The adiabatic compressibility is most accessible via measurement of speed of sound. The relationship between adiabatic compressibility and speed of sound, v , is:

$$v^2 = \frac{1}{\rho \kappa_S} \quad (6.4)$$

Isothermal compressibility can be related to the speed of sound via equations (6.3) and (6.4) and can be rearranged as the isothermal derivative of density with pressure:

$$\begin{aligned} \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T &= \frac{1}{V \rho^2} \left(\frac{\partial \rho}{\partial P} \right)_T = \frac{1}{\rho v^2} + \frac{TV \alpha_P^2}{C_P} \\ \left(\frac{\partial \rho}{\partial P} \right)_T &= \frac{1}{v^2} + \frac{T \alpha_P^2}{C_P} \end{aligned} \quad (6.5)$$

Some groups ([106] and [38]) integrate equation (6.5) to represent the density change as a function of the speed of sound.

$$\rho(P, T) = \rho(P_0, T) + \int_{P_0}^P \frac{dP}{v^2} + T \int_{P_0}^P \frac{\alpha_P^2}{C_P} dP \quad (6.6)$$

where P_0 is the reference pressure. Dzida et al. [106] and Payri [38] et al. ignore the second term, claiming it only accounts for a small error in density. Both have been used to predict the density of biodiesel or diesel systems.

When predicting adiabatic compressibility of mixtures, there are two routes that can be taken: empirical constants can be fitted to the experimental data, or an equation of state model can be used. Both Fort and Moore [40] and Jain et al. [39] use very simple empirical parameters to fit the excess compressibility of binary mixtures to concentration:

$$\frac{\kappa_S^E}{x_1 x_2} = A + B(x_1 - x_2) + C(x_1 - x_2)^2 \quad (6.7)$$

where κ_S^E is the excess adiabatic compressibility, x_1 is the mole fraction of component 1, x_2 is the mole fraction of component 2, and A , B , and C are fitted empirical constants. Wang and Nur [107] and Berryman [108] use a volumetric average and assumption of ideal mixing to fit the speed of sound.

Multiple research groups fit the density data of mixtures using the Tait equation [36, 37, 106]. They can obtain fits with <3% error this way, however, each mixture composition is fit with different parameters, so the method is not predictive to other types or batches of fuels.

Instead of using empirical relations, an equation of state (EOS) model can be used to predict the density and speed of sound. An EOS model directly relates the density of the fluid to the physical properties of the solution, which allows for mixtures to be predicted from pure component properties using mixing rules that have already been developed. Application of an EOS to fuels requires the development of a surrogate to represent the fuel. Surrogates are mixtures of components with well-known properties that, when mixed with the correct ratios, give good predictions of the physical properties of the fuel.

Many equations of state have been used to model speed of sound. The Tao-Mason EOS is similar to the van der Waals EOS with a slight modification to the attractive term [109-111]. This equation can produce predictions with <3% in density for heavy alkanes, but it still has four parameters which would need to be fitted. Another option is the Goharshadi-Morsali-Abbaspour (GMA) EOS [112-114]. It has higher accuracy than Tao-Mason, with errors of <1% for alkanes, but has six fitted parameters, with no mixing rules. The Peng-Robinson equation has been used to predict the speed of sound in the gas phase, but it gives large errors for liquid densities [46]. The GERG equation can fit the data to within experimental uncertainties for multiple physical

properties [115]. It is a highly complicated equation that requires a large number of data sets to accurately predict mixture properties. While it is too complicated for easy use for surrogate mixtures, it is used in the REFPROP program [116] available from NIST and can be used to predict properties of binary mixtures of limited components for model evaluation.

The statistical associating fluid theory (SAFT) model has many different modifications, some of which have been used to predict speed of sound and compressibility. The original SAFT overpredicts the speed of sound by approximately 30%, and PC-SAFT underpredicts speed of sound by 10-15% [42, 43]. PC-SAFT can be improved by re-regressing the constants for alkanes using the speed of sound as well as density and saturated pressure data, and the errors are reduced to an average of 3.26% [43]. Soft-SAFT gives variable predictions depending on the type of fluid. Perfluoroalkanes were modeled very well [117], but alkanes and alcohols had higher errors [44].

Finally, the SAFT-BACK equation is reported to give very good prediction of speed of sound data for pure fluids [45, 46, 118, 119]. The BACK modification uses a hard convex body form for the radial distribution function. The SAFT-BACK equation is also referred to as the SAFT-CP equation [120], but the two equations are identical except for the parameter values used. Two equations, the SAFT-BACK equation, and the Elliott, Suresh, Donohue (ESD) equation, have been chosen for evaluation.

6.2 Calculation Methods

6.2.1 ESD equation of state

The ESD equation of state (EOS) is a cubic equation which more accurately predicts the repulsive forces than the van der Waals form used in the popular Peng-Robinson equation. The

ESD equation has been used to predict phase equilibria of pure fluids and mixtures, including polymers, but has not been used for speed of sound prediction. The ESD is defined as:

$$Z = \frac{PV}{RT} = 1 + \frac{2.1q\eta}{1 - 1.9\eta} + \frac{1.9\eta}{1 - 1.9\eta} - \frac{9.5qY\eta}{1 + 1.7745Y\eta} \quad (6.8)$$

Where Z is compressibility factor, V is volume, P is pressure, R is the gas constant, T is temperature, and q , η , and Y are all variables defined as:

$$q = 1 + 1.90476(c - 1) \quad (6.9)$$

$$\eta = \frac{b}{V} \quad (6.10)$$

$$Y = e^{\epsilon/(kT)} + 1.0617 \quad (6.11)$$

where b is the packing fraction, c is a shape parameter which gives an indication of how spherical the molecule is, ϵ is the attractive term, and k is the Boltzmann constant.

The ESD is a cubic equation; it can be re-arranged to have the form of a third degree polynomial in Z . This is beneficial because it is simpler to calculate the roots of a polynomial, rather than solve a more complex equation. When the ESD is rearranged it has the form:

$$Z^3 + a_2Z^2 + a_1Z + a_0 = 0 \quad (6.12)$$

$$a_2 = -1.9 \frac{bP}{RT} + 1.7745Y \frac{bP}{RT} - 1 \quad (6.13)$$

$$a_1 = -3.37155Y \left(\frac{bP}{RT} \right)^2 - 1.7745Y \frac{bP}{RT} - 2.1q \frac{bP}{RT} + 9.5qY \frac{bP}{RT} \quad (6.14)$$

$$a_0 = -21.77645qY \left(\frac{bP}{RT} \right)^2 \quad (6.15)$$

6.2.2 SAFT-BACK equation of state

The SAFT-BACK EOS [118] is a modification of the statistical associating fluid theory (SAFT) model. The SAFT equation [121] calculates the Helmholtz energy of a fluid by considering individual segments of molecules. Molecules are broken up into spherical sites, whose energy is independently calculated. These sites are then assembled into chains, and the energy of the assembly is calculated. The sites are then allowed to interact with both other sites

on the same molecule, and sites on other molecules, and this contribution is added to the energy.

SAFT-BACK differs from SAFT in the way that the individual spheres are modeled, and this modification allows good prediction all the way to the critical point for pure n-alkanes [45, 118].

It is defined in terms of the Helmholtz energy:

$$A^{res} = A - A^{ideal} = A^{hcb} + A^{chain,hcb} + A^{dis} + A^{chain,dis} \quad (6.16)$$

$$\frac{A^{hcb}}{RT} = m \left[\frac{\alpha^2}{(1-\eta)^2} - \frac{\alpha^2 - 3\alpha}{1-\eta} - (1-\alpha^2) \ln(1-\eta) - 3\alpha \right] \quad (6.17)$$

$$\frac{A^{chain,hcb}}{RT} = (1-m) \ln[g^{hcb}(d)] \quad (6.18)$$

$$\frac{A^{dis}}{RT} = m \sum_i \sum_j D_{ij} \left(\frac{u}{kT} \right)^i \left(\frac{\eta}{\tau} \right)^j \quad (6.19)$$

$$\frac{A^{chain,dis}}{RT} = m \frac{\lambda A^{chain,hcb}}{A^{hcb}} \sum_i \sum_j D_{ij} \left(\frac{u}{kT} \right)^i \left(\frac{\eta}{\tau} \right)^j = \lambda \frac{\left(\frac{A^{chain,hcb}}{RT} \right) \left(\frac{A^{dis}}{RT} \right)}{\left(\frac{A^{hcb}}{RT} \right)} \quad (6.20)$$

where A is Helmholtz energy, k is the Boltzmann constant, m is the number of segments per molecule, α is a shape parameter, η is the packing fraction, $g^{hcb}(d)$ is the hard convex body radial distribution function, D_{ij} is a power law expansion coefficient [122], u is the attractive energy, and τ is a constant. η , $g^{hcb}(d)$, u , and τ are defined as:

$$\eta = \frac{1}{6} \pi N_{AV} m \rho d^3 = b \rho = \frac{b}{V} \quad (6.21)$$

$$g^{hcb}(d) = \frac{1}{1-\eta} + \frac{3\alpha(1+\alpha)\eta}{(1-\eta)^2(1+3\alpha)} + \frac{2\alpha^2\eta^2}{(1-\eta)^3(1+3\alpha)} \quad (6.22)$$

$$u = u^0 \left(1 + \frac{\varepsilon}{kT} \right) \quad (6.23)$$

$$\tau = \frac{\sqrt{2}\pi}{6} \quad (6.24)$$

where ρ is the molar density, b is a constant which lumps together the other constants in equation (6.21), N_{AV} is Avogadro's number, d is the temperature dependent segment diameter, and ε is a constant which determines the temperature dependence of u . ε/k is set to 1 for small molecules

(methane in this work) and 10 for larger molecules. σ is the temperature independent segment diameter. d and σ are defined as:

$$d = \sigma[1 - 0.12e^{(-3u^0/(kT))}] \quad (6.25)$$

$$v^{00} = \frac{1}{6}\pi N_{AV}\sigma^3 \quad (6.26)$$

Helmholtz energy is related to pressure by:

$$Z = \rho \left(\frac{\partial \left(\frac{A}{RT} \right)}{\partial \rho} \right)_{N,T} = \eta \left(\frac{\partial \left(\frac{A}{RT} \right)}{\partial \eta} \right)_{N,T} \quad (6.27)$$

This makes Z a function of each of the five terms used to make up the Helmholtz energy such that:

$$Z = Z^{ideal} + Z^{hcb} + Z^{chain,hcb} + Z^{dis} + Z^{chain,dis} \quad (6.28)$$

$$Z^{ideal} = 1 \quad (6.29)$$

$$Z^{hcb} = m \left[\frac{(1 + 3\alpha)\eta + (3\alpha^2 - 3\alpha - 2)\eta^2 + (1 - \alpha^2)\eta^3}{(1 - \eta)^3} \right] \quad (6.30)$$

$$Z^{chain,hcb} = \frac{(1 - m)\eta}{(1 - \eta)} \left[1 + \frac{3\alpha(1 + \alpha)}{(1 + 3\alpha)(1 - \eta)^2 g^{hcb}(d)} + \frac{4\alpha^2\eta}{(1 + 3\alpha)(1 - \eta)^3 g^{hcb}(d)} \right] \quad (6.31)$$

$$Z^{dis} = m \sum_i \sum_j j D_{ij} \left[\frac{u}{kT} \right]^i \left[\frac{\eta}{\tau} \right]^j \quad (6.32)$$

$$Z^{chain,dis} = \lambda \left[\frac{A^{chain,hcb}}{A^{hcb}} Z^{dis} + \frac{A^{dis}}{A^{hcb}} Z^{chain,hcb} - \frac{A^{chain,hcb} A^{dis}}{(A^{hcb})^2} Z^{hcb} \right] \quad (6.33)$$

6.2.3 Calculation method

The relation between adiabatic compressibility and speed of sound is given in equation (6.4). Equations (6.3) is used to relate the adiabatic to the isothermal compressibility using heat capacity:

$$\frac{\kappa_T}{\kappa_S} = \frac{C_P}{C_V} \quad (6.3)$$

where κ_T is the isothermal compressibility, C_P is the constant pressure heat capacity, and C_V is the constant volume heat capacity. The relationship between C_P and C_V is:

$$C_P - C_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P \quad (6.34)$$

Thus, equations (6.3) and (6.4) can be rearranged:

$$v^2 = \sqrt{\frac{C_P}{C_V} \left(\frac{1}{\rho \kappa_T} \right)} \quad (6.35)$$

The speed of sound propagation through a fluid depends highly on the density of the fluid. The density of the fluid is also dependent on the temperature and pressure of the system. The steep slope of the isotherm on the P - V diagram in the liquid region relates to the isothermal compressibility, which has a significant impact on the speed of sound (equation (6.35)).

Values for C_P for pure liquids are readily available at atmospheric pressure in the literature. Values for both C_P and C_V as an ideal gas can also be found. To calculate values of C_P and C_V at elevated pressures, however, an adjustment needs to be applied to the heat capacity values. There are three options for this step. If there are experimental values for C_P available at the correct pressure, these values can be used and C_V can be found using equation (6.34). For ranges where there is no literature data available, the route can use C_V instead. In the case of the two models that have been evaluated, one path is easier than the other for each model.

$$C_V - C_V^{IG} = \left(\frac{\partial C_V}{\partial V} \right)_T = \int_0^\rho T \left(\frac{\partial^2 P}{\partial T^2} \right)_V \frac{\partial \rho}{\rho^2} \quad (6.36)$$

$$C_V - C_V^{IG} = -T \left(\frac{\partial^2 A^{res}}{\partial T^2} \right) \quad (6.37)$$

where C_V^{IG} is the ideal gas constant volume heat capacity, and A^{res} is the residual Helmholtz energy as shown in equation (6.16). All the required derivatives are presented in Appendix H.

6.2.4 Extension to mixtures

The mixing rules from Maghari and Hamzehloo [120] were used for the prediction of the speed of sound of mixtures of hydrocarbons. The segment terms and the chain terms are treated differently. The different treatment allows for mixtures of molecules of different size and chain length.

For the hard convex body and dispersion terms, the mixing rules are:

$$m = \sum_i x_i m_i \quad (6.38)$$

$$\alpha = \sum_i x_i \alpha_i \quad (6.39)$$

$$\eta = \rho \sum_i x_i m_i v_i^{oo} \left[1 - 0.12 \left(\frac{-3u_i^0}{kT} \right) \right]^3 \quad (6.40)$$

$$u_{ij} = (u_i u_j)^{1/2} \quad (6.41)$$

$$u = \frac{\sum_i \sum_j x_i x_j m_i m_j u_{ij}}{\sum_i \sum_j x_i x_j m_i m_j} \quad (6.42)$$

For the hard convex body chain term, the mixing rule and the radial distribution function are given by:

$$\frac{A^{chain,hcb}}{RT} = \sum_i x_i (1 - m_i) \ln[g_{ii}^{hcb}(d_{ii})] \quad (6.43)$$

$$g_{ii}^{hcb}(d_{ii}) = \frac{1}{1 - \eta} + \frac{3\alpha_i \eta (1 + \alpha_i)}{(1 + 3\alpha_i)(1 - \eta)^2} + \frac{4\alpha_i^2 \eta^2}{(1 + 3\alpha_i)(1 - \eta)^3} \quad (6.44)$$

6.3 Results and Discussion

6.3.1 Model selection

Both the ESD equation and the SAFT-BACK equation were used to predict the density for n-butane and n-decane at various temperatures and pressures. At room temperature, the ESD equation does fairly well at predicting the density (Figure 6.1 and Figure 6.2). However, as pressure and temperature increase, the ESD fails to predict the density accurately. The slope of

the isotherm at room temperature is too low, which leads to incorrect values for the derivative properties, and the errors will propagate and lead to an underprediction of the speed of sound. The SAFT-BACK equation is better at predicting density, and matches both the values and the slope particularly well. For this reason, only the SAFT-BACK EOS will be used here to calculate the speed of sound.

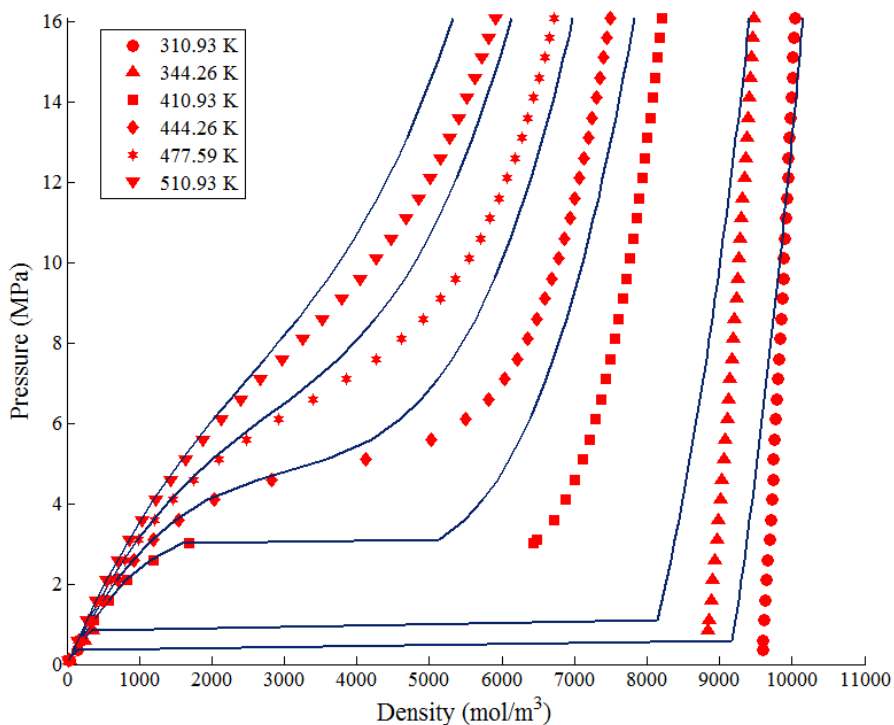


Figure 6.1. Prediction of the density of n-butane at various temperatures and pressures using the ESD EOS. Correlated values from the NIST Webbook [123] shown as points, ESD prediction shown as lines.

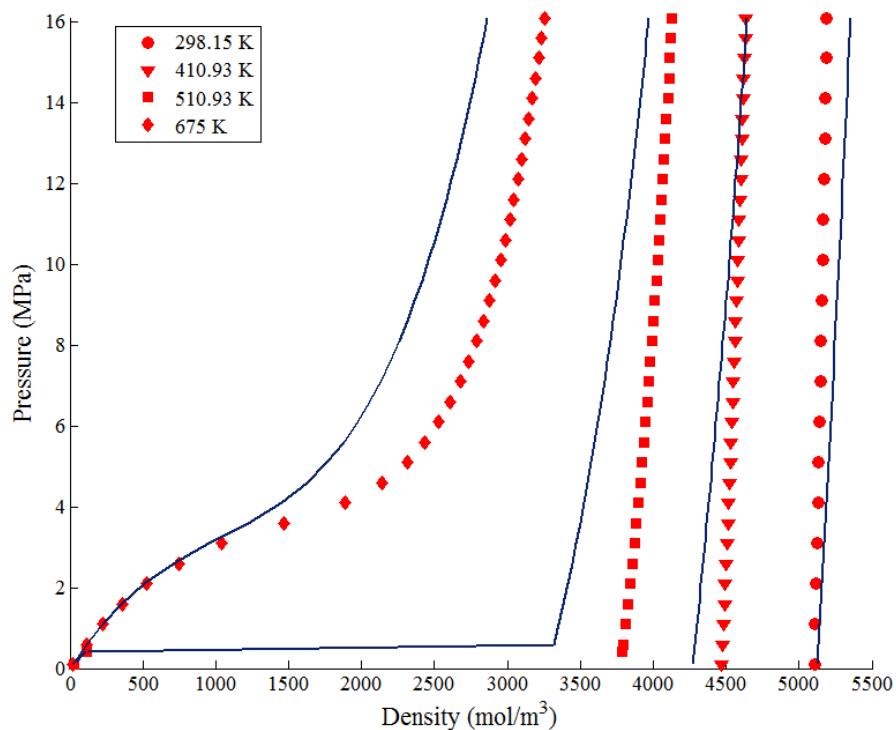


Figure 6.2. Prediction of the density of n-decane at various temperatures and pressures using the ESD EOS. Correlated values from the NIST Webbook [123] shown as points, ESD prediction shown as lines.

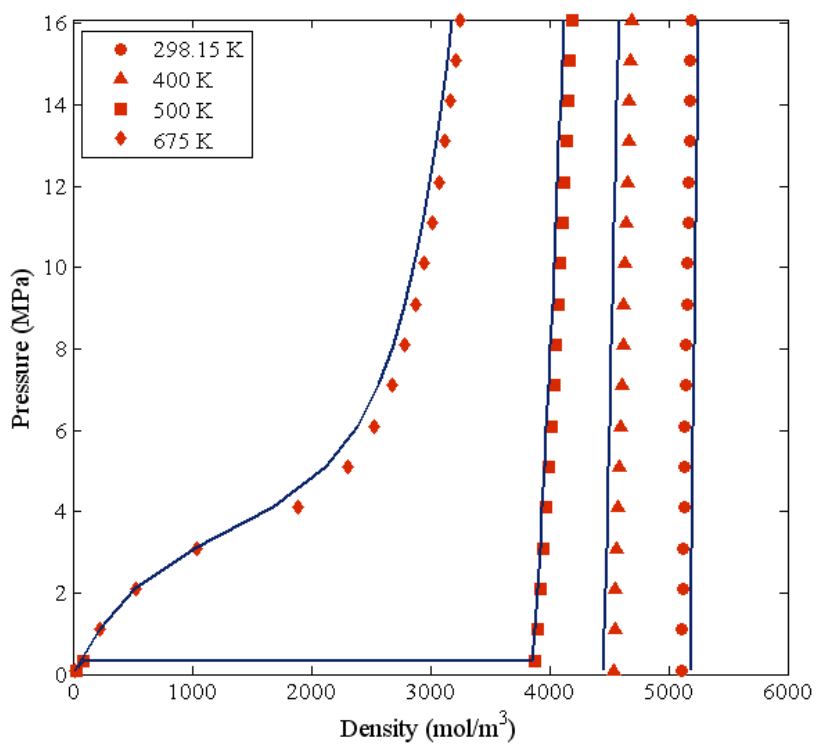


Figure 6.3. Prediction of the density of n-butane at various temperatures and pressures using the SAFT-BACK EOS. Correlated values from the NIST Webbook [123] shown as points, SAFT-BACK prediction shown as lines.

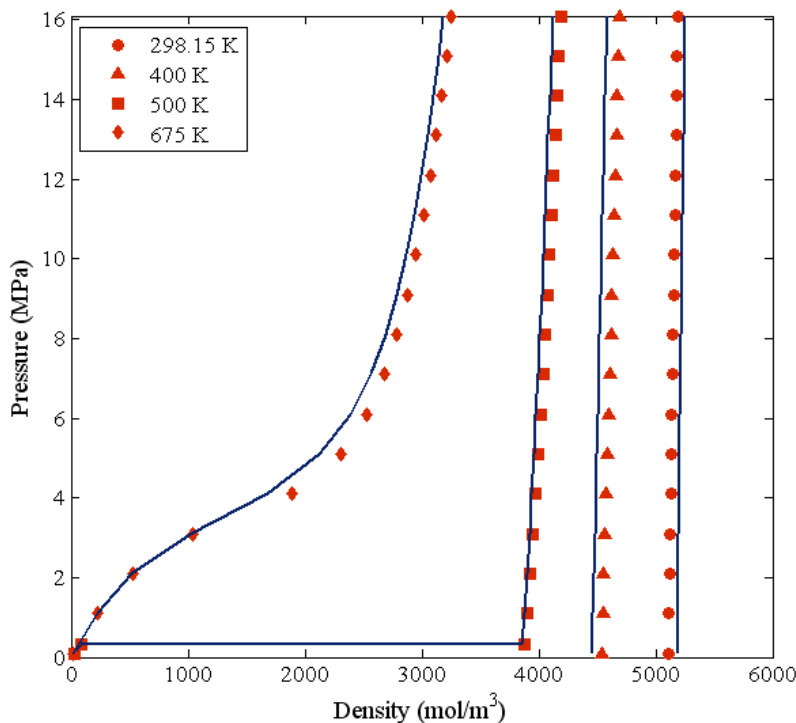


Figure 6.4. Prediction of the density of n-decane at various temperatures and pressures using the SAFT-BACK EOS. Correlated values from the NIST Webbook [123] shown as points, SAFT-BACK prediction shown as lines.

6.3.2 Density prediction for pure fluids

The SAFT-BACK equation was used to predict the density of 8 pure n-alkanes, ranging in size from methane to n-dodecane. The smaller alkanes are shown in Figure 6.5, and the larger alkanes in Figure 6.6. For the smaller molecules, methane through butane, the prediction of the density is highly accurate (Figure 6.5), with the exception of ethane (Figure 6.5 (b)). The errors were usually smaller than the size of the markers, but ethane is slightly more inaccurate. In particular, the slope of the density at the lower temperatures for these molecules are very accurate (circle markers), with the exception of ethane. However, for the larger molecules (decane and dodecane), the prediction exhibits large errors (Figure 6.6 (c) and (d)). Both the slope and values predicted are incorrect at the lower temperatures for the two largest molecules, and for the case of dodecane, the predictions are incorrect across all temperatures. The fluid is predicted as being too incompressible for the liquid phase.

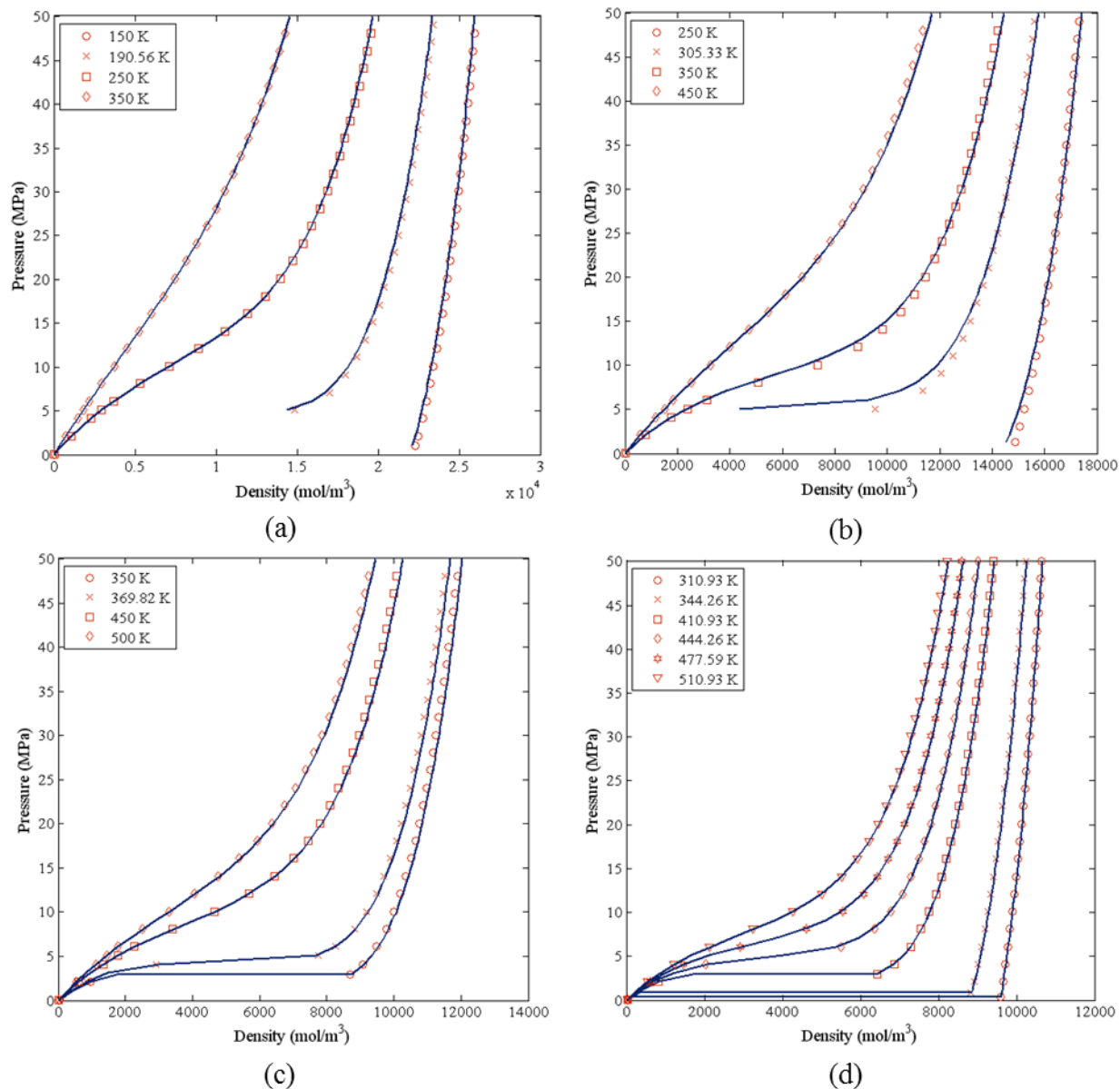


Figure 6.5. Density and pressure for various small alkanes predicted using the SAFT-BACK equation at multiple temperatures. GERG correlation values shown as points [123] and predictions shown as lines. Individual molecules are (a) methane, (b) ethane, (c) propane, and (d) butane.

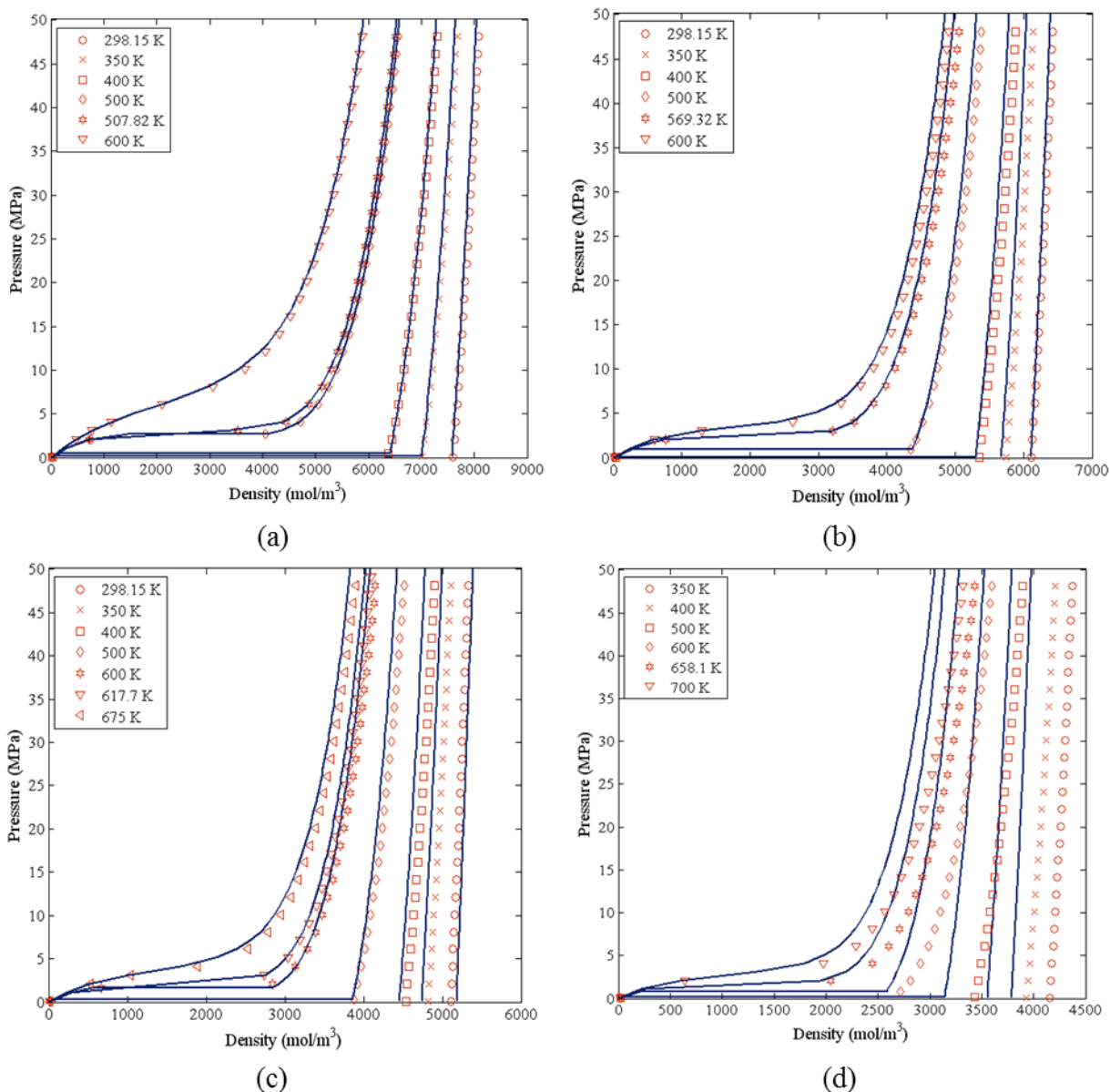


Figure 6.6. Density and pressure for various larger alkanes predicted using the SAFT-BACK equation at multiple temperatures. GERG correlation values shown as points [123] and predictions shown as lines. Individual molecules are (a) hexane, (b) octane, (c) decane, and (d) dodecane.

6.3.3 Speed of sound prediction for pure fluids

The speed of sound for the same molecules were also predicted. For the small molecules, the predictions are accurate for all but ethane (Figure 6.7). Ethane has larger errors at the lower temperatures, due to a combination of the inaccurate density predictions. But again, as the molecules get larger, the error significantly increases (Figure 6.8). For the density, both hexane

and octane were predicted well, but for speed of sound, only the hexane is predicted well for only the higher temperatures. The results reported by Maghari [45] appear to have a much higher accuracy than those reported here, but percent absolute deviations were not reported in that paper. However, we were unable to reproduce Maghari's results given the coefficients and equations stated in his paper. Because of this discrepancy, we carefully evaluated our derivatives term-by-term against numerical results and found excellent agreement to five significant figures. Our results were close to that of Chen [118] for density (1.98% AAD compared to Chen's 2.05% AAD for decane), but Chen does not evaluate speed of sound. Literature data for dodecane was not available at the time of the Chen publishing, and so the dodecane coefficients were not optimized with data. In addition, Chen only evaluates temperatures down to 447 K, and the more significant speed of sound errors are found at the lower temperatures.

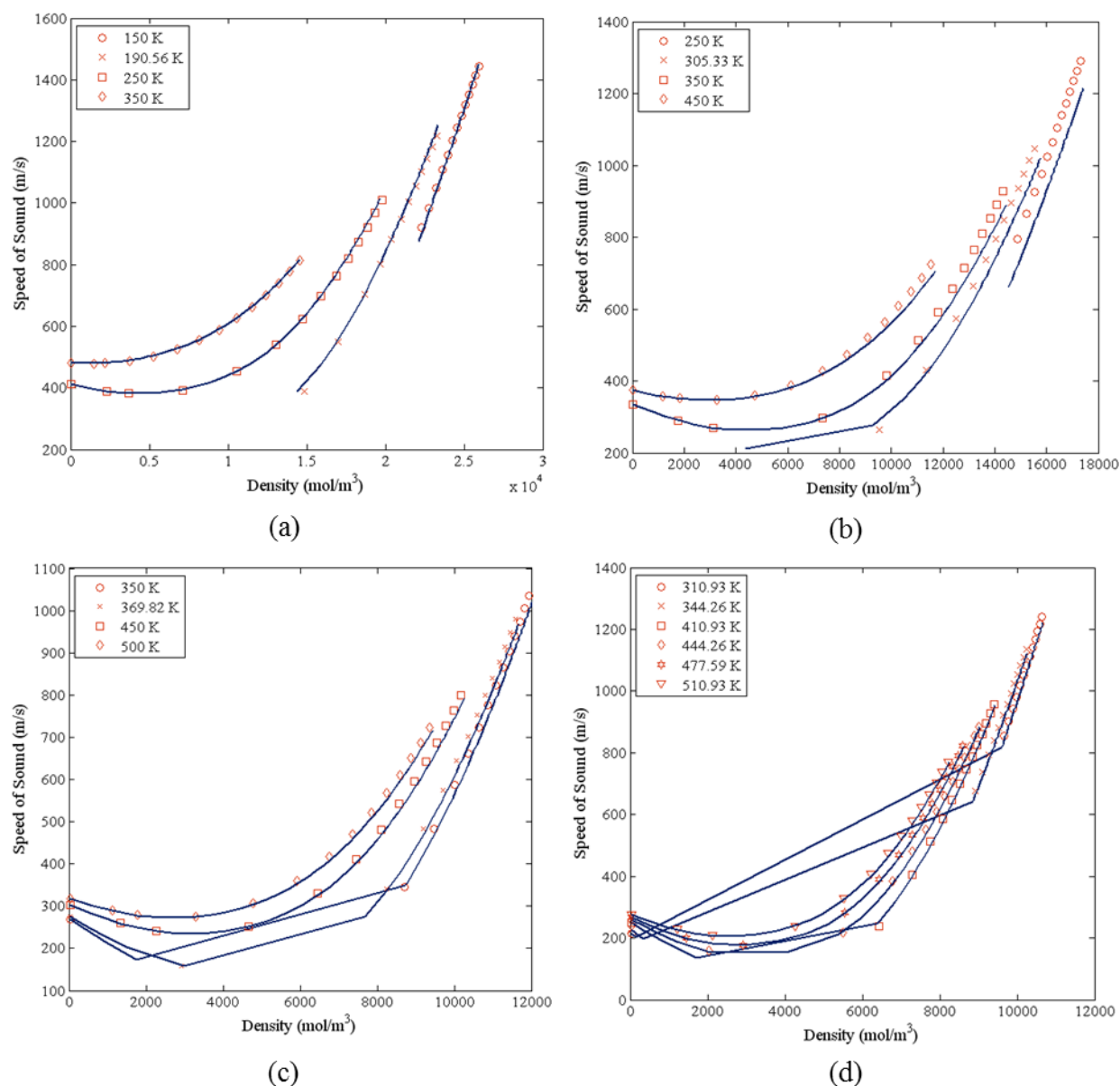


Figure 6.7. Speed of sound for various small alkanes predicted using the SAFT-BACK equation at multiple temperatures. GERG correlation values shown as points [116] and predictions shown as lines. Individual molecules are (a) methane, (b) ethane, (c) propane, and (d) butane.

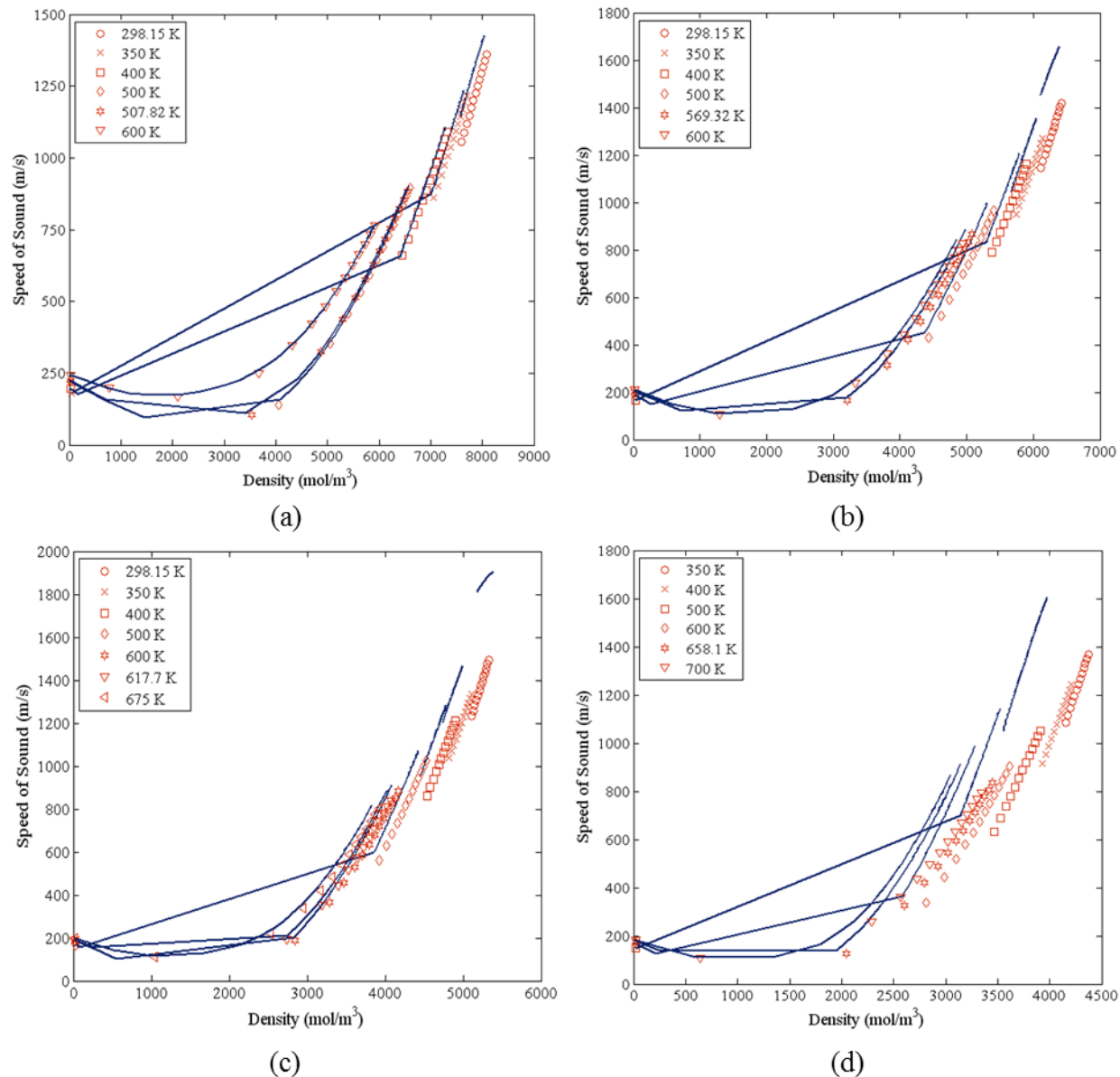


Figure 6.8. Speed of sound for various larger alkanes predicted using the SAFT-BACK equation at multiple temperatures. GERG correlation values shown as points [116] and predictions shown as lines. Individual molecules are (a) hexane, (b) octane, (c) decane, and (d) dodecane.

One of the potential sources of the inaccuracies in the speed of sound is the prediction of C_V and C_P . The calculation process uses the ideal gas C_V , which is corrected using the second derivative of Helmholtz energy with respect to temperature (equation (6.37)). The predicted C_V is then converted to C_P using the derivatives of volume and pressure with respect to temperature (equation (6.34)). In the case of methane and butane, the prediction of C_V becomes much more

inaccurate as temperature decreases and pressure increases (Figure 6.9 (a) and Figure 6.10 (a)). The derivatives used to convert C_V to C_P fortuitously cancel the error in C_V in the case of methane and butane. However, as the molecules become bigger, the error in the second derivative becomes much larger, especially at lower temperatures (Figure 6.11 and Figure 6.12 (a)). In the cases of octane and dodecane, the low temperature C_V has the completely wrong slope as well. Because the error is so large, the cancellation of errors is no longer able to compensate, and the prediction of speed of sound deteriorates.

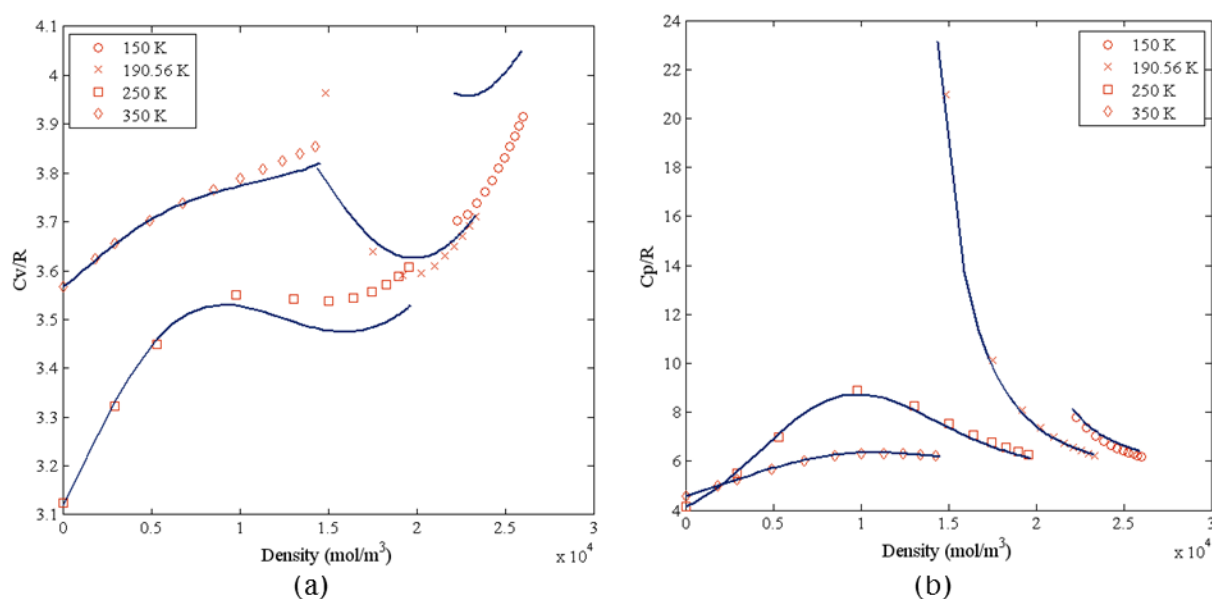
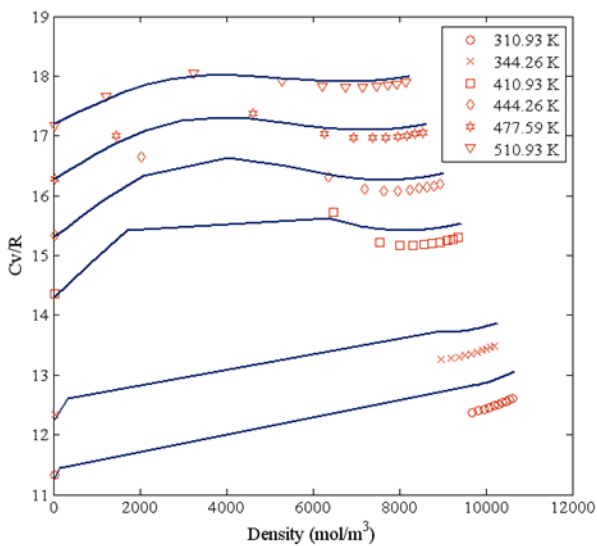
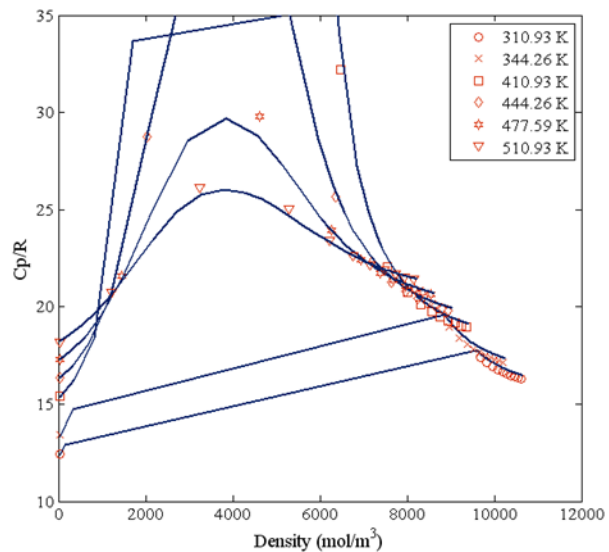


Figure 6.9. Predicted heat capacities for methane at multiple temperatures. GERG correlation values from [116].

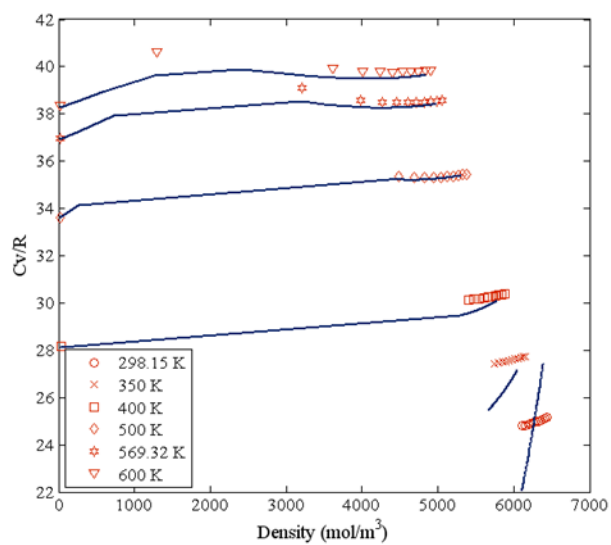


(a)

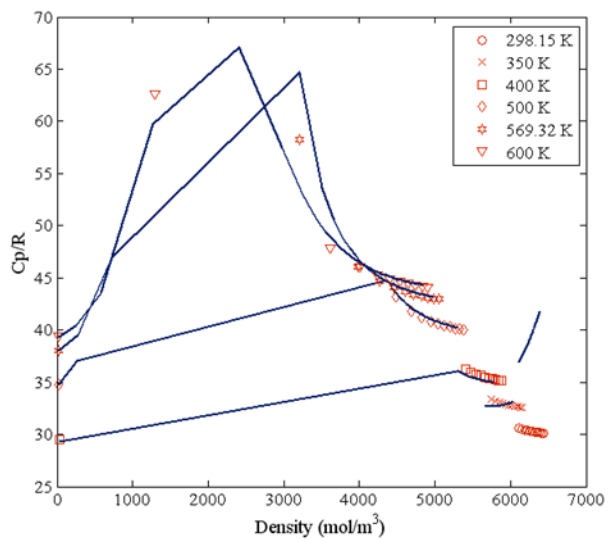


(b)

Figure 6.10. Predicted heat capacities for butane at multiple temperatures. GERG correlation values from [116].



(a)



(b)

Figure 6.11. Predicted heat capacities for octane at multiple temperatures. GERG correlation values from [116].

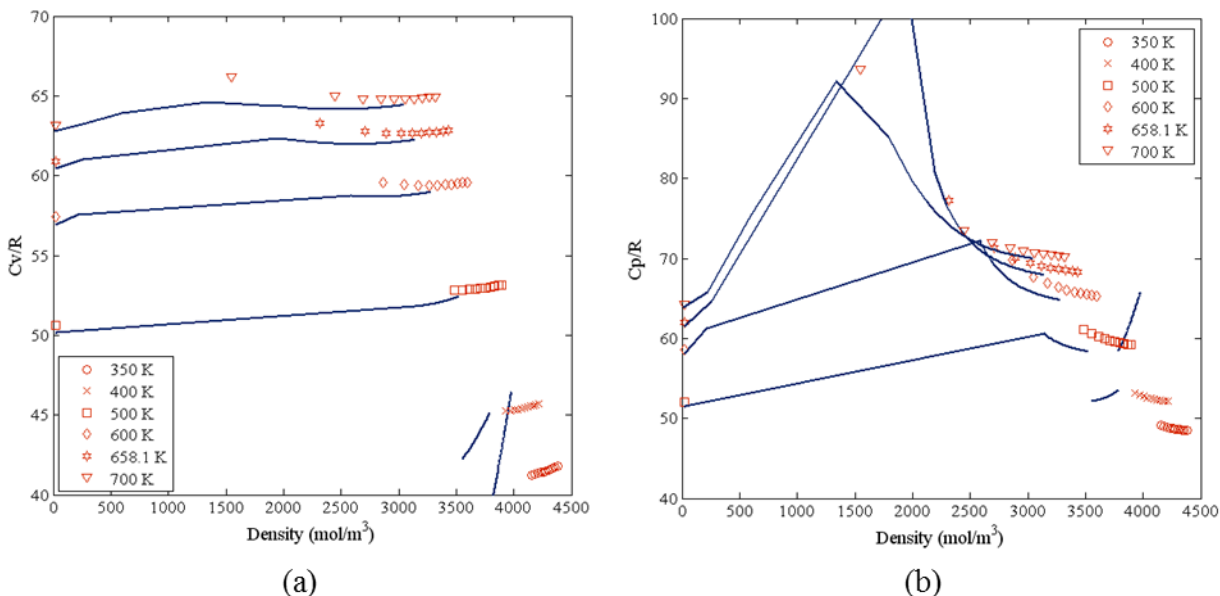


Figure 6.12. Predicted heat capacities for dodecane at multiple temperatures. GERG correlation values from [116].

In an attempt to find the source of these errors, the roots of the SAFT-BACK equation were examined. Normally, the equation is used to find the correct density for a given temperature and pressure, but it can also be used to calculate the pressure at various theoretical densities (Figure 6.13 and Figure 6.14). Plotting an isotherm provides visualization of the theoretical density roots at a given pressure. In the case of a cubic equation, such as the ESD equation, there can be one or three unique real solutions or “roots” at a given pressure. For the SAFT-BACK equation, there can be up to five real roots at a given pressure. The behavior of the SAFT EOS roots has been discussed in detail in the literature [124, 125].

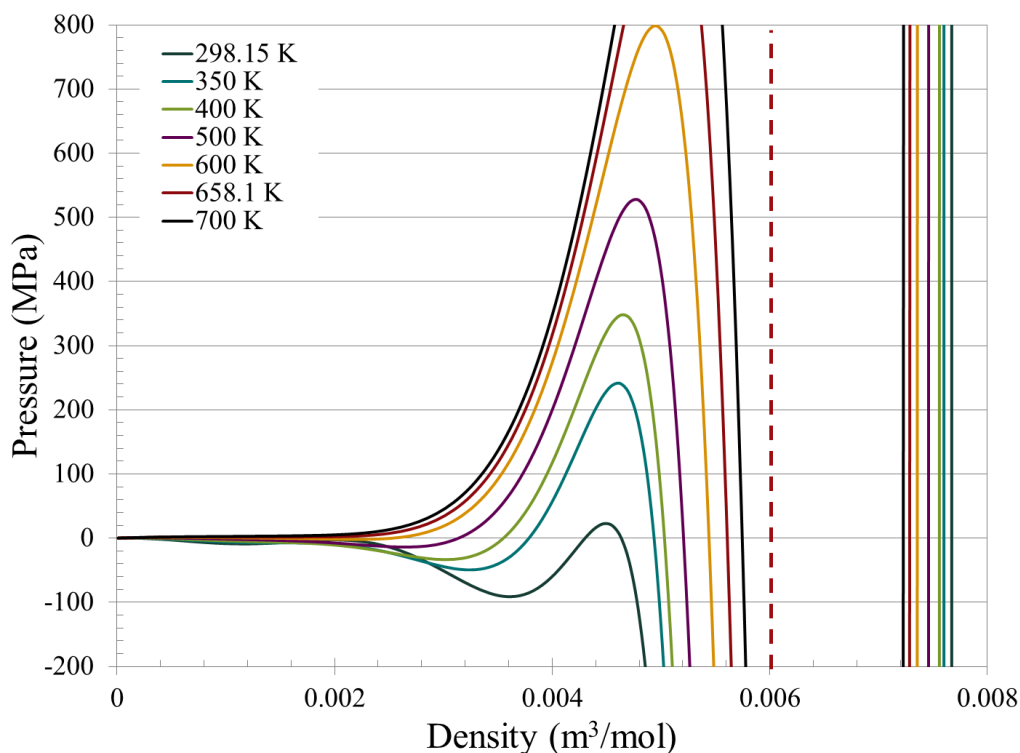


Figure 6.13. Pressure predicted by SAFT-BACK at multiple temperatures for dodecane at various densities. The segments at high molar volume are connected through a minimum that is off scale. Red dotted line represents the close-packed density.

The liquid densities of interest for dodecane shown in Figure 6.13 are to the left of the red dotted line, which represents the close-packed density. The hump that is seen around 0.0044 m³/mol represents the saturated liquid (3rd and 4th) roots, and the height of it decreases with decreasing temperature (Figure 6.13). For this work, we seek to model liquids up to 50 MPa. When the height of this hump decreases below the pressure of interest, these roots disappear as solutions, and the only root remaining is the nonphysical 5th root. This helps to explain the why the predictions become spurious as the temperature decreases.

A similar trend can be seen for multiple components at room temperature (Figure 6.14). The liquid densities of interest for propane shown in Figure 6.14 are to the left of the maximum pressure hump at 700 MPa. This pressure high enough for propane that experimental conditions for propane can be represented by the SAFT-BACK as shown in Figure 6.14. In order to represent compressed liquids, this pressure maximum must be above the experimental pressures.

However, the 5th root is above the close-packed density for propane (0.024 m³/mol), and as such should not be considered as a realistic root. In the case of all molecules shown in Figure 6.14, this 5th root is above the close-packed density for each molecule.

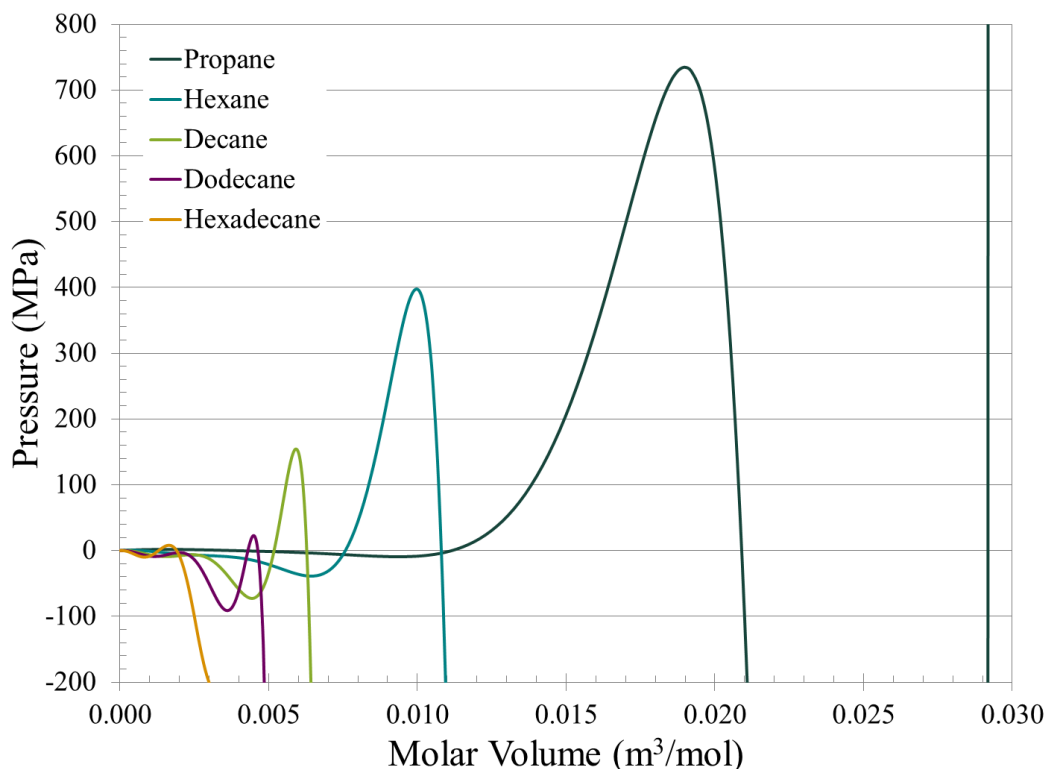


Figure 6.14. Pressure predicted by SAFT-BACK at 298.15 K for multiple n-alkanes at various densities. Curves for all molecules except propane have been truncated after the 4th root, to improve visibility. The two segments at high molar volume for propane are connected through a minimum that is off scale.

A distinct trend in the height of the stable liquid region “hump” at 298.15 K can be seen in Figure 6.14. An enlarged image is shown in Figure 6.15. As the molecule size increases, the height of the hump decreases strongly. As the size of the molecule increases, the maximum pressure that be represented at 298.15 K decreases. For hexadecane, a molecule representative of a jet/diesel fuel component, the liquid molar volume below 10 MPa is in the range of 0.0016 m³/mol, but above about 10 MPa, the only molar volume root jumps to the range of 0.0058 m³/mol (the nonphysical 5th root) and is a nonphysical solution.

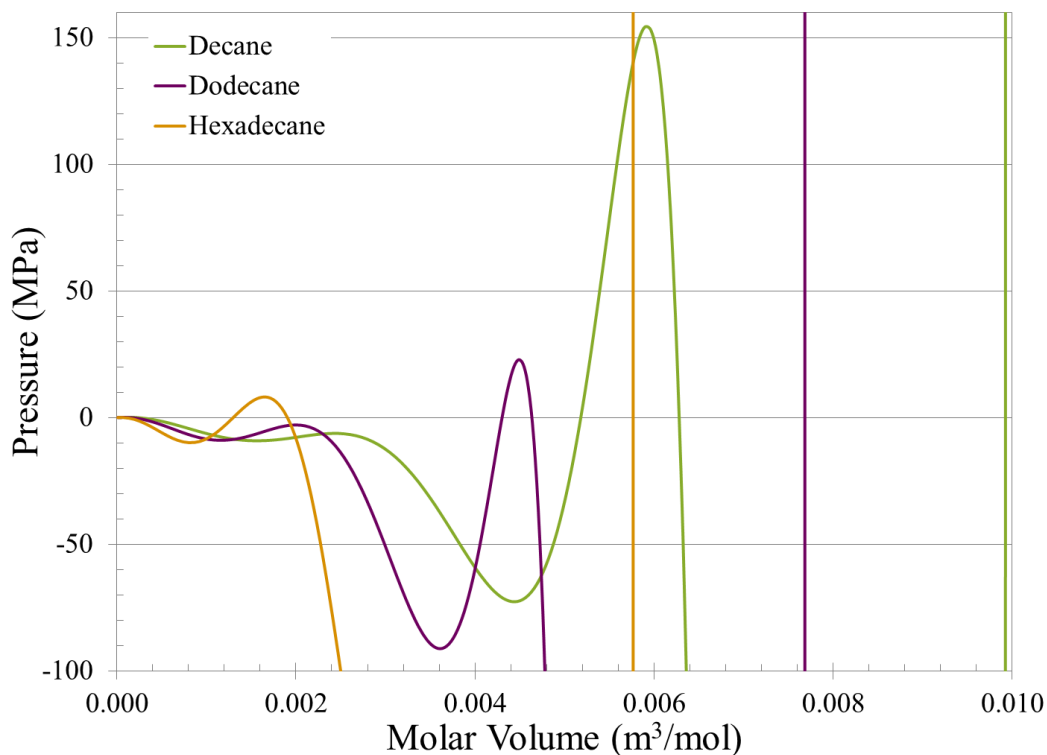


Figure 6.15. Zoomed in version of Figure 6.14 to show detail in the pressure range of interest for the three largest alkanes. All roots are shown in this version of the figure, and segments are connected through a minimum which is off scale.

6.3.4 Speed of sound prediction for mixtures

The speed of sound for binary mixtures was predicted using the compounds for which the SAFT-BACK worked moderately well. Mixtures included ethane/butane and propane/hexane, and were evaluated at multiple compositions and temperatures. It was found that the mixing rules work moderately well. As long as the individual compounds were predicted well at the selected temperatures, the mixtures were predicted accurately (Figure 6.16 and Figure 6.17). These results are similar to those shown by Maghari [120]. Maghari's results are again more accurate than we were able to reproduce at the higher molecular weights, but we have very similar results at the low molecular weights.

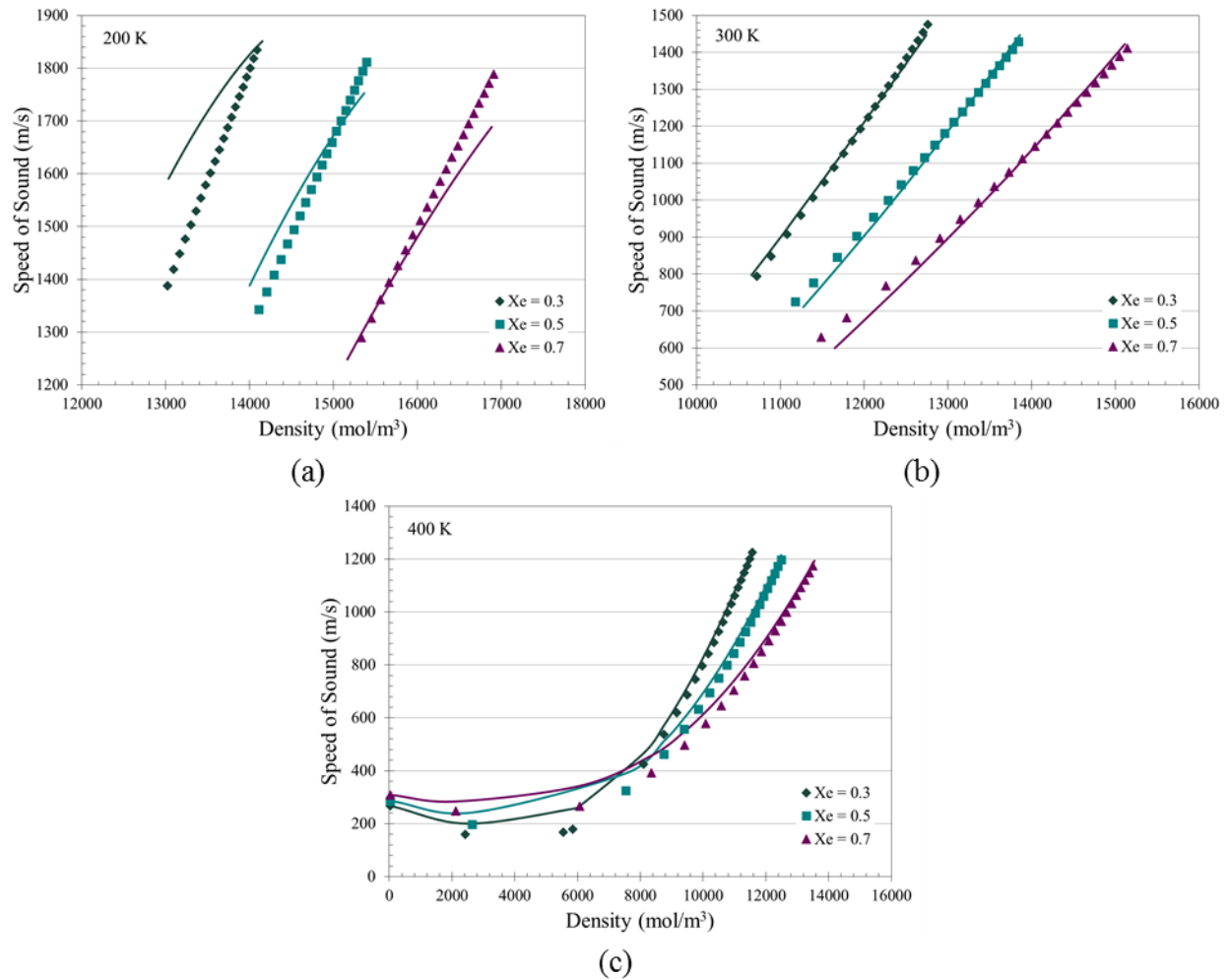


Figure 6.16. Speed of sound predicted for mixtures of ethane and butane at various temperatures, compared to GERG correlation values from [116]. (a) 200 K, (b) 300 K, and (c) 400 K.

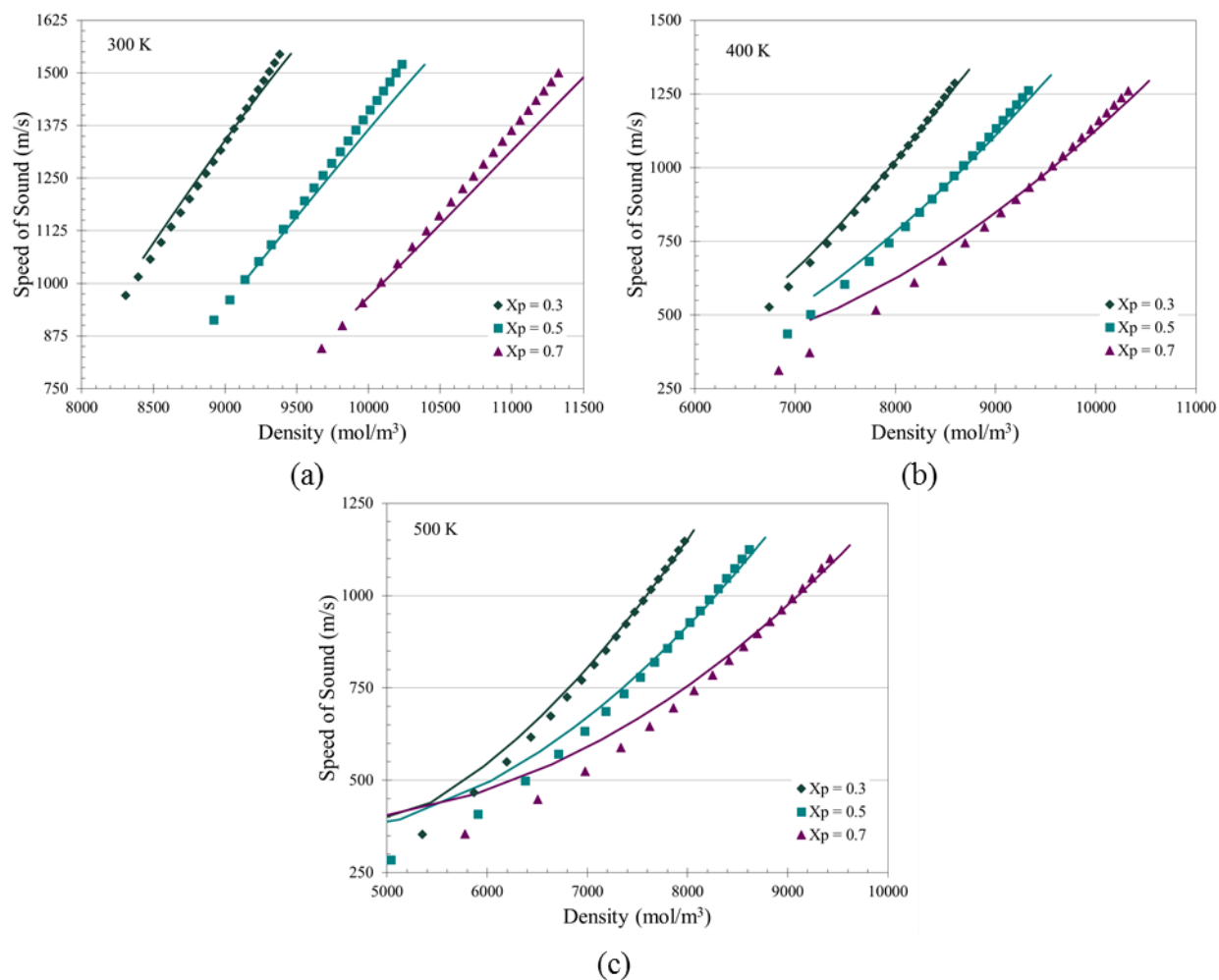


Figure 6.17. Speed of sound predicted for mixtures of propane and hexane at various temperatures, compared to GERG correlation values from [116]. (a) 300 K, (b) 400 K, and (c) 500 K.

6.4 Conclusions

Density and speed of sound were predicted for multiple n-alkanes and some binary mixtures. Both the ESD and SAFT-BACK equations were evaluated for density, and the SAFT-BACK equation was found to work better for all molecules selected. The SAFT-BACK equation was then used to predict the density, speed of sound, and heat capacities for eight n-alkanes, ranging in size from methane to n-dodecane. Density was predicted well for molecules smaller than octane, and speed of sound for molecules smaller than hexane. The slope of C_V is predicted incorrectly, which causes the fluid to be predicted as too compressible. This leads to the speed of

sound being overpredicted for the larger molecules. The mixtures are well predicted in the temperature and pressure ranges where the pure fluids are well predicted. The SAFT-BACK equation works well for small molecules and high temperatures, but fails for larger molecules near room temperature because the only real volume root at high pressure is the nonphysical root that is smaller than the close-packed volume.

APPENDICES

APPENDIX A

Cloud point and pour point data for all mixtures

This appendix gives all the raw data and adjusted data for the cloud point and pour point temperature measurements.

Table A.1. Cloud point temperatures for mixtures of USD and various additives (Part 1).

Additive	Mass % Additive	Cloud Point Temperature (°C)	Additive	Mass % Additive	Cloud Point Temperature (°C)
USD only	0.0	-27.1	4-Heptanone	24.2	-16.7
	0.0	-26.8		24.2	-16.6
Dihexyl ketone	9.7	-4.7		24.2	-16.7
	9.7	-5.2		48.9	-17
	9.7	-8.1		48.9	-17.1
	14.6	0.3		48.9	-16.9
	14.6	0		74.1	-19.3
	14.6	0.7		74.1	-19
	24.4	9.6		74.1	-19.1
	24.4	8.9		84.4	-22
	24.4	9.9		84.4	-21.5
Dibutyl succinate	16.5	-14.4		84.4	-21.9
	16.5	-14.2	Butyl nonanoate	5.0	-15.5
	16.5	-14.2		5.0	-15.4
	27.1	-13.3		5.0	-15
	27.1	-13.4		15.0	-16
	27.1	-13.4		15.0	-15.8
	27.1	-13.9		15.0	-15.8
	27.1	-13.8		24.9	-16.4
	27.1	-13.9		24.9	-16
	52.8	-11		24.9	-16.1
	52.8	-11.3		49.9	-17.6
	52.8	-11.8		49.9	-18.3
	52.8	-11.8		49.9	-18.3
	52.8	-12.2		74.9	-23.2
	77.0	-11		74.9	-22.8
	77.0	-10		74.9	-23.1
	77.0	-11.5		85.0	-27.8
	86.4	-11.3		85.0	-25.5
	86.4	-11.6		85.0	-26
	86.4	-12.1	Dihexyl ether	23.6	-17.6
	91.0	-17.7		23.6	-17.7
	91.0	-15.9		23.6	-17.6
	91.0	-16.2		73.6	-27.4
	91.0	-15.9		73.6	-27.2
				73.6	-27.3

Table A.2. Cloud point temperatures for mixtures of USD and various additives (Part 2).

Additive	Mass % Additive	Cloud Point Temperature (°C)	Additive	Mass % Additive	Cloud Point Temperature (°C)
Isobutyl nonanoate	25.4	-16.1	Hexanes	20.6	-21.6
	25.4	-16.4		20.6	-21.6
	25.4	-16.2		20.6	-21.6
	50.5	-18		43.7	-26.7
	50.5	-18		43.7	-26.4
	50.5	-18.2		43.7	-26.8
	75.4	-21.5		70.0	-35.1
	75.4	-22.1		70.0	-35
	75.4	-22.4		70.0	-34.6
Diisobutyl succinate	27.1	-13.5	Dibutyl ether	81.5	-41.1
	27.1	-13.6		81.5	-39.5
	27.1	-13.4		23.1	-18.3
	52.8	-11.8		23.1	-18.3
	52.8	-11.2		23.1	-18.2
	52.8	-11.9		73.0	-29.1
	77.0	-10.6		73.0	-29.2
	77.0	-11.5		73.0	-29.1
	77.0	-10.5	Ethyl hexyl nonanoate	24.9	-15.8
Butyl butyrate	15.3	-15.9		24.9	-15.7
	15.3	-16		24.9	-15.9
	15.3	-15.9		74.9	-22.7
	25.4	-16.7		74.9	-23.1
	25.4	-16.4		74.9	-22.7
	25.4	-16.6			
	50.5	-18			
	50.5	-17.9			
	50.5	-18			
	75.4	-21.1			
	75.4	-21			
	75.4	-20.9			
	85.3	-23.9			
	85.3	-24.2			
	85.3	-24.2			

Table A.3. Cloud point temperatures for mixtures of HAD and various additives (Part 1).

Additive	Mass % Additive	Cloud Point Temperature (°C)	Additive	Mass % Additive	Cloud Point Temperature (°C)
HAD only	0	-14.3	4-Heptanone	48.9	-29.8
	0	-15.2		48.9	-29.8
Diethyl ketone	9.7	-7		48.9	-29.7
	9.7	-7.6		74.1	-33
	9.7	-9		74.1	-33
	24.4	6.8		79.3	-34
	24.4	7.2		79.3	-34.2
	24.4	6.1		79.3	-34.1
Dibutyl succinate	16.5	-25.9	Butyl nonanoate	5.0	-27.6
	16.5	-26.1		5.0	-27.6
	16.5	-26.1		5.0	-27.7
	27.1	-26		15.0	-28.5
	27.1	-25.9		15.0	-28
	27.1	-25.6		15.0	-28.2
	52.8	-24.1		24.9	-28.5
	52.8	-24.9		24.9	-28.4
	52.8	-24.2		24.9	-28.5
	77.0	-23.6		49.9	-30.5
	77.0	-23.6		49.9	-31.1
	77.0	-23.7		49.9	-30.4
	77.0	-23.4		74.9	-35.7
	77.0	-23.3		74.9	-35.6
	86.4	-25.6		74.9	-35.8
	86.4	-25.5	Diethyl ether	85.0	-38.5
	86.4	-25.6		85.0	-38.5
	91.0	-28		85.0	-38
	91.0	-27.9		23.6	-30
	91.0	-28		23.6	-30.1
	95.5	-34.6		23.6	-29.9
	95.5	-33.5		73.6	-38.9
	95.5	-34.2		73.6	-38.5
				73.6	-38.7

Table A.4. Cloud point temperatures for mixtures of HAD and various additives (Part 2).

Additive	Mass % Additive	Cloud Point Temperature (°C)	Additive	Mass % Additive	Cloud Point Temperature (°C)
Isobutyl nonanoate	25.4	-28.8	Hexanes	20.6	-34.1
	25.4	-28.6		20.6	-34
	25.4	-28.6		20.6	-33.7
	50.5	-30.5		43.7	-39.8
	50.5	-30.4		43.7	-40.1
	50.5	-30.7		43.7	-39.5
	75.4	-35.4		70.0	-48.9
	75.4	-35.9		70.0	-48.7
	75.4	-35.7		70.0	-48.4
Diisobutyl succinate	27.1	-25.6	Dibutyl ether	81.5	-54.2
	27.1	-25.6		81.5	-53.8
	27.1	-25.7		81.5	-54.3
	52.8	-23.7		23.1	-31.8
	52.8	-24.2		23.1	-31.5
	52.8	-23.8		23.1	-31.3
	77.0	-23		73.0	-42.9
	77.0	-22.9		73.0	-42.3
	77.0	-23.3		73.0	-42.8
Butyl butyrate	15.3	-28.6	Ethyl hexyl nonanoate	24.9	-28.2
	15.3	-28.6		24.9	-28.4
	15.3	-28.5		24.9	-28.8
	25.4	-28.8		49.9	-30.5
	25.4	-28.8		49.9	-31.1
	25.4	-28.9		49.9	-30.9
	50.5	-30.9		74.9	-36.2
	50.5	-31		74.9	-36.5
	50.5	-31		74.9	-35.9
	75.4	-35.5	Butyl ethyl hexanoate	24.9	-28.9
	75.4	-35.4		24.9	-29.2
	75.4	-34.9		24.9	-29.3
	85.3	-38.2		49.9	-31
	85.3	-37.8		49.9	-31.3
	85.3	-37		49.9	-31.5
				74.9	-35.9
				74.9	-36
				74.9	-35.8

Table A.5. Cloud point (CP), adjusted cloud point (CP*), and cold filter plugging point (CFPP) temperatures for mixtures of canola FAME in the HAD+ fuel. The cloud point data was collected using ASTM D2500, and CFFP data collected by ASTM D6371. The cloud point data is adjusted for comparison with ASTM D7683 using Cloud point (D2500) = Cloud point (D7683) + 1.68.

Mass% Canola FAME	CP (°C)	CP* (°C)	CFPP (°C)
0.0	-24	-25.7	-38
0.0	-24	-25.7	-36
10.3	-20	-21.7	-35
10.3	-20	-21.7	-34
15.4	-20	-21.7	-33
20.5	-19	-20.7	-31
20.5	-19	-20.7	-31
30.7	-16	-17.7	-28
30.7	-16	-17.7	-28
40.8	-15	-16.7	-21
40.8	-15	-16.7	-21
60.8	-9	-10.7	-19
80.5	-7	-8.7	-14
100.0	-6	-7.7	-10

Table A.6. Cloud point (CP) and adjusted cloud point (CP*) temperatures for mixtures of dibutyl succinate in the HAD* fuel. The cloud point data was collected using ASTM D2500. The cloud point data is adjusted for comparison with ASTM D7683 using Cloud point (D2500) = Cloud point (D7683) + 1.68.

Mass % Dibutyl Succinate	CP (°C)	CP* (°C)
0	-26	-27.7
0.0	-25	-26.7
11.3	-25	-26.7
22.3	-24	-25.7
22.3	-24	-25.7
33.0	-24	-25.7
43.3	-23	-24.7
53.4	-22	-23.7
63.2	-21	-22.7
72.8	-21	-22.7
82.1	-21	-22.7
91.2	-24	-25.7
91.2	-22	-23.7
100.0	-29	-29

Table A.7. Cloud point (CP), adjusted cloud point (CP*), and cold filter plugging point (CFPP) temperatures for mixtures of dibutyl succinate in the HAD+ fuel. The cloud point data was collected using ASTM D2500. The cloud point data is adjusted for comparison with ASTM D7683 using $\text{Cloud point (D2500)} = \text{Cloud point (D7683)} + 1.68$.

Mass % Dibutyl Succinate	CP (°C)	CP* (°C)	CFPP (°C)
0.0	-24	-25.7	-38
0.0	-24	-25.7	-36
11.3	-23	-24.7	-41
22.3	-23	-24.7	-41
33.0	-22	-23.7	-41
43.3	-21	-22.7	-42
53.4	-20	-21.7	-43
63.2	-20	-21.7	-42
72.8	-19	-20.7	-42
82.1	-20	-21.7	-41
91.2	-23	-24.7	-41
100.0	-29	-29	-41

Table A.8. Cold filter plugging point (CFPP) temperatures for mixtures of butyl nonanoate in the HAD fuel.

Mass % Butyl Nonanoate	CFPP (°C)
0.0	-38
0.0	-36
10.0	-32
10.0	-32
29.9	-33
29.9	-33
49.9	-35
49.9	-35
69.9	-47
69.9	-42
89.9	-50
89.9	-49

APPENDIX B

Tabulated data for the prediction of physical properties

This appendix tabulates the values of all the constants given in Chapter 3, as well as the predicted data for all compounds.

Table B.1. Constants for the regression of Cp/R for the lower temperature range.

	Dibutyl Succinate	Methyl Oleate	Methyl Stearate	Cetane	Heptamethyl- nonane	TGME
A ₁	32.619	-5.455	-2.430	-10.191	-12.176	-9.185
A ₂	6.004	0.245	0.239	0.234	0.241	0.198
A ₃	-0.187	-1.83E-04	-1.75E-04	-1.98E-04	-1.92E-04	-2.07E-04
A ₄	-6.91E-04	7.46E-08	7.36E-08	9.58E-08	8.04E-08	1.26E-07
A ₅	1.40E-04	-1.31E-11	-1.43E-11	-1.97E-11	-1.40E-11	-3.25E-11

Table B.2. Constants for the regression of Cp/R for the high temperature range.

	Dibutyl Succinate	Methyl Oleate	Methyl Stearate	Cetane	Heptamethyl- nonane	TGME
A ₁	36.700	47.343	49.352	36.630	40.981	33.656
A ₂	7.31E-02	0.115	0.121	0.109	0.103	6.99E-02
A ₃	-2.91E-05	-4.58E-05	-4.81E-05	-4.39E-05	-4.07E-05	-2.77E-05
A ₄	5.28E-09	8.30E-09	8.72E-09	8.01E-09	7.35E-09	5.01E-09
A ₅	-3.59E-13	-5.64E-13	-5.93E-13	-5.48E-13	-4.98E-13	-3.40E-13

Table B.3. Constants for the regression of H/RT for the low temperature range.

	Dibutyl Succinate	Methyl Oleate	Methyl Stearate	Cetane	Heptamethyl- nonane	TGME
A ₁	32.619	-5.455	-2.430	-10.191	-12.176	-9.185
A ₂	6.004	0.245	2.39E-01	2.34E-01	0.241	0.198
A ₃	-0.187	-1.83E-04	-1.75E-04	-1.98E-04	-1.92E-04	-2.07E-04
A ₄	-6.91E-04	7.46E-08	7.36E-08	9.58E-08	8.04E-08	1.26E-07
A ₅	1.40E-04	-1.31E-11	-1.43E-11	-1.97E-11	-1.40E-11	-3.25E-11
A ₆	-6.31E+07	-7.78E+03	-8.51E+03	-5.79E+03	-5.55E+03	-4.45E+03

Table B.4. Constants for the regression of H/RT for the high temperature range.

	Dibutyl Succinate	Methyl Oleate	Methyl Stearate	Cetane	Heptamethyl- nonane	TGME
A ₁	36.700	47.343	49.352	36.630	40.981	33.656
A ₂	0.073	0.115	0.121	0.109	0.103	0.070
A ₃	-2.91E-05	-4.58E-05	-4.81E-05	-4.39E-05	-4.07E-05	-2.77E-05
A ₄	5.28E-09	8.30E-09	8.72E-09	8.01E-09	7.35E-09	5.01E-09
A ₅	-3.59E-13	-5.64E-13	-5.93E-13	-5.48E-13	-4.98E-13	-3.40E-13
A ₆	-1.39E+04	-1.88E+04	-1.97E+04	-1.54E+04	-1.64E+04	-1.29E+04

Table B.5. Constants for the regression of S/T for the low temperature range.

	Dibutyl Succinate	Methyl Oleate	Methyl Stearate	Cetane	Heptamethyl- nonane	TGME
A ₁	32.619	-5.455	-2.430	-10.191	-12.176	-9.185
A ₂	6.004	0.245	0.239	2.34E-01	0.241	0.198
A ₃	-0.187	-1.83E-04	-1.75E-04	-1.98E-04	-1.92E-04	-2.07E-04
A ₄	-6.91E-04	7.46E-08	7.36E-08	9.58E-08	8.04E-08	1.26E-07
A ₅	1.40E-04	-1.31E-11	-1.43E-11	-1.97E-11	-1.40E-11	-3.25E-11
A ₇	-2.64E+05	-34.423	-50.396	-3.703	5.274	1.538

Table B.6. Constants for the regression of S/T for the high temperature range.

	Dibutyl Succinate	Methyl Oleate	Methyl Stearate	Cetane	Heptamethyl- nonane	TGME
A ₁	36.700	47.343	49.352	36.630	40.981	33.656
A ₂	0.073	0.115	0.121	0.109	0.103	0.070
A ₃	-2.91E-05	-4.58E-05	-4.81E-05	-4.39E-05	-4.07E-05	-2.77E-05
A ₄	5.28E-09	8.30E-09	8.72E-09	8.01E-09	7.35E-09	5.01E-09
A ₅	-3.59E-13	-5.64E-13	-5.93E-13	-5.48E-13	-4.98E-13	-3.40E-13
A ₇	-2.30E+02	-3.02E+02	-3.15E+02	-2.39E+02	-2.62E+02	-2.11E+02

Table B.7. Predicted data for the viscosity of various compounds extrapolated to the critical point (Part 1).

Dibutyl Succinate		Methyl Oleate		Methyl Stearate	
Temperature (K)	Viscosity (Pa*s)	Temperature (K)	Viscosity (Pa*s)	Temperature (K)	Viscosity (Pa*s)
250	2.34E-02	293	1.04E-02	310	6.73E-03
260	1.64E-02	300	8.53E-03	320	5.19E-03
270	1.18E-02	310	6.53E-03	330	4.07E-03
280	8.73E-03	320	5.08E-03	340	3.23E-03
290	6.57E-03	330	4.02E-03	350	2.60E-03
300	5.04E-03	340	3.22E-03	360	2.12E-03
310	3.94E-03	350	2.61E-03	370	1.75E-03
320	3.12E-03	360	2.14E-03	380	1.46E-03
330	2.51E-03	370	1.78E-03	390	1.22E-03
340	2.04E-03	380	1.49E-03	400	1.04E-03
350	1.68E-03	390	1.26E-03	410	8.86E-04
360	1.40E-03	400	1.07E-03	420	7.63E-04
370	1.18E-03	410	9.24E-04	430	6.62E-04
380	1.00E-03	420	7.99E-04	440	5.77E-04
390	8.58E-04	430	6.97E-04	450	5.07E-04
400	7.40E-04	440	6.11E-04	460	4.48E-04
410	6.43E-04	450	5.39E-04	470	3.97E-04
420	5.63E-04	460	4.78E-04	480	3.55E-04
430	4.95E-04	470	4.26E-04	490	3.18E-04
440	4.39E-04	480	3.81E-04	500	2.86E-04
450	3.90E-04	490	3.43E-04	510	2.59E-04
460	3.49E-04	500	3.10E-04	520	2.35E-04
470	3.14E-04	510	2.81E-04	530	2.14E-04
480	2.84E-04	520	2.56E-04	540	1.95E-04
490	2.57E-04	530	2.34E-04	550	1.79E-04
500	2.34E-04	540	2.15E-04	560	1.65E-04
510	2.14E-04	550	1.97E-04	570	1.52E-04
520	1.96E-04	560	1.82E-04	580	1.41E-04
530	1.80E-04	570	1.68E-04	590	1.30E-04
540	1.66E-04	580	1.56E-04	600	1.21E-04
550	1.54E-04	590	1.45E-04	610	1.13E-04
560	1.43E-04	600	1.35E-04	620	1.06E-04
570	1.33E-04	610	1.27E-04	630	9.88E-05
580	1.24E-04	620	1.18E-04	640	9.27E-05
590	1.16E-04	630	1.11E-04	650	8.71E-05
600	1.09E-04	640	1.05E-04	660	8.20E-05
610	1.02E-04	650	9.84E-05	670	7.74E-05
620	9.60E-05	660	9.29E-05	680	7.31E-05
630	9.05E-05	670	8.78E-05	690	6.92E-05
640	8.54E-05	680	8.32E-05	700	6.56E-05
650	8.08E-05	690	7.89E-05	710	6.23E-05
660	7.66E-05	700	7.49E-05	720	5.93E-05
670	7.27E-05	710	7.13E-05	730	5.64E-05
680	6.91E-05	720	6.79E-05	740	5.38E-05
690	6.58E-05	730	6.47E-05	750	5.14E-05
700	6.28E-05	740	6.18E-05	760	4.91E-05
710	5.99E-05	750	5.91E-05	770	4.70E-05
		760	5.66E-05	780	4.50E-05
		764	5.56E-05	781	4.48E-05

Table B.8. Predicted data for the viscosity of various compounds extrapolated to the critical point (Part 2).

Cetane		Heptamethylnonane		TGME	
Temperature (K)	Viscosity (Pa*s)	Temperature (K)	Viscosity (Pa*s)	Temperature (K)	Viscosity (Pa*s)
291	3.47E-03	163	2.44E+01	231	5.04E-02
300	2.86E-03	170	1.12E+01	240	3.24E-02
310	2.34E-03	180	4.06E+00	250	2.06E-02
320	1.94E-03	190	1.64E+00	260	1.35E-02
330	1.63E-03	200	7.28E-01	270	9.16E-03
340	1.38E-03	210	3.48E-01	280	6.38E-03
350	1.18E-03	220	1.78E-01	290	4.56E-03
360	1.02E-03	230	9.68E-02	300	3.33E-03
370	8.87E-04	240	5.52E-02	310	2.49E-03
380	7.77E-04	260	2.05E-02	320	1.89E-03
390	6.85E-04	270	1.32E-02	330	1.46E-03
400	6.08E-04	280	8.76E-03	340	1.14E-03
410	5.43E-04	290	5.98E-03	350	9.10E-04
420	4.88E-04	300	4.19E-03	360	7.33E-04
430	4.40E-04	310	3.01E-03	370	5.97E-04
440	3.99E-04	320	2.20E-03	380	4.92E-04
450	3.63E-04	330	1.64E-03	390	4.09E-04
460	3.32E-04	340	1.25E-03	400	3.43E-04
470	3.04E-04	360	7.52E-04	410	2.91E-04
480	2.80E-04	370	5.96E-04	420	2.48E-04
490	2.59E-04	380	4.78E-04	430	2.13E-04
500	2.40E-04	390	3.88E-04	440	1.85E-04
510	2.23E-04	410	2.64E-04	450	1.61E-04
520	2.08E-04	420	2.20E-04	460	1.41E-04
530	1.95E-04	430	1.86E-04	470	1.24E-04
540	1.82E-04	440	1.58E-04	480	1.10E-04
550	1.71E-04	460	1.16E-04	490	9.81E-05
560	1.61E-04	470	1.01E-04	500	8.78E-05
570	1.52E-04	480	8.77E-05	510	7.89E-05
580	1.44E-04	490	7.69E-05	520	7.12E-05
590	1.36E-04	500	6.78E-05	530	6.45E-05
600	1.29E-04	510	6.00E-05	540	5.86E-05
610	1.23E-04	520	5.34E-05	550	5.34E-05
620	1.17E-04	530	4.77E-05	560	4.89E-05
630	1.11E-04	540	4.28E-05	570	4.49E-05
640	1.06E-04	560	3.49E-05	580	4.14E-05
650	1.02E-04	570	3.17E-05	590	3.82E-05
660	9.75E-05	580	2.89E-05	600	3.54E-05
670	9.35E-05	590	2.64E-05	610	3.28E-05
680	8.97E-05	600	2.42E-05	620	3.05E-05
690	8.63E-05	610	2.22E-05	630	2.85E-05
700	8.30E-05	620	2.05E-05	640	2.66E-05
710	8.00E-05	630	1.89E-05	650	2.49E-05
720	7.71E-05	640	1.75E-05	657	2.38E-05
723	7.63E-05	660	1.51E-05		
		670	1.41E-05		
		680	1.32E-05		
		690	1.23E-05		
		692	1.22E-05		

Table B.9. Predicted data for the heat capacity of various compounds extrapolated to the critical point (Part 1).

Dibutyl Succinate		Methyl Oleate		Methyl Stearate	
Temperature (K)	Heat Capacity (J/kgK)	Temperature (K)	Heat Capacity (J/kgK)	Temperature (K)	Heat Capacity (J/kgK)
250	1.87E+03	293	2.09E+03	310	2.10E+03
260	1.89E+03	300	2.11E+03	320	2.13E+03
270	1.92E+03	310	2.14E+03	330	2.16E+03
280	1.94E+03	320	2.17E+03	340	2.19E+03
290	1.97E+03	330	2.20E+03	350	2.22E+03
300	1.99E+03	340	2.23E+03	360	2.25E+03
310	2.02E+03	350	2.25E+03	370	2.28E+03
320	2.05E+03	360	2.28E+03	380	2.31E+03
330	2.08E+03	370	2.31E+03	390	2.34E+03
340	2.10E+03	380	2.34E+03	400	2.37E+03
350	2.13E+03	390	2.37E+03	410	2.40E+03
360	2.16E+03	400	2.40E+03	420	2.43E+03
370	2.19E+03	410	2.43E+03	430	2.46E+03
380	2.22E+03	420	2.46E+03	440	2.49E+03
390	2.24E+03	430	2.48E+03	450	2.52E+03
400	2.27E+03	440	2.51E+03	460	2.55E+03
410	2.30E+03	450	2.54E+03	470	2.58E+03
420	2.33E+03	460	2.57E+03	480	2.61E+03
430	2.36E+03	470	2.60E+03	490	2.63E+03
440	2.39E+03	480	2.62E+03	500	2.66E+03
450	2.41E+03	490	2.65E+03	510	2.69E+03
460	2.44E+03	500	2.68E+03	520	2.72E+03
470	2.47E+03	510	2.71E+03	530	2.75E+03
480	2.50E+03	520	2.74E+03	540	2.78E+03
490	2.53E+03	530	2.76E+03	550	2.80E+03
500	2.56E+03	540	2.79E+03	560	2.83E+03
510	2.58E+03	550	2.82E+03	570	2.86E+03
520	2.61E+03	560	2.84E+03	580	2.89E+03
530	2.64E+03	570	2.87E+03	590	2.92E+03
540	2.67E+03	580	2.90E+03	600	2.94E+03
550	2.70E+03	590	2.93E+03	610	2.97E+03
560	2.73E+03	600	2.96E+03	620	3.00E+03
570	2.76E+03	610	2.99E+03	630	3.03E+03
580	2.79E+03	620	3.02E+03	640	3.06E+03
590	2.83E+03	630	3.05E+03	650	3.09E+03
600	2.86E+03	640	3.08E+03	660	3.13E+03
610	2.90E+03	650	3.11E+03	670	3.16E+03
620	2.94E+03	660	3.15E+03	680	3.20E+03
630	2.98E+03	670	3.19E+03	690	3.24E+03
640	3.04E+03	680	3.23E+03	700	3.28E+03
650	3.10E+03	690	3.28E+03	710	3.33E+03
660	3.17E+03	700	3.34E+03	720	3.39E+03
670	3.28E+03	710	3.42E+03	730	3.47E+03
680	3.43E+03	720	3.52E+03	740	3.58E+03
690	3.68E+03	730	3.67E+03	750	3.74E+03
700	4.25E+03	740	3.93E+03	760	4.04E+03
710	6.85E+03	750	4.54E+03	770	4.86E+03
		760	8.17E+03	775	6.25E+03

Table B.10. Predicted data for the heat capacity of various compounds extrapolated to the critical point (Part 2).

Cetane		Heptamethylnonane		TGME	
Temperature (K)	Heat Capacity (J/kgK)	Temperature (K)	Heat Capacity (J/kgK)	Temperature (K)	Heat Capacity (J/kgK)
291	2.16E+03	163	1.49E+03	231	2.11E+03
300	2.19E+03	170	1.52E+03	240	2.12E+03
310	2.23E+03	180	1.56E+03	250	2.14E+03
320	2.27E+03	190	1.60E+03	260	2.15E+03
330	2.31E+03	200	1.64E+03	270	2.17E+03
340	2.35E+03	210	1.68E+03	280	2.19E+03
350	2.38E+03	220	1.73E+03	290	2.21E+03
360	2.42E+03	230	1.77E+03	300	2.24E+03
370	2.46E+03	240	1.82E+03	310	2.26E+03
380	2.50E+03	260	1.91E+03	320	2.28E+03
390	2.53E+03	270	1.95E+03	330	2.30E+03
400	2.57E+03	280	2.00E+03	340	2.33E+03
410	2.61E+03	290	2.04E+03	350	2.35E+03
420	2.64E+03	300	2.09E+03	360	2.38E+03
430	2.68E+03	310	2.13E+03	370	2.40E+03
440	2.71E+03	320	2.18E+03	380	2.42E+03
450	2.75E+03	330	2.22E+03	390	2.45E+03
460	2.79E+03	340	2.26E+03	400	2.47E+03
470	2.82E+03	360	2.35E+03	410	2.50E+03
480	2.86E+03	370	2.39E+03	420	2.52E+03
490	2.89E+03	380	2.44E+03	430	2.55E+03
500	2.92E+03	390	2.48E+03	440	2.57E+03
510	2.96E+03	400	2.52E+03	450	2.60E+03
520	2.99E+03	410	2.56E+03	460	2.63E+03
530	3.03E+03	420	2.60E+03	470	2.65E+03
540	3.06E+03	430	2.64E+03	480	2.68E+03
550	3.10E+03	440	2.68E+03	490	2.71E+03
560	3.13E+03	460	2.76E+03	500	2.73E+03
570	3.17E+03	470	2.80E+03	510	2.76E+03
580	3.20E+03	480	2.84E+03	520	2.79E+03
590	3.24E+03	490	2.88E+03	530	2.82E+03
600	3.28E+03	500	2.92E+03	540	2.86E+03
610	3.32E+03	510	2.95E+03	550	2.90E+03
620	3.36E+03	520	2.99E+03	560	2.94E+03
630	3.41E+03	530	3.03E+03	570	2.98E+03
640	3.46E+03	540	3.07E+03	580	3.03E+03
650	3.52E+03	560	3.15E+03	590	3.10E+03
660	3.59E+03	570	3.19E+03	600	3.18E+03
670	3.67E+03	580	3.23E+03	610	3.29E+03
680	3.79E+03	590	3.28E+03	620	3.45E+03
690	3.96E+03	600	3.33E+03	630	3.72E+03
700	4.26E+03	610	3.38E+03	640	4.29E+03
710	4.98E+03	620	3.44E+03	650	6.47E+03
720	1.05E+04	630	3.50E+03		
		640	3.59E+03		
		660	3.86E+03		
		670	4.14E+03		
		680	4.86E+03		
		690	1.26E+04		

Table B.11. Predicted gas phase heat capacities for various compounds. Units are J/kgK .

Temperature (K)	Dibutyl Succinate	Methyl Oleate	Methyl Stearate	Cetane	Heptamethyl- nonane	TGME
1000	3079.94	3474.89	3615.14	3991.84	4026.39	3231.88
1250	3335.16	3787.03	3940.80	4376.07	4392.90	3504.67
1500	3507.66	3998.34	4161.31	4631.37	4643.60	3690.17
1750	3627.26	4144.93	4314.26	4805.96	4818.62	3819.31
2000	3712.44	4249.38	4423.24	4929.11	4943.87	3911.57
2250	3774.78	4325.78	4502.95	5018.52	5035.74	3979.21
2500	3821.49	4383.05	4562.70	5085.17	5104.75	4029.98
2750	3857.26	4426.91	4608.45	5136.00	5157.69	4068.92
3000	3885.20	4461.16	4644.18	5175.56	5199.06	4099.36
3250	3907.40	4488.37	4672.57	5206.90	5231.97	4123.56
3500	3925.29	4510.30	4695.44	5232.12	5258.52	4143.07
3750	3939.92	4528.23	4714.15	5252.70	5280.23	4159.05
4000	3952.02	4543.06	4729.63	5269.70	5298.21	4172.26
4250	3962.14	4555.47	4742.56	5283.91	5313.23	4183.31
4500	3970.70	4565.94	4753.48	5295.88	5325.93	4192.64
4750	3977.96	4574.86	4762.79	5306.08	5336.74	4200.59
5000	3984.21	4582.51	4770.77	5314.82	5346.03	4207.43

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APPENDIX C

Distillation Curve Data

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This appendix provides supporting data for Chapter 4. The measured temperature is corrected to atmospheric pressure using the Sydney Young equation as cited in Chapter 4.

Table C.1. Uncorrected and corrected distillation data for JP-8. Data taken with an atmospheric pressure of 737 mmHg.

Volume Distilled (mL)	Measured T (°C)	Pressure Correction (°C)	Corrected T (°C)
0	166.5	1.213	167.7
100	182.5	1.257	183.8
200	185.9	1.267	187.2
300	188.5	1.274	189.8
400	191.2	1.281	192.5
500	194.8	1.291	196.1
600	196.5	1.296	197.8
700	199.1	1.303	200.4
800	201	1.308	202.3
900	205	1.319	206.3
1000	208	1.328	209.3
1100	211	1.336	212.3
1200	214	1.344	215.3
1300	218	1.355	219.4
1400	222	1.366	223.4
1500	227	1.380	228.4
1600	232	1.394	233.4
1700	238	1.410	239.4
1800	244	1.427	245.4
1900	255	1.457	256.5

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Table C.2. Uncorrected and corrected distillation data for IPK. Data taken with an atmospheric pressure of 746 mmHg.

Volume Distilled (mL)	Measured T (°C)	Pressure Correction (°C)	Corrected T (°C)
0	161.8	0.7305	162.5
100	169.6	0.7436	170.3
200	170.8	0.7456	171.5
300	171.9	0.7474	172.6
400	172.8	0.7489	173.5
500	174.2	0.7513	175.0
600	175.2	0.7530	176.0
700	176.6	0.7553	177.4
800	178	0.7577	178.8
900	179.4	0.7600	180.2
1000	181	0.7627	181.8
1100	182.8	0.7657	183.6
1200	184.7	0.7689	185.5
1300	186.8	0.7725	187.6
1400	189.2	0.7765	190.0
1500	191.9	0.7810	192.7
1600	195.1	0.7864	195.9
1700	198.9	0.7928	199.7
1800	205	0.8030	205.8
1900	214	0.8182	214.8

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Table C.3. Uncorrected and corrected distillation data for HRJ. Data taken with an atmospheric pressure of 746 mmHg.

Volume Distilled (mL)	Measured T (°C)	Pressure Correction (°C)	Corrected T (°C)
0	160.2	0.7278	160.9
100	183.6	0.7671	184.4
200	191.4	0.7802	192.2
300	197	0.7896	197.8
400	201	0.7963	201.8
500	207	0.8064	207.8
600	211	0.8131	211.8
700	215	0.8198	215.8
800	220	0.8282	220.8
900	224	0.8350	224.8
1000	229	0.8434	229.8
1100	232	0.8484	232.8
1200	237	0.8568	237.9
1300	241	0.8635	241.9
1400	245	0.8702	245.9
1500	250	0.8786	250.9
1600	255	0.8870	255.9
1700	259	0.8938	259.9
1800	264	0.9022	264.9
1900	270	0.9122	270.9

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Table C.4. Uncorrected and corrected distillation data for SPK2. Data taken with an atmospheric pressure of 758 mmHg.

Volume Distilled (mL)	Measured T (°C)	Pressure Correction (°C)	Corrected T (°C)
0	159.7	0.0519	159.8
100	165.1	0.0526	165.2
200	165.8	0.0527	165.9
300	166.1	0.0527	166.2
400	166.8	0.0528	166.9
500	167.4	0.0528	167.5
600	168.1	0.0529	168.2
700	168.8	0.0530	168.9
800	169.5	0.0531	169.6
900	170.4	0.0532	170.5
1000	171.5	0.0533	171.6
1100	172.4	0.0534	172.5
1200	173.7	0.0536	173.8
1300	174.8	0.0537	174.9
1400	176.7	0.0540	176.8
1500	178.1	0.0541	178.2
1600	180.7	0.0544	180.8
1700	182.5	0.0547	182.6
1800	186.1	0.0551	186.2
1900	191.4	0.0557	191.5

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Table C.5. Uncorrected and corrected distillation data for HRJ-8. Data taken with an atmospheric pressure of 753 mmHg.

Volume Distilled (mL)	Measured T (°C)	Pressure Correction (°C)	Corrected T (°C)
0	147.4	0.3531	147.8
100	173.4	0.3750	173.8
200	177.2	0.3782	177.6
300	181	0.3814	181.4
400	184.9	0.3846	185.3
500	189.4	0.3884	189.8
600	195.2	0.3933	195.6
700	200	0.3973	200.4
800	208	0.4040	208.4
900	215	0.4099	215.4
1000	222	0.4158	222.4
1100	230	0.4225	230.4
1200	240	0.4309	240.4
1300	249	0.4385	249.4
1400	256	0.4444	256.4
1500	263	0.4502	263.5
1600	270	0.4561	270.5
1700	275	0.4603	275.5
1800	279	0.4637	279.5
1900	283	0.4670	283.5

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Table C.6. Uncorrected and corrected distillation data for HRJ-8. Data taken with an atmospheric pressure of 749.6 mmHg.

Volume Distilled (mL)	Measured T (°C)	Pressure Correction (°C)	Corrected T (°C)
0	146.2	0.5232	146.7
100	176.2	0.5606	176.8
200	179.9	0.5652	180.5
300	183.3	0.5695	183.9
400	186.5	0.5735	187.1
500	190.4	0.5783	191.0
600	194.1	0.5829	194.7
700	198.4	0.5883	199.0
800	203	0.5940	203.6
900	206	0.5978	206.6
1000	211	0.6040	211.6
1100	216	0.6103	216.6
1200	221	0.6165	221.6
1300	226	0.6228	226.6
1400	231	0.6290	231.6
1500	237	0.6365	237.6
1600	243	0.6440	243.6
1700	251	0.6540	251.7
1800	260	0.6652	260.7
1900	270	0.6777	270.7

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Table C.7. Uncorrected and corrected distillation data for HRD. Data taken with an atmospheric pressure of 743.8 mmHg.

Volume Distilled (mL)	Measured T (°C)	Pressure Correction (°C)	Corrected T (°C)
0	164	0.850	164.8
100	230	0.978	231.0
200	242	1.001	243.0
300	254	1.024	255.0
400	262	1.040	263.0
500	268	1.052	269.1
600	273	1.061	274.1
700	278	1.071	279.1
800	282	1.079	283.1
900	285	1.085	286.1
1000	288	1.091	289.1
1100	290	1.094	291.1
1200	293	1.100	294.1
1300	295	1.104	296.1
1400	297	1.108	298.1
1500	299	1.112	300.1
1600	301	1.116	302.1
1700	304	1.122	305.1
1800	307	1.128	308.1
1900	313	1.139	314.1

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APPENDIX D

Database of Potential Surrogate Components

This appendix provides the database of compounds used for surrogate development in Chapter 4. Property information was collected from DIPPR and the NIST Webbook as cited in Chapter 4. Most cetane values are from the Murphy Compendium of Cetane Numbers as cited in Chapter 4, except the compendium did not report values for many isoparaffins. For the isoparaffins only, the values reported in Ghosh and Jaffe were used.

Table D.1. Selected properties of potential surrogate components – n-paraffins, mono-aromatics, di-aromatics, and naphthenes.

Name	Molecular class	Molecular Weight (g/mol)	Melting Temperature (°C)	Boiling Temperature (°C)	Cetane Number
n-Hexane	n-Paraffin	86.18	-95.32	68.88	43.9
n-Heptane	n-Paraffin	100.2	-90.58	98.58	52.5
n-Octane	n-Paraffin	114.23	-56.77	125.83	64.4
n-Nonane	n-Paraffin	128.26	-53.49	150.97	73
n-Decane	n-Paraffin	142.28	-29.64	174.31	76.7
n-Undecane	n-Paraffin	156.31	-25.58	196.08	81.1
n-Dodecane	n-Paraffin	170.33	-9.58	216.47	82.5
n-Tridecane	n-Paraffin	184.36	-5.39	235.62	89.5
n-Tetradecane	n-Paraffin	198.39	5.86	253.73	95
n-Pentadecane	n-Paraffin	212.41	9.92	270.84	96
n-Hexadecane	n-Paraffin	226.44	18.16	287.01	100
n-Heptadecane	n-Paraffin	240.47	21.98	302.3	105
n-Octadecane	n-Paraffin	254.49	28.16	316.86	106.3
n-Nonadecane	n-Paraffin	268.52	31.89	330.05	110
n-Eicosane	n-Paraffin	282.55	36.43	343.93	110
n-Heneicosane	n-Paraffin	296.57	40.2	356.65	100
Benzene	mono-Aromatic	78.11	5.53	80.24	6.8
Toluene	mono-Aromatic	92.14	-94.97	110.78	7.4
Ethylbenzene	mono-Aromatic	106.17	-94.95	136.35	8
p-Xylene	mono-Aromatic	106.17	13.26	138.51	1
o-Xylene	mono-Aromatic	106.17	-25.17	144.58	9
n-Propylbenzene	mono-Aromatic	120.19	-99.6	159.39	7.6
Mesitylene	mono-Aromatic	120.19	-44.73	159.39	7.6
n-Butylbenzene	mono-Aromatic	134.22	-87.85	183.46	10
m-Diethylbenzene	mono-Aromatic	134.22	-83.89	181.29	0
n-Pentylbenzene	mono-Aromatic	148.24	-75	205.61	9
Hexylbenzene	mono-Aromatic	162.27	-61.15	226.26	26
Cyclohexylbenzene	mono-Aromatic	160.26	6.99	240.27	9
n-Heptylbenzene	mono-Aromatic	176.3	-48	246.25	34.7
n-Octylbenzene	mono-Aromatic	190.32	-36	264.55	35.3
n-Decylbenzene	mono-Aromatic	218.38	-14.38	298.04	56.8
Methyl Naphthalene	di-Aromatic	142.2	-30.48	244.83	0
Ethylcyclohexane	Naphthene	112.21	-111.31	131.95	34.1
n-Propylcyclohexane	Naphthene	126.24	-94.9	156.9	40
trans-Decalin	Naphthene	138.25	-30.36	187.46	40
n-Butylcyclohexane	Naphthene	140.27	-74.73	181.13	61.8
1,1-Diethylcyclohexane	Naphthene	140.27	-100	176.82	61.8
iso-Butylcyclohexane	Naphthene	140.27	-94.8	171.45	61.8
sec-Butylcyclohexane	Naphthene	140.27	-110	179.49	61.8
Bicyclohexyl	Naphthene	166.3	3.63	239.19	50
n-Decylcyclohexane	Naphthene	224.43	-1.73	297.75	90

Table D.2. Selected properties of potential surrogate components – isoparaffins.

Name	Molecular class	Molecular Weight (g/mol)	Melting Temperature (°C)	Boiling Temperature (°C)	Cetane Number
Isobutane	Isoparaffin	58.12	-159.61	-11.57	20
Isopentane	Isoparaffin	72.15	-159.9	27.99	24.28
3-Methylpentane	Isoparaffin	86.18	-162.9	63.42	29.09
2,3-Dimethylbutane	Isoparaffin	86.18	-127.96	58.13	11.8
3-Methylhexane	Isoparaffin	100.2	-119.4	92	32.83
3-Ethylpentane	Isoparaffin	100.2	-118.6	93.62	32.83
2,4-Dimethylpentane	Isoparaffin	100.2	-119.24	80.64	13.94
2,2,3-Trimethylbutane	Isoparaffin	100.2	-24.58	81.03	13.94
2,5-Dimethylhexane	Isoparaffin	114.23	-91.15	109.26	15.37
2,3,4-Trimethylpentane	Isoparaffin	114.23	-109.2	113.62	15.37
2-Methyl-3-Ethylpentane	Isoparaffin	114.23	-114.95	115.8	15.37
2-Methyloctane	Isoparaffin	128.26	-80.1	143.45	41.38
3-Methyloctane	Isoparaffin	128.26	-107.6	144.38	41.38
4-Methyloctane	Isoparaffin	128.26	-113.2	142.59	41.38
2,4-Dimethyl-3-ethylpentane	Isoparaffin	128.26	-122.36	136.87	25.17
3-Ethylheptane	Isoparaffin	128.26	-114.9	143.35	41.38
2,7-Dimethyloctane	Isoparaffin	142.28	-54	160.02	29.8
3,3,5-Trimethylheptane	Isoparaffin	142.28	-108.15	155.83	29.8
2,2,5,5-Tetramethylhexane	Isoparaffin	142.28	-12.6	137.61	29.8
2,2,3,3-Tetramethylhexane	Isoparaffin	142.28	-54	160.46	29.8
2-Methylnonane	Isoparaffin	142.28	-74.65	167.15	46.73
3-Methylnonane	Isoparaffin	142.28	-84.8	167.95	46.73
4-Methylnonane	Isoparaffin	142.28	-98.7	165.85	46.73
5-Methylnonane	Isoparaffin	142.28	-87.7	165.3	46.73
3-Methylundecane	Isoparaffin	170.33	-58	210.95	49.58
2,2,4,4,6,6,8-Heptamethylnonane	Isoparaffin	226.44	-110.15	246.5	60
Squalane	Isoparaffin	422.81	-38	447	60

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APPENDIX E

Near-IR and Fourier Transform IR Spectra for all Fuel Distillations and Mixtures

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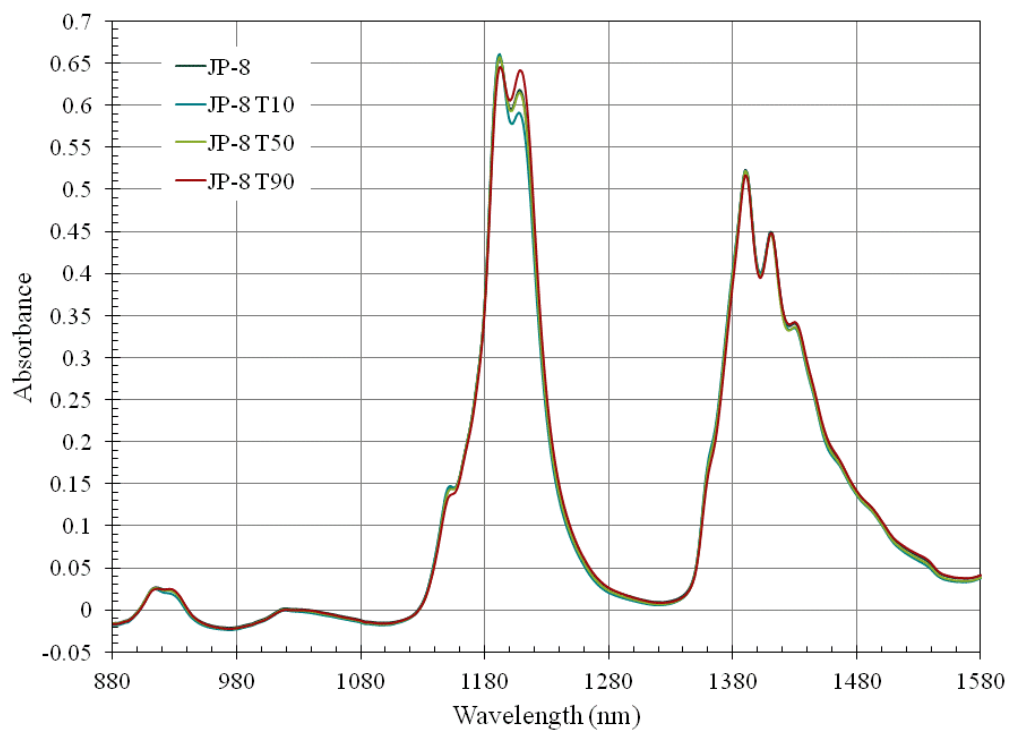


Figure E.1. NIR spectra for the JP-8 fuel and its distillation fractions.

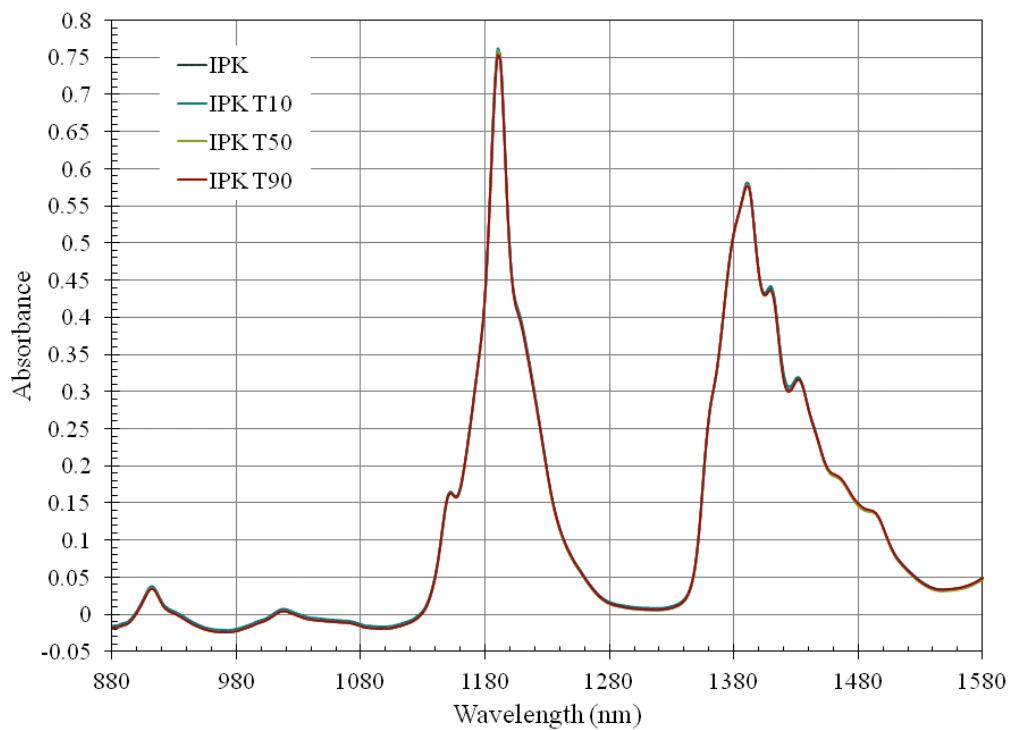


Figure E.2. NIR spectra for the IPK fuel and its distillation fractions

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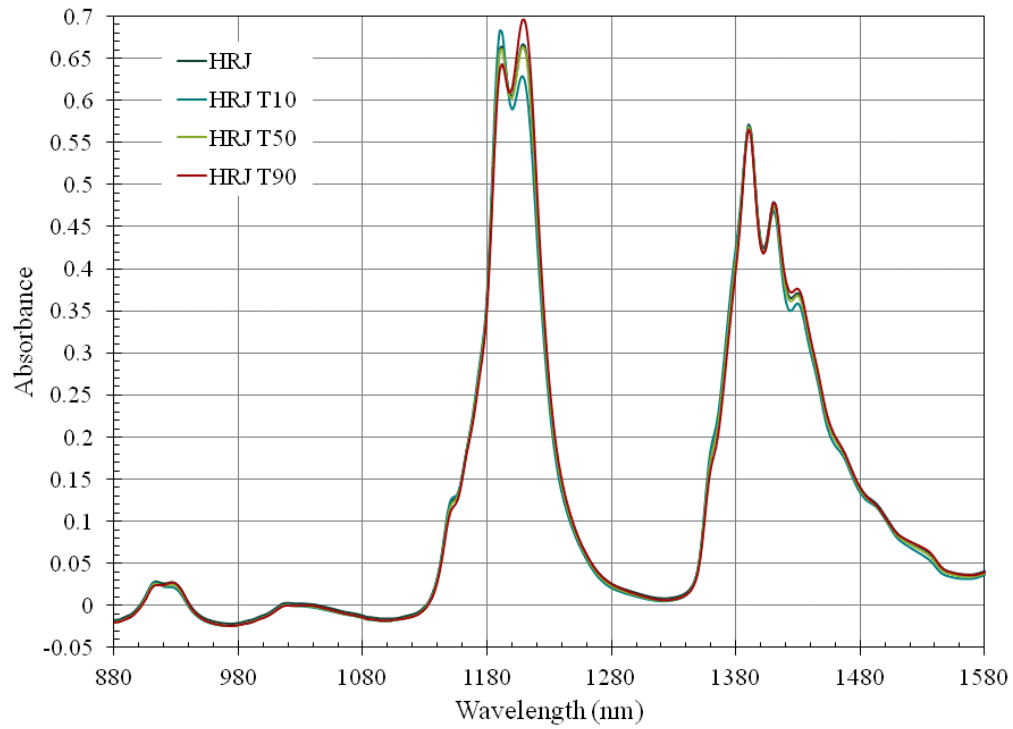


Figure E.3. NIR spectra for the HRJ fuel and its distillation fractions

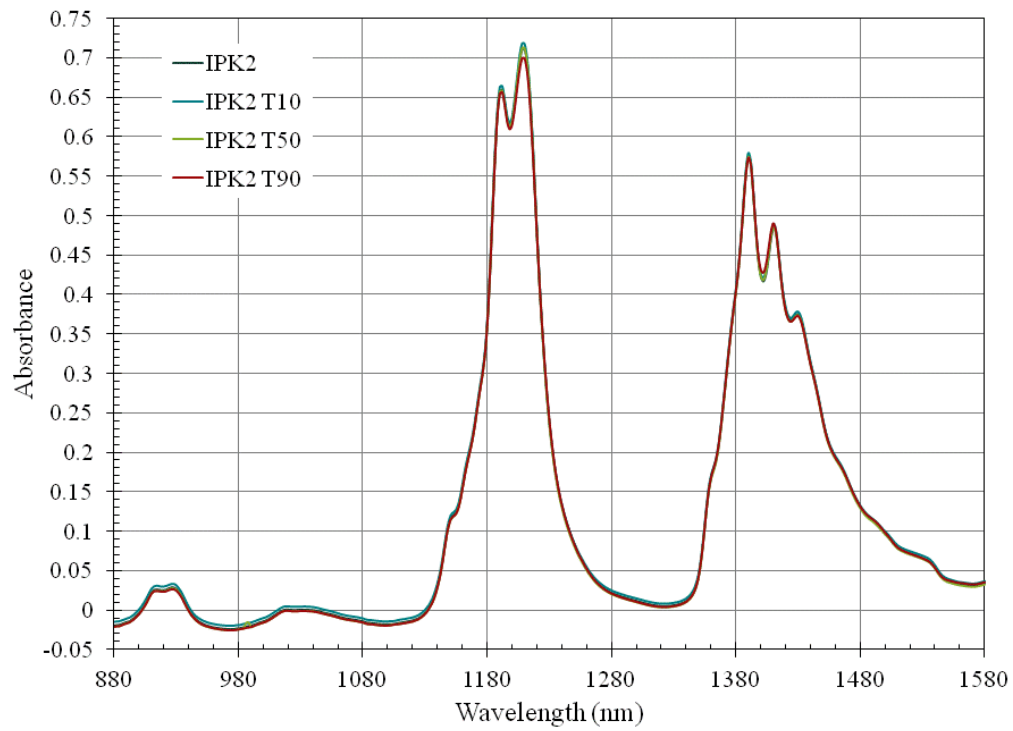


Figure E.4. NIR spectra for the SPK2 fuel and its distillation fractions

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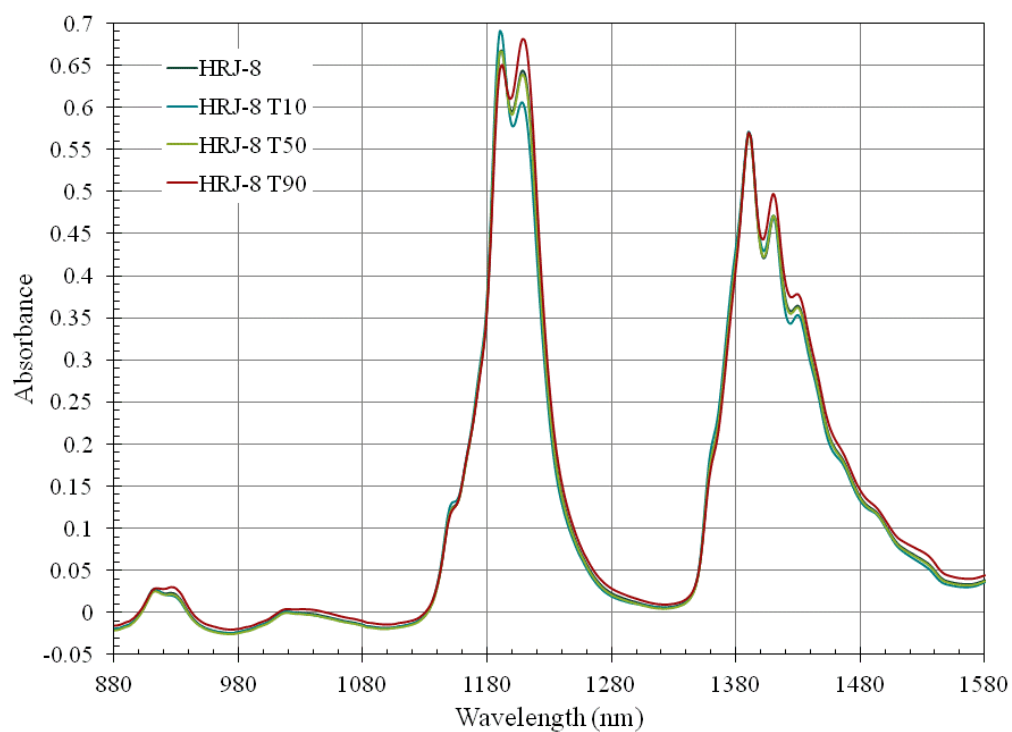


Figure E.5. NIR spectra for the HRJ-8 fuel and its distillation fractions

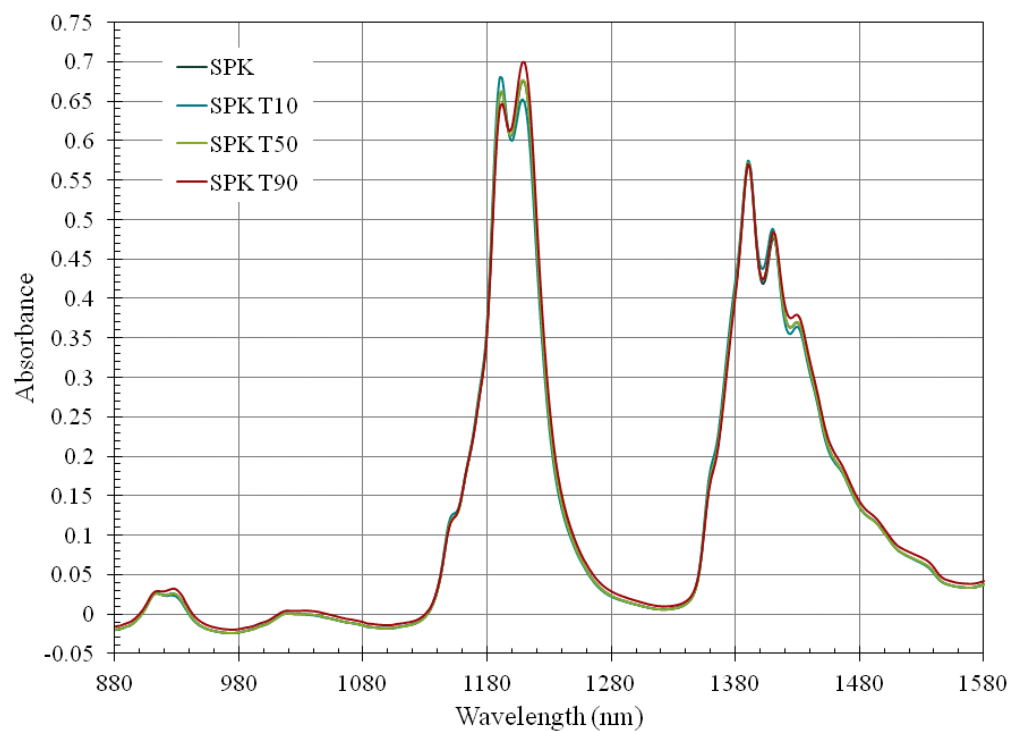


Figure E.6. NIR spectra for the SPK fuel and its distillation fractions

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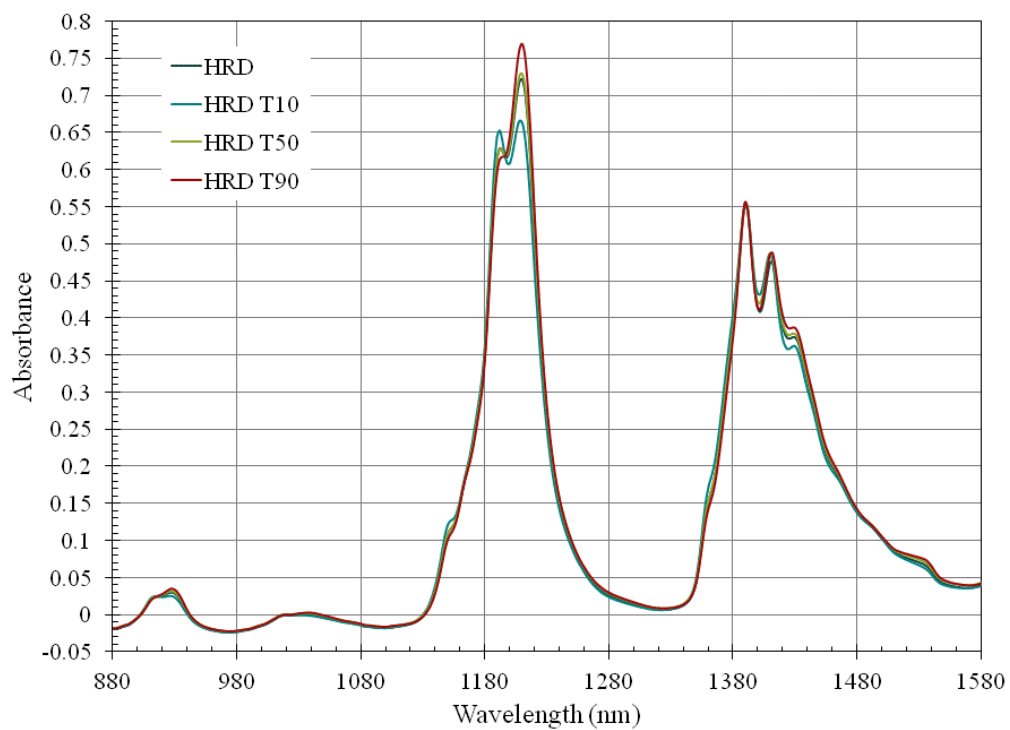


Figure E.7. NIR spectra for the HRD fuel and its distillation fractions

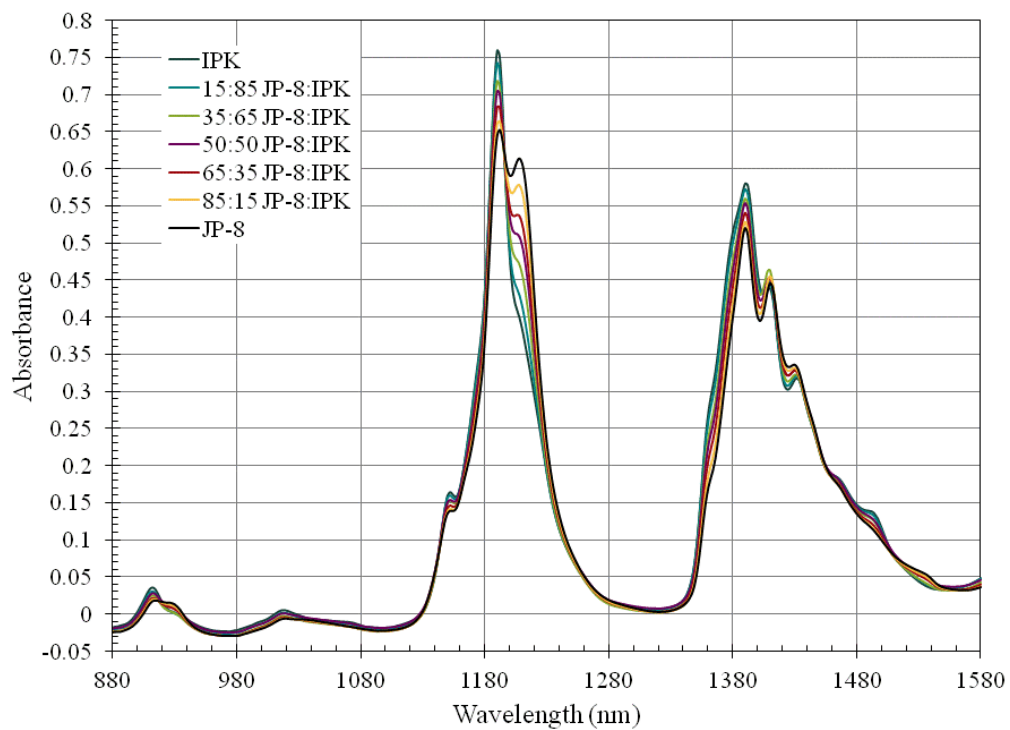


Figure E.8. NIR spectra for mixtures of JP-8 and IPK.

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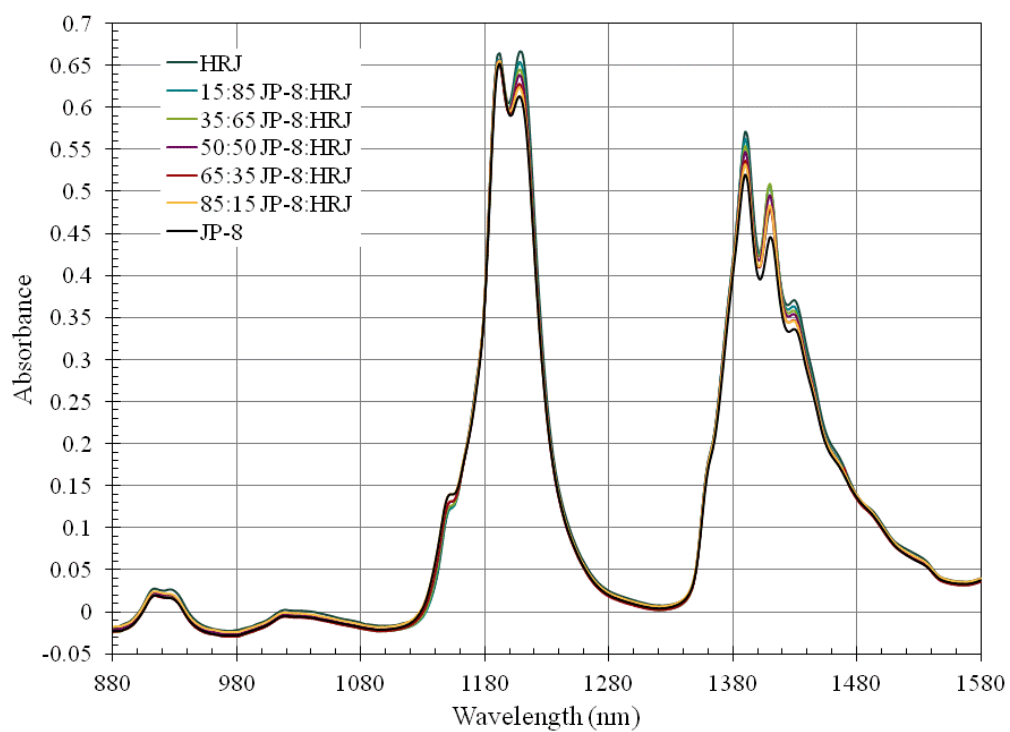


Figure E.9. NIR spectra for mixtures of JP-8 and HRJ.

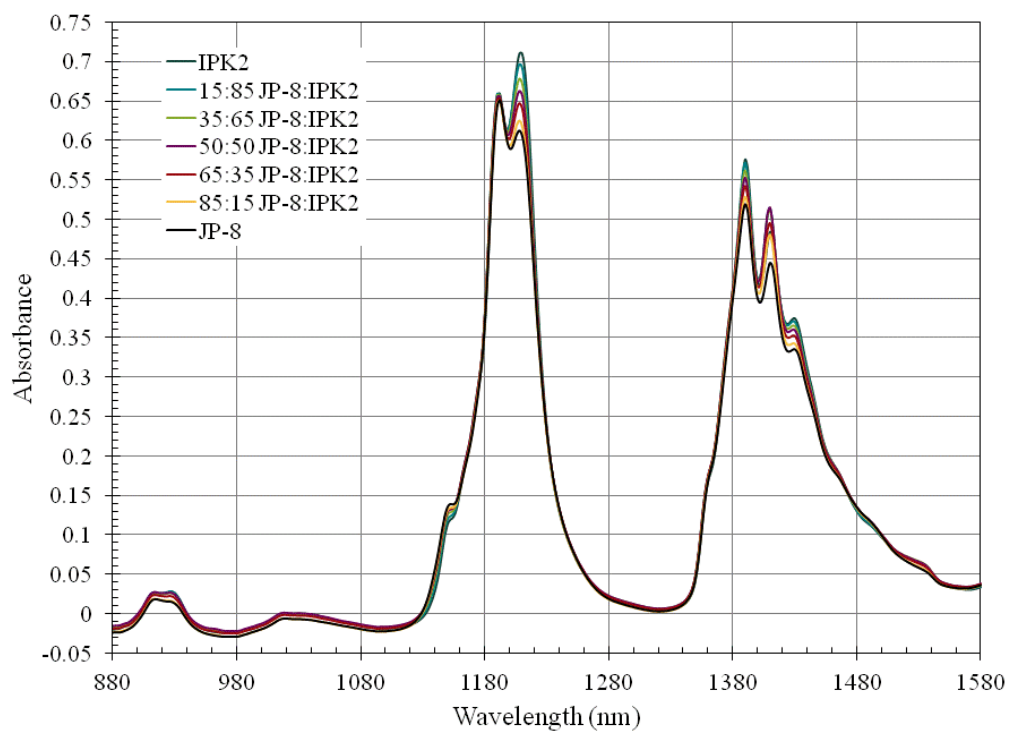


Figure E.10. NIR spectra for mixtures of JP-8 and SPK2.

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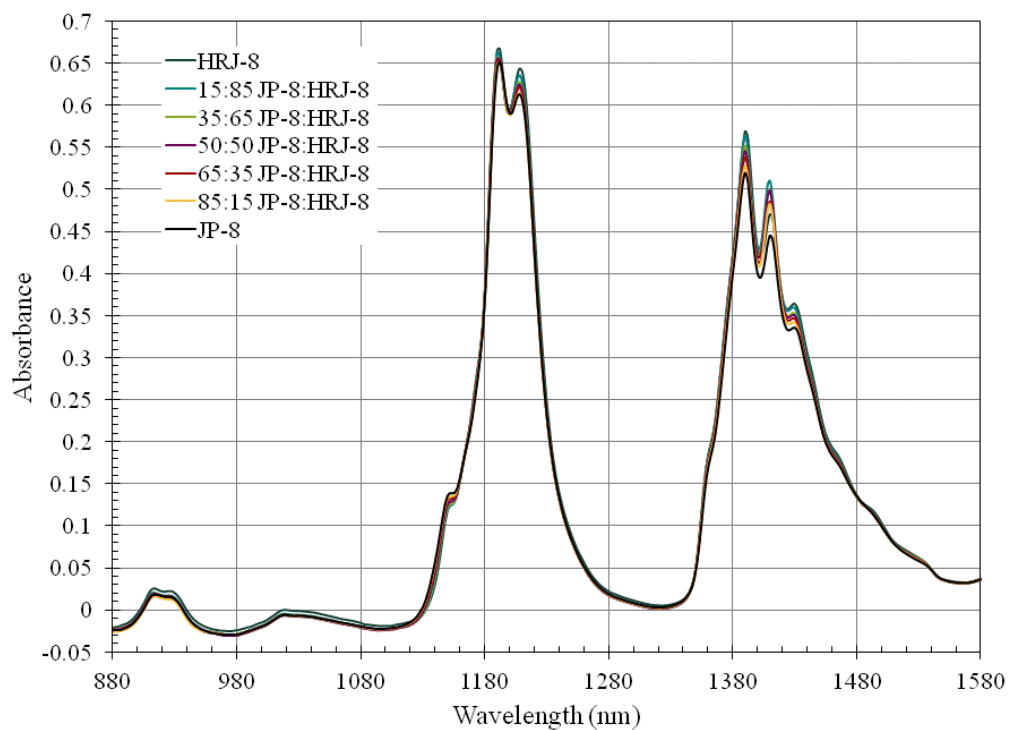


Figure E.11. NIR spectra for mixtures of JP-8 and HRJ-8.

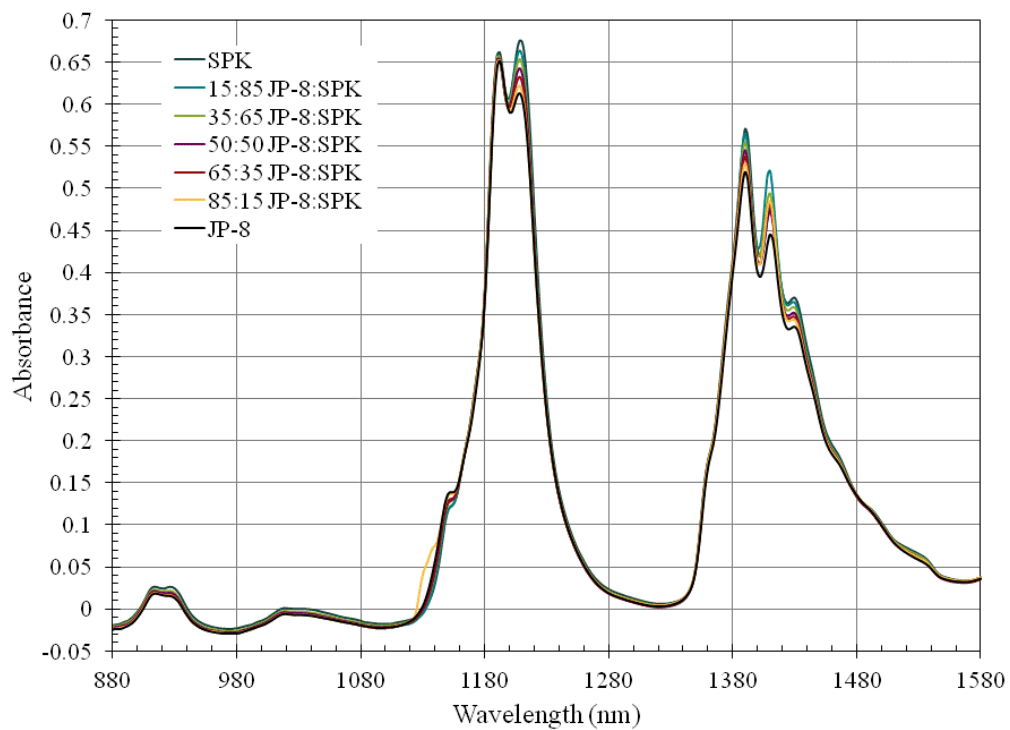


Figure E.12. NIR spectra for mixtures of JP-8 and SPK.

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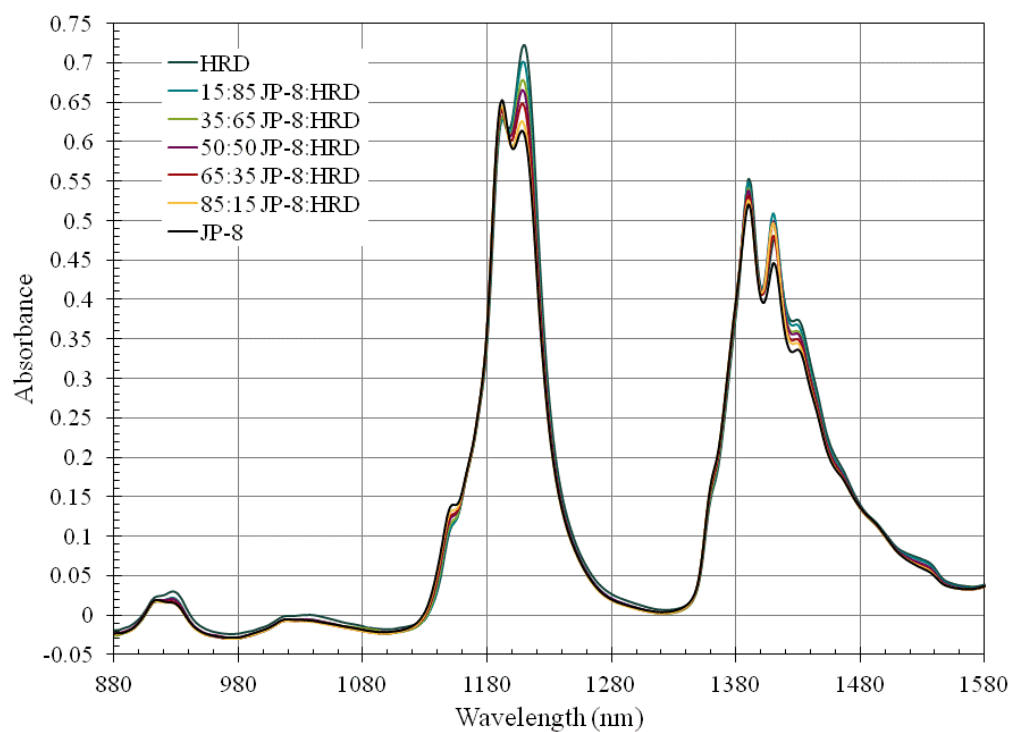


Figure E.13. NIR spectra for mixtures of JP-8 and HRD.

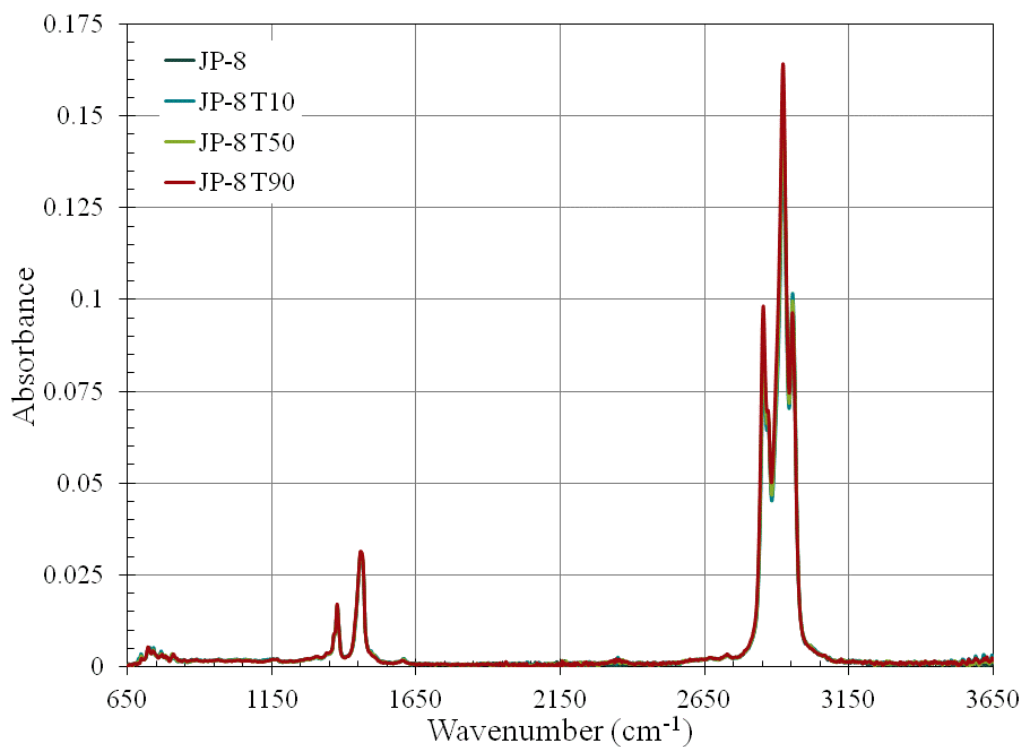


Figure E.14. FTIR spectra for the JP-8 fuel and its distillation fractions.

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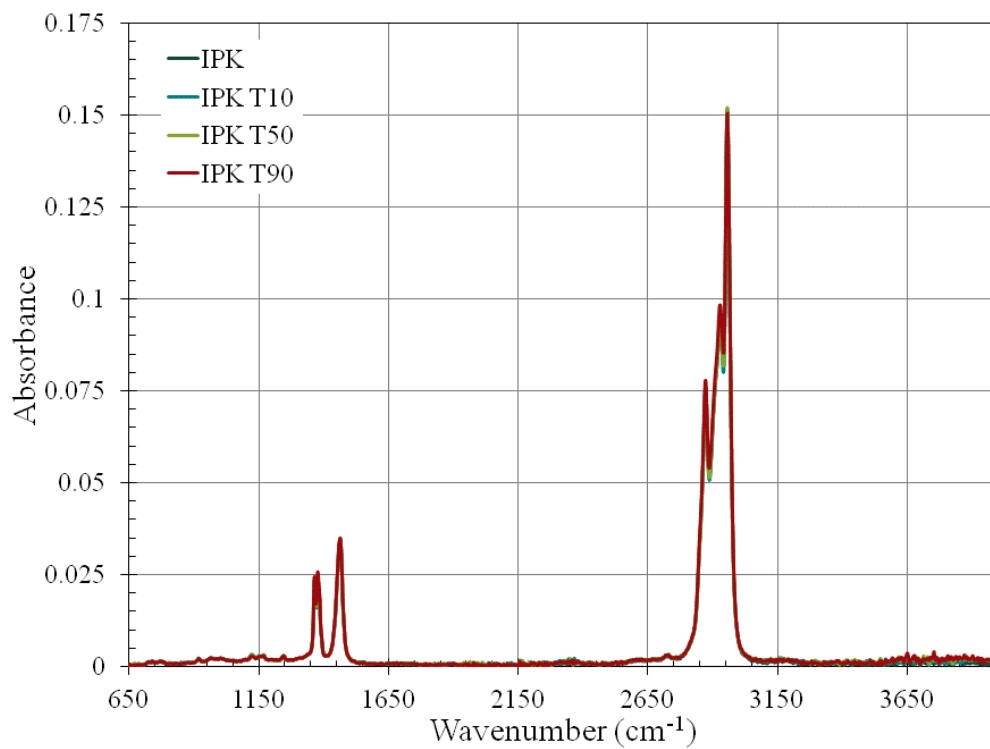


Figure E.15. FTIR spectra for the IPK fuel and its distillation fractions.

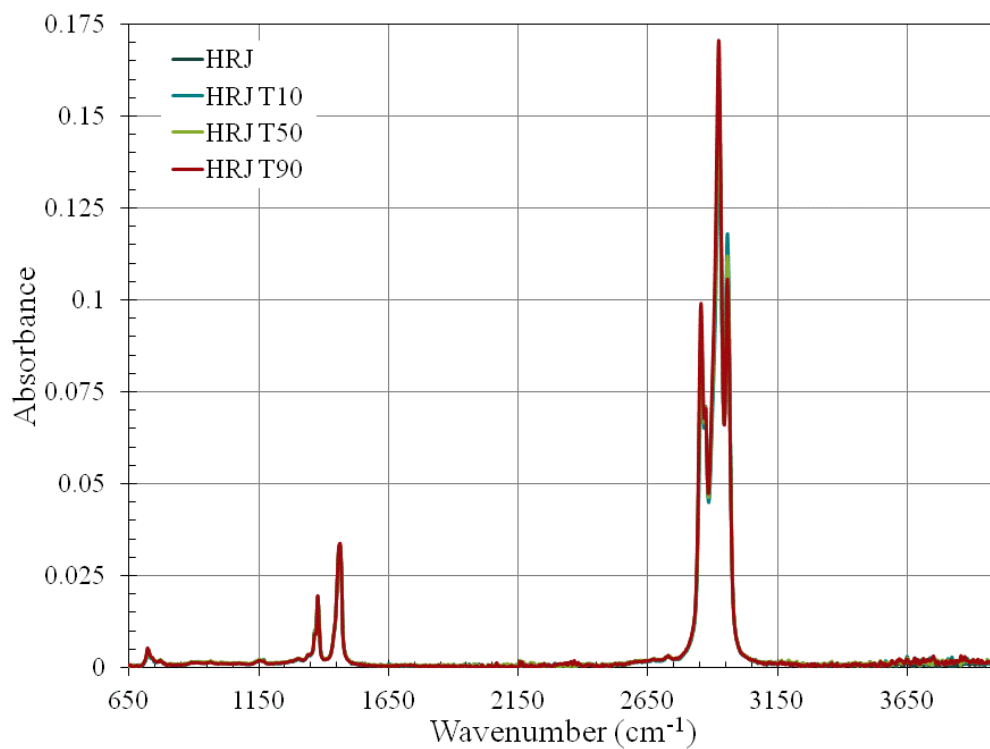


Figure E.16. FTIR spectra for the HRJ fuel and its distillation fractions.

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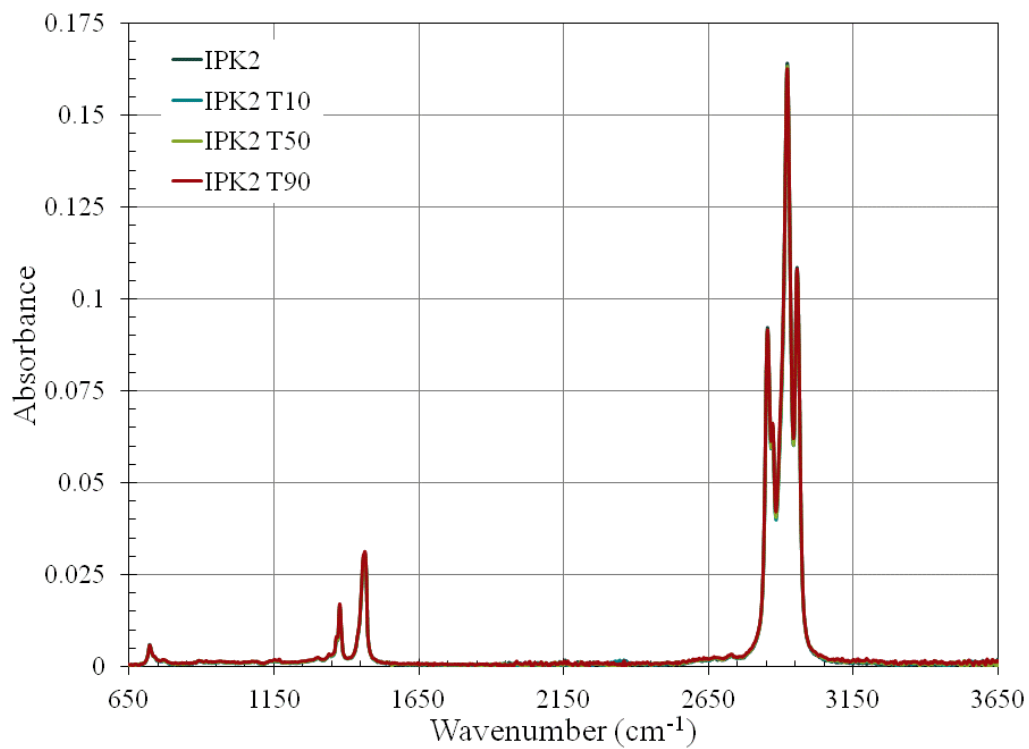


Figure E.17. FTIR spectra for the SPK2 fuel and its distillation fractions.

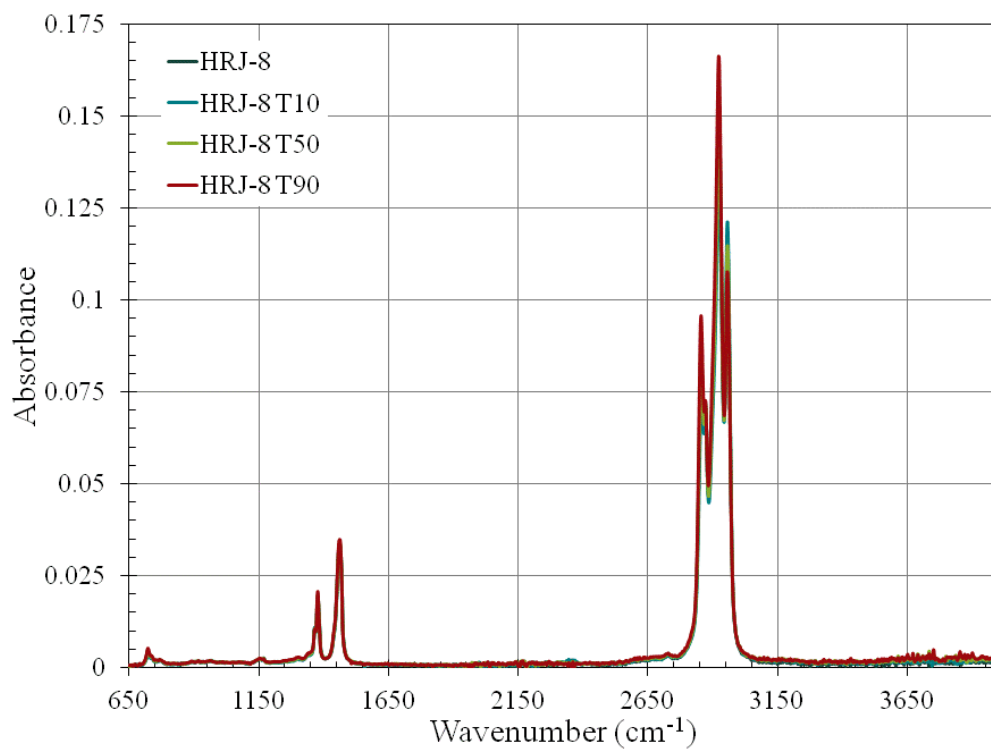


Figure E.18. FTIR spectra for the HRJ-8 fuel and its distillation fractions.

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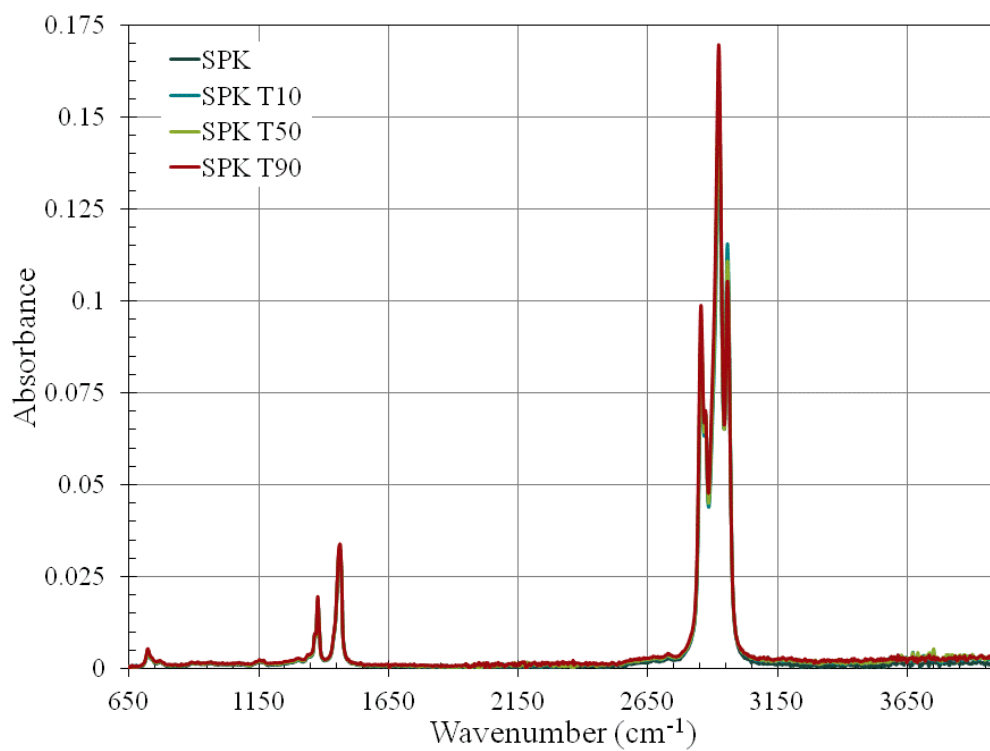


Figure E.19. FTIR spectra for the SPK fuel and its distillation fractions.

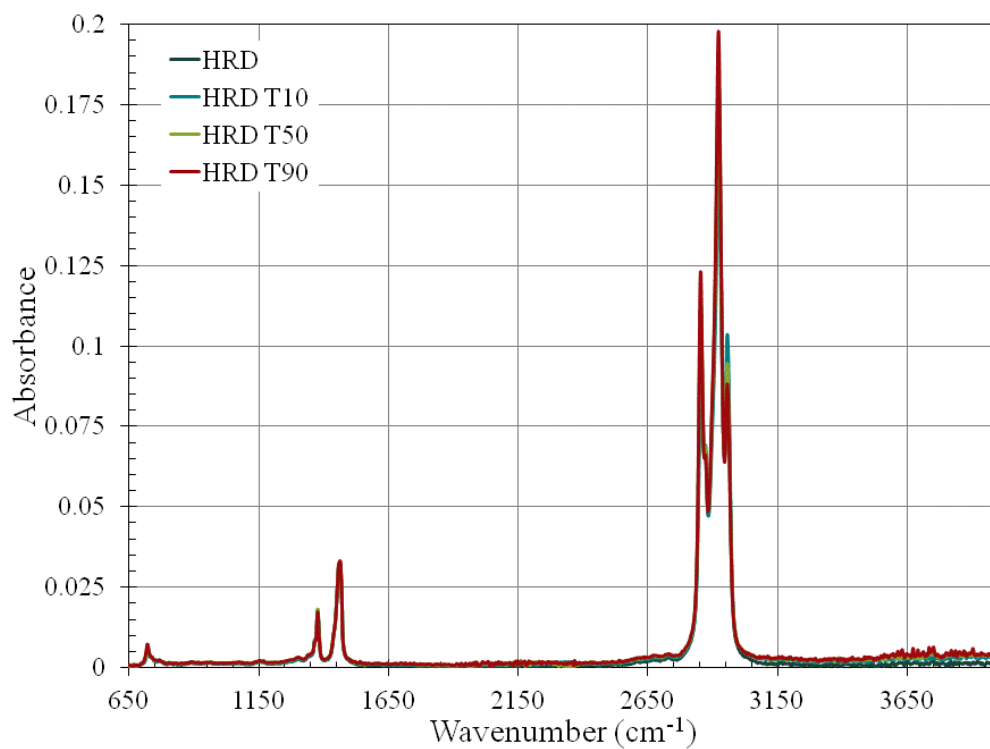


Figure E.20. FTIR spectra for the HRD fuel and its distillation fractions.

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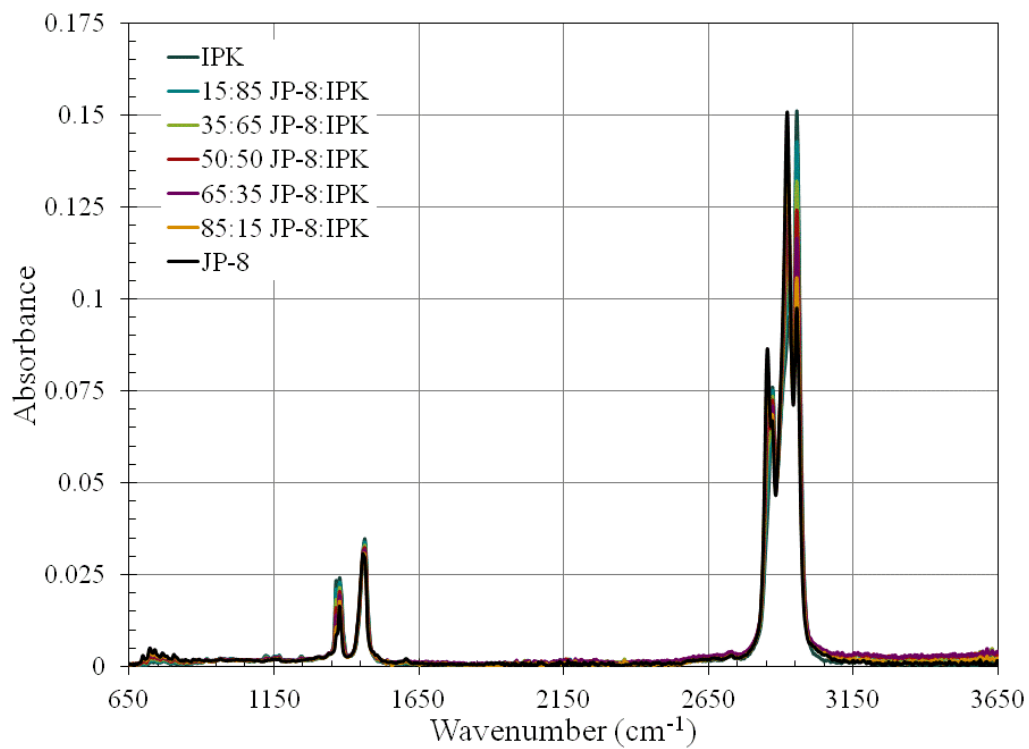


Figure E.21. FTIR spectra for mixtures of JP-8 and IPK.

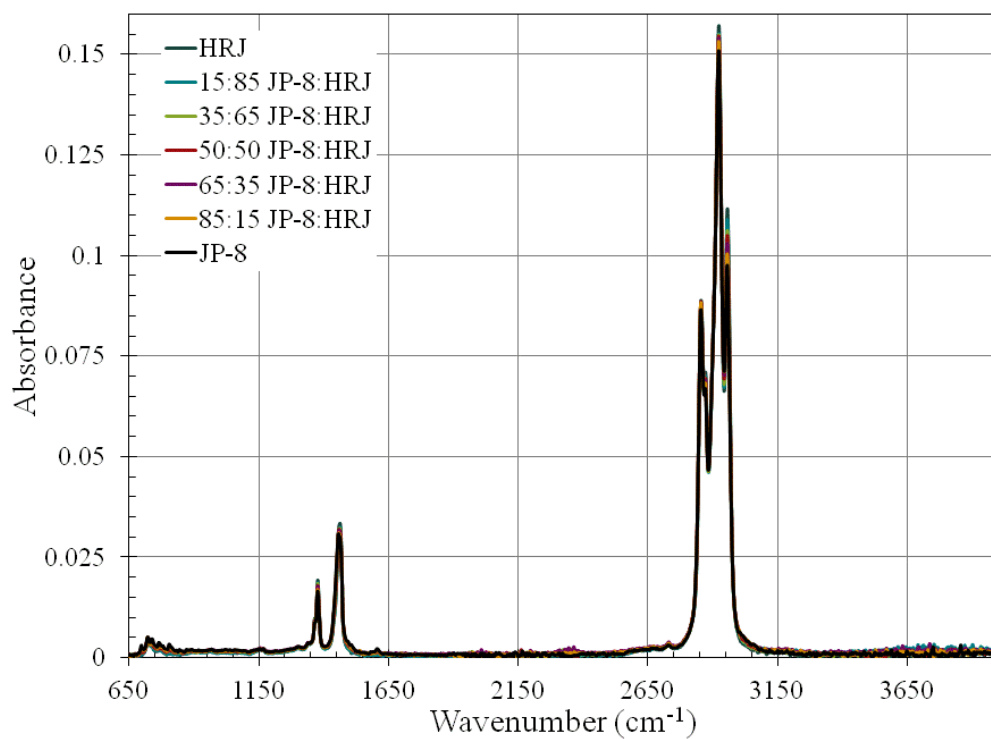


Figure E.22. FTIR spectra for mixtures of JP-8 and HRJ.

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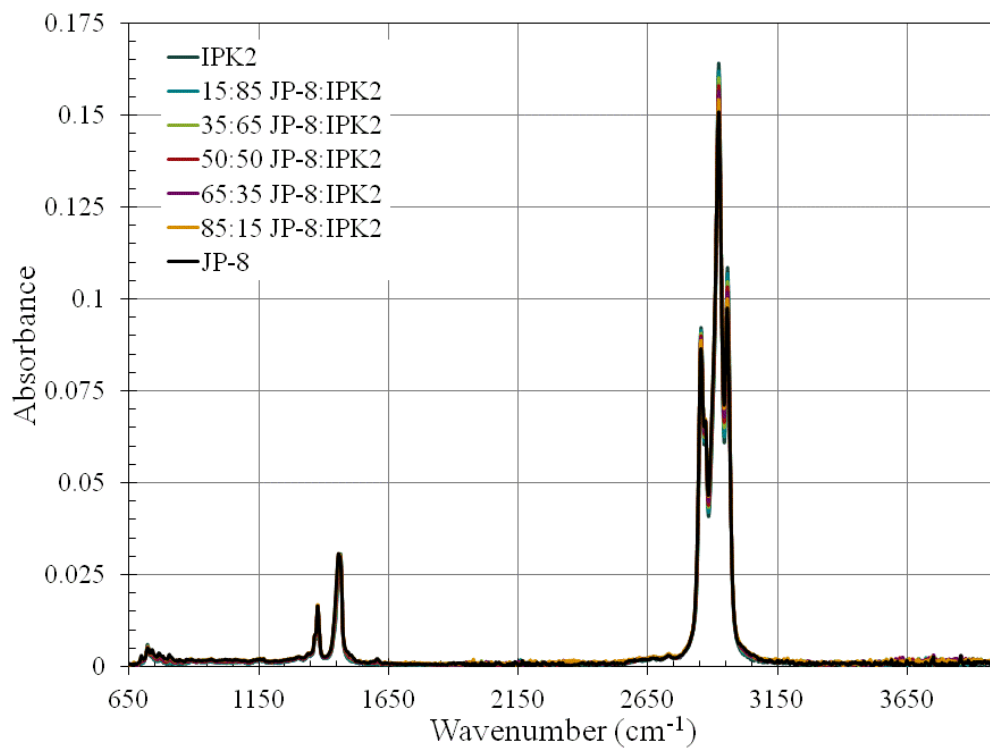


Figure E.23. FTIR spectra for mixtures of JP-8 and SPK2.

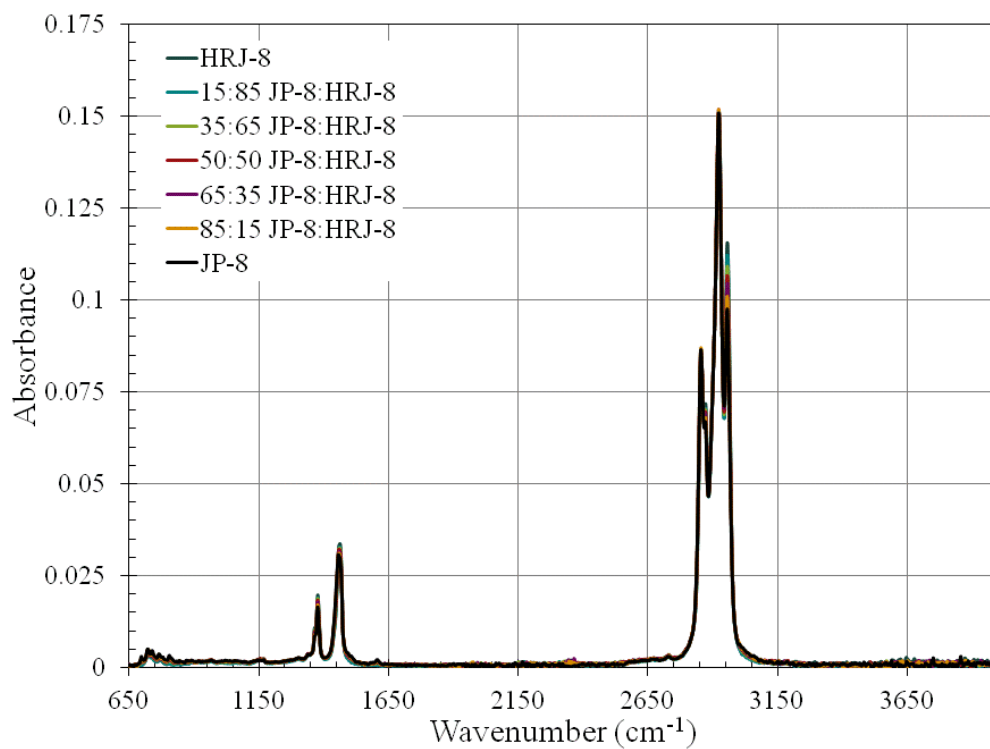


Figure E.24. FTIR spectra for mixtures of JP-8 and HRJ-8.

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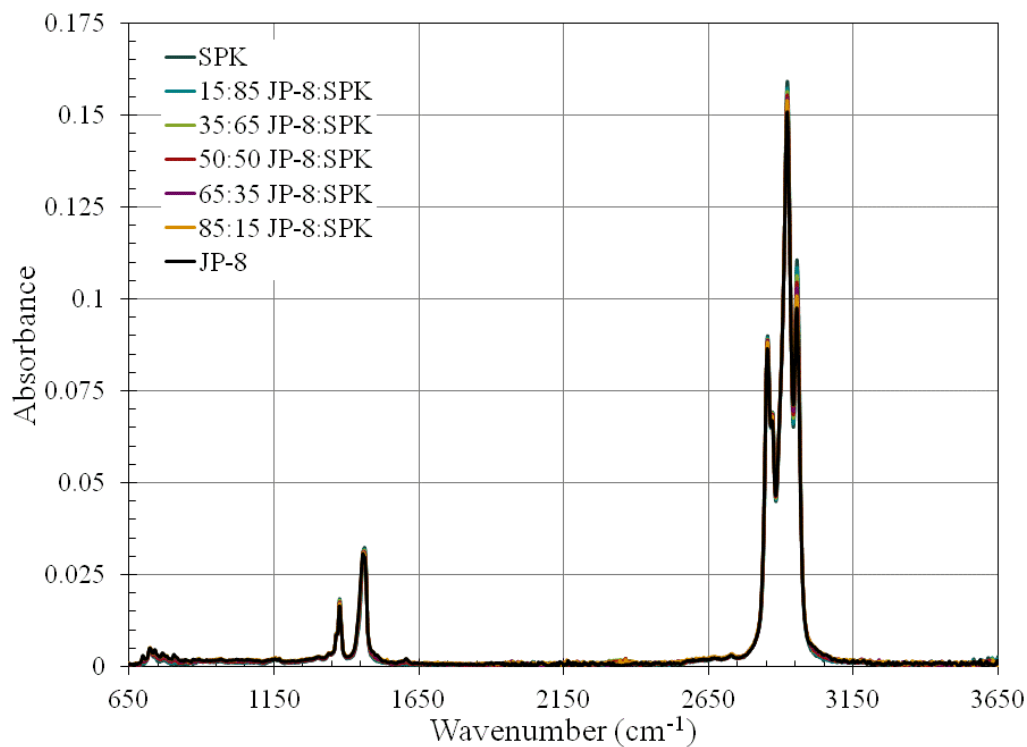


Figure E.25. FTIR spectra for mixtures of JP-8 and SPK.

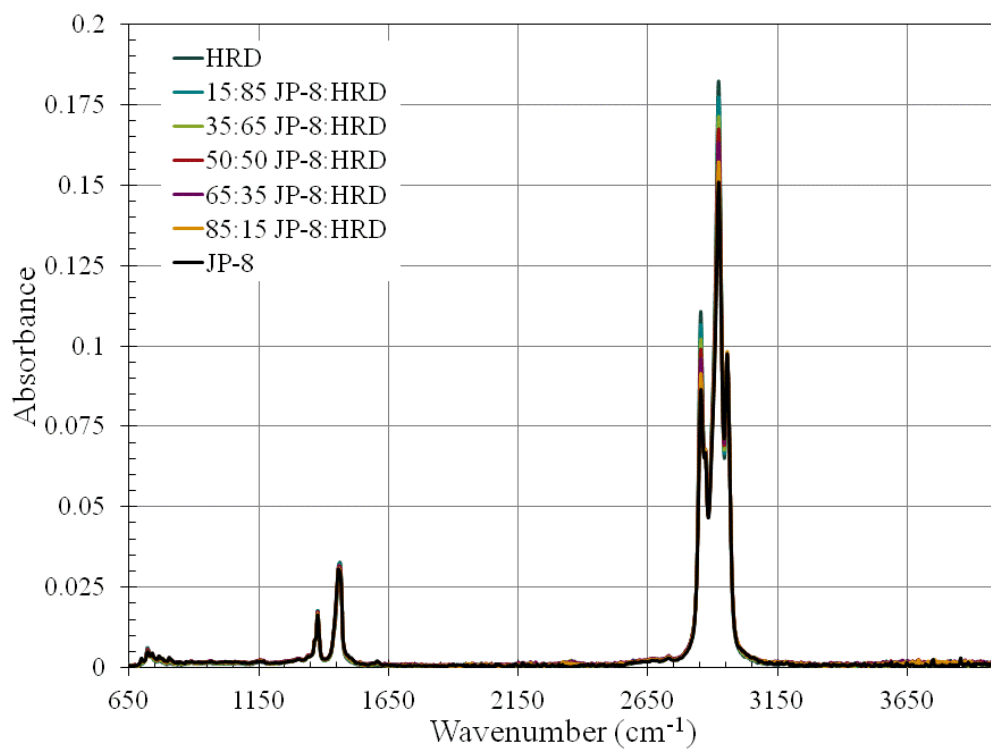


Figure E.26. FTIR spectra for mixtures of JP-8 and HRD.

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APPENDIX F

Proof of Pseudocomponent Mixtures for Cetane Number Prediction and Tabulated Cetane Numbers and Beta Values

F.1 Proof of Pseudocomponent Model

To represent a fuel as one component rather than multiple, it first needs to be shown that a mixture can be represented with a pseudocomponent and still give the same results.

To reiterate, the Ghosh and Jaffe equation states that the cetane number of a mixture can be predicted using:

$$CN = \frac{\sum_i v_i \beta_i CN_i}{\sum_i v_i \beta_i} \quad (F.1)$$

where CN is the mixture cetane number, v_i is the volume fraction of component i , CN_i is the cetane number of pure i , and β_i is an adjustable parameter.

A 4 component system is considered such that:

$$CN = \frac{v_1 \beta_1 CN_1 + v_2 \beta_2 CN_2 + v_3 \beta_3 CN_3 + v_4 \beta_4 CN_4}{v_1 \beta_1 + v_2 \beta_2 + v_3 \beta_3 + v_4 \beta_4} \quad (F.2)$$

The first 3 components could be condensed into a pseudocomponent mixture, designated by x . The resulting equation is:

$$CN = \frac{v_x \beta_x CN_x + v_4 \beta_4 CN_4}{v_x \beta_x + v_4 \beta_4} \quad (F.3)$$

where v_x is defined as the sum of the volume fractions in the lump:

$$v_x = 1 - v_4 = v_1 + v_2 + v_3 \quad (F.4)$$

β_x is defined as the volume average of the individual β s such that:

$$\beta_x = \frac{v_1}{v_x} \beta_1 + \frac{v_2}{v_x} \beta_2 + \frac{v_3}{v_x} \beta_3 = \frac{1}{v_x} (v_1 \beta_1 + v_2 \beta_2 + v_3 \beta_3) \quad (F.5)$$

The cetane number of the lump is defined using the original equation such that:

$$\begin{aligned}
 CN_x &= \frac{\frac{v_1}{v_x} \beta_1 CN_1 + \frac{v_2}{v_x} \beta_2 CN_2 + \frac{v_3}{v_x} \beta_3 CN_3}{\frac{v_1}{v_x} \beta_1 + \frac{v_2}{v_x} \beta_2 + \frac{v_3}{v_x} \beta_3} \\
 &= \frac{v_1 \beta_1 CN_1 + v_2 \beta_2 CN_2 + v_3 \beta_3 CN_3}{v_1 \beta_1 + v_2 \beta_2 + v_3 \beta_3}
 \end{aligned} \tag{F.6}$$

where in equation (F.6), $1/v_x$ is factored out of both the numerator and denominator, so it cancels out and the equation is simplified. The lump cetane number, CN_x , in equation (F.6) can be used in the original equation of Ghosh and Jaffe, represented by equation (F.1). When equations (F.4), (F.5), and (F.6) are plugged into equation (F.3),

$$\begin{aligned}
 CN &= \frac{v_x \left[\frac{1}{v_x} (v_1 \beta_1 + v_2 \beta_2 + v_3 \beta_3) \right] \left[\frac{v_1 \beta_1 CN_1 + v_2 \beta_2 CN_2 + v_3 \beta_3 CN_3}{v_1 \beta_1 + v_2 \beta_2 + v_3 \beta_3} \right] + v_4 \beta_4 CN_4}{v_x \left[\frac{1}{v_x} (v_1 \beta_1 + v_2 \beta_2 + v_3 \beta_3) \right] + v_4 \beta_4} \\
 &= \frac{v_1 \beta_1 CN_1 + v_2 \beta_2 CN_2 + v_3 \beta_3 CN_3 + v_4 \beta_4 CN_4}{v_1 \beta_1 + v_2 \beta_2 + v_3 \beta_3 + v_4 \beta_4}
 \end{aligned} \tag{F.7}$$

Once everything has been canceled out, the original equation returns. Therefore, any number of components can be grouped into one pseudocomponent lump using the volume averaging method for β shown above, and the Ghosh and Jaffe equation will still be valid. This also means that a mixture of two fuels can be treated as a binary mixture of two representative pseudocomponents. These pseudocomponents take the form of:

$$v_x = \sum v_i \tag{F.8}$$

$$\beta_x = \sum \frac{v_i}{v_x} \beta_i \tag{F.9}$$

$$CN_x = \sum_i \frac{\frac{v_i}{v_x} \beta_i CN_i}{\beta_x} \tag{F.10}$$

F.2 Tabulated Cetane Numbers and Blending Values

β values are used by each functionality class as indicated by Ghosh and Jaffe referenced in Chapter 4.

Table F.1. Cetane numbers and β values for n-paraffins and mono-isoparaffins used for cetane number surrogates.

Molecular Class	Carbon Number	Cetane Number	β Value
n-Paraffin	C5	31.72	0.5212
n-Paraffin	C6	39.97	0.5212
n-Paraffin	C7	54.61	0.5212
n-Paraffin	C8	61.56	0.5212
n-Paraffin	C9	85.4	0.5212
n-Paraffin	C10	80.91	0.5212
n-Paraffin	C11	84.74	0.5212
n-Paraffin	C12	83.15	0.5212
n-Paraffin	C13	88	0.5212
n-Paraffin	C14	100.4	0.5212
n-Paraffin	C15	96.3	0.5212
n-Paraffin	C16	100	0.5212
Mono-Isoparaffin	C5	27.1135	7.3717
Mono-Isoparaffin	C6	30.17	7.3717
Mono-Isoparaffin	C7	33.2265	7.3717
Mono-Isoparaffin	C8	36.283	7.3717
Mono-Isoparaffin	C9	39.3395	7.3717
Mono-Isoparaffin	C10	42.396	7.3717
Mono-Isoparaffin	C11	45.4525	7.3717
Mono-Isoparaffin	C12	48.509	7.3717
Mono-Isoparaffin	C13	51.5655	7.3717
Mono-Isoparaffin	C14	54.622	7.3717
Mono-Isoparaffin	C15	57.6785	7.3717
Mono-Isoparaffin	C16	60.735	7.3717
Mono-Isoparaffin	C17	63.7915	7.3717
Mono-Isoparaffin	C18	66.848	7.3717
Mono-Isoparaffin	C19	69.9045	7.3717
Mono-Isoparaffin	C20	72.961	7.3717
Mono-Isoparaffin	C21	76.0175	7.3717
Mono-Isoparaffin	C22	79.074	7.3717
Mono-Isoparaffin	C23	82.1305	7.3717
Mono-Isoparaffin	C24	85.187	7.3717
Mono-Isoparaffin	C25	88.2435	7.3717

Table F.2. Cetane numbers and β values for multi-isoparaffins and mono-cycloparaffins used for cetane number surrogates.

Molecular Class	Carbon Number	Cetane Number	β Value
Multi-Isoparaffin	C5	14.88	7.3717
Multi-Isoparaffin	C6	17.75	7.3717
Multi-Isoparaffin	C7	20.61	7.3717
Multi-Isoparaffin	C8	23.48	7.3717
Multi-Isoparaffin	C9	26.34	7.3717
Multi-Isoparaffin	C10	29.21	7.3717
Multi-Isoparaffin	C11	32.07	7.3717
Multi-Isoparaffin	C12	34.94	7.3717
Multi-Isoparaffin	C13	37.8	7.3717
Multi-Isoparaffin	C14	40.67	7.3717
Multi-Isoparaffin	C15	43.53	7.3717
Multi-Isoparaffin	C16	46.4	7.3717
Multi-Isoparaffin	C17	49.26	7.3717
Multi-Isoparaffin	C18	52.13	7.3717
Multi-Isoparaffin	C19	54.99	7.3717
Multi-Isoparaffin	C20	57.86	7.3717
Multi-Isoparaffin	C21	60.72	7.3717
Multi-Isoparaffin	C22	63.59	7.3717
Multi-Isoparaffin	C23	66.45	7.3717
Multi-Isoparaffin	C24	69.32	7.3717
Multi-Isoparaffin	C25	72.18	7.3717
Mono-cycloparaffin	C6	18.5	0.0727
Mono-cycloparaffin	C7	24.9	0.0727
Mono-cycloparaffin	C8	34.1	0.0727
Mono-cycloparaffin	C9	40	0.0727
Mono-cycloparaffin	C10	61.8	0.0727
Mono-cycloparaffin	C11	62	0.0727
Mono-cycloparaffin	C12	64.5	0.0727
Mono-cycloparaffin	C13	78.5	0.0727
Mono-cycloparaffin	C14	83.7	0.0727
Mono-cycloparaffin	C15	90	0.0727
Mono-cycloparaffin	C16	90	0.0727

Table F.3. Cetane numbers and β values for mono- and di-aromatics used for cetane number surrogates.

Molecular Class	Carbon Number	Cetane Number	β Value
Mono-Aromatic	C6	10.7	3.1967
Mono-Aromatic	C7	2.6	3.1967
Mono-Aromatic	C8	7.4	3.1967
Mono-Aromatic	C9	7.6	3.1967
Mono-Aromatic	C10	10	3.1967
Mono-Aromatic	C11	9	3.1967
Mono-Aromatic	C12	9	3.1967
Mono-Aromatic	C13	37.5	3.1967
Mono-Aromatic	C14	39.2	3.1967
Mono-Aromatic	C15	50.1	3.1967
Mono-Aromatic	C16	56.8	3.1967
Mono-Aromatic	C17	56.3	3.1967
Mono-Aromatic	C18	62.8	3.1967
Mono-Aromatic	C19	50.5	3.1967
Mono-Aromatic	C20	40	3.1967
Di-Aromatic	C10	22.6	3.1967
Di-Aromatic	C11	0	3.1967
Di-Aromatic	C12	5	3.1967
Di-Aromatic	C13	10	3.1967
Di-Aromatic	C14	14	3.1967
Di-Aromatic	C15	16	3.1967
Di-Aromatic	C16	16.5	3.1967
Di-Aromatic	C17	17	3.1967
Di-Aromatic	C18	17.5	3.1967
Di-Aromatic	C19	18	3.1967
Di-Aromatic	C20	18.5	3.1967
Di-Aromatic	C21	19	3.1967
Di-Aromatic	C22	19.5	3.1967
Di-Aromatic	C23	20	3.1967

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APPENDIX G

Regression Code and Coefficients

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G.1 R Code

This section is written in the programming language used in the R statistical software. A “#” before a line indicates a comment. To use this code, copy this section into an R script, and highlight the desired sections to run. Functionality is built in to work with both FTIR and NIR data sets.

#Prior to a run, the “pls” package must be loaded. This package contains all the functions used in this code beyond the basic math set.

#The dataset must be in a “.csv” file (comma separated file) with no headers. Each row contains the data for an individual run. The first column must be the cetane numbers, with the absorbance values for the run continuing the row. Every run needs to have the absorbance values recorded at the same wavelengths, and the data needs to be lined up so that each column represents the absorbance at that wavelength for all runs. So each experiment needs to be contained in a single row, with the form “CN(1), AB(1,1), AB(2,1), AB(3,1)” with CN(1) representing the experimental cetane number for run 1, AB(1,1) representing the absorbance value at wavelength 1 for run 1, AB(2,1) the absorbance at wavelength 2 for run 1, ect. The wavelengths or wavenumbers should not be included in the file as headers, the first line should begin with the first run.

#Read in dataset

ALL<-

read.table("C:\\Documents\\research\\TARDEC\\NIR\\NIRbranched.csv",header=F,sep=",")

#set up length of test and train segments

n<-nrow(ALL)

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train<-29 # This number sets the length of the training set. Must be changed based on each
#dataset

test<-train+1

#start to divide up matrix into training and testing sets

cetane<-as.matrix(ALL[,1])

cetane.train<-as.matrix(cetane[1:train, ])

cetane.test<-as.matrix(cetane[test:n, ])

#NIR is used as the name of the absorbance matrix no matter if the data is from FTIR or NIR
#tests.

NIR<-as.matrix(ALL[, -1])

#These next two sections are used if the background needs to be removed prior to processing
#set up restrictions on FTIR

#NIR1<-as.matrix(NIR[, 1001:1201])

#NIR2<-as.matrix(NIR[, 2481:2261])

#NIR3<-as.matrix(NIR[, 3101:3351])

#NIR<-cbind(NIR1,NIR2,NIR3)

#set up restriction on NIR

#NIR<-as.matrix(NIR[, 1:241])

NIR.train<-as.matrix(NIR[1:train, ])

NIR.test<-as.matrix(NIR[test:n, ])

#mean center and get means of each set of data

cetane.train.mc<-stdize(as.matrix(cetane.train), center=T, scale=F)

NIR.train.mc<-stdize(as.matrix(NIR.train), center=T, scale=F)
```

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```
cetane.train.m<-mean(cetane.train)

cetane.test.m<-mean(cetane.test)

NIR.train.m<-apply(NIR.train, 2, mean)

NIR.test.m<-apply(NIR.test, 2, mean)

#The first term passed to the command plsr must be the cetane numbers, and the second the set
#of the absorbance values. The number "7" here indicates the number of regression components;
#this can be omitted for a run using as many components as possible. CV indicates cross
#validation is used, and jackknife = T indicates that a jackknife analysis will be performed. The
#combination of cross validation and the jackknife function allow the user to determine how
#many regression components are likely to be required. Only the two data sets are essential for a
#successful run.

#run PLS regression

run1<-plsr(cetane.train.mc ~NIR.train.mc, 7, validation="CV", jackknife=T)

#store the coefficients developed from the PLS regression

b<-coef(run1)

#calculate the intercept

int.train<-cetane.train.m - NIR.train.m%*%b

int.train<-as.numeric(int.train)

#calculate predicted cetane numbers

pred.cetane.train<-NIR.train%*%b + int.train

pred.cetane.test<-NIR.test%*%b + int.train

#plots
```

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```
plot(cetane.train, pred.cetane.train, xlab="Experimental Cetane Number", ylab="Predicted  
Cetane Number", pch=16, ylim=c(0,70), xlim=c(0,70))  
  
abline(0,1)  
  
points(cetane.test, pred.cetane.test, pch=1)  
  
legend(locator(1), c("Training Set - Neat Fuels and Distil Fracs", "Predicted Set - Branched  
Pures"), pch=c(16, 1), bty="n")  
  
#calculate errors  
  
error.train<-mean(abs(cetane.train-pred.cetane.train)/cetane.train)  
  
error.test<-mean(abs(cetane.test-pred.cetane.test)/cetane.test)
```

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G.2 Regression Coefficients and Intercepts**Table G.1.** Regression coefficients (RC) for the full NIR dataset (1 of 2). WL – wavelength (cm).

WL	RC	WL	RC	WL	RC	WL	RC	WL	RC
1580	1.3495	1486	4.0406	1392	3.9509	1298	-1.7035	1204	-0.5761
1578	0.7817	1484	3.4568	1390	8.3996	1296	-2.2367	1202	-7.3471
1576	0.7743	1482	2.7162	1388	11.7782	1294	-2.2884	1200	-9.9210
1574	0.1134	1480	2.5615	1386	12.1773	1292	-2.1919	1198	-15.6617
1572	-0.3155	1478	2.5739	1384	9.8899	1290	-1.9271	1196	-23.6260
1570	-0.4616	1476	2.6391	1382	6.7177	1288	-2.1413	1194	-24.2429
1568	-0.7108	1474	3.0366	1380	2.2804	1286	-1.8661	1192	-19.9482
1566	-0.7323	1472	4.0960	1378	0.3369	1284	-1.9043	1190	-12.8851
1564	-1.5372	1470	5.0070	1376	2.9835	1282	-1.9381	1188	-6.1841
1562	-1.4701	1468	6.1543	1374	4.2527	1280	-1.7098	1186	0.2765
1560	-1.4174	1466	6.9749	1372	1.9286	1278	-1.5186	1184	3.5726
1558	-1.4316	1464	7.3132	1370	2.3970	1276	-1.4065	1182	3.9910
1556	-1.2010	1462	6.7570	1368	3.5341	1274	-1.4508	1180	2.2543
1554	-1.3526	1460	6.2610	1366	2.0615	1272	-1.4846	1178	-1.7970
1552	-1.3140	1458	5.1715	1364	0.3791	1270	-1.1898	1176	-1.7434
1550	-0.7676	1456	4.9368	1362	-0.5797	1268	-0.9025	1174	0.0255
1548	-1.2465	1454	5.6515	1360	-0.4488	1266	-0.7632	1172	1.2130
1546	-1.5134	1452	6.8256	1358	0.8889	1264	-0.3877	1170	2.0854
1544	-1.7518	1450	8.1703	1356	0.7937	1262	-0.3197	1168	1.3752
1542	-2.2914	1448	9.4246	1354	1.8494	1260	-0.3100	1166	-0.5765
1540	-2.4225	1446	10.5724	1352	1.6961	1258	-0.2008	1164	-1.5472
1538	-2.4603	1444	11.2651	1350	0.2704	1256	1.7973	1162	-3.2731
1536	-1.8978	1442	12.2013	1348	-2.0822	1254	0.9685	1160	-4.8744
1534	-1.6894	1440	12.8093	1346	-3.5335	1252	1.2670	1158	-6.4400
1532	-1.4529	1438	10.0746	1344	-3.9346	1250	2.0183	1156	-9.5675
1530	-1.0833	1436	9.5507	1342	-3.9927	1248	2.0143	1154	-11.6079
1528	-0.4580	1434	11.2473	1340	-3.8717	1246	2.5523	1152	-12.8190
1526	-0.6821	1432	13.3870	1338	-3.6813	1244	2.7637	1150	-12.8729
1524	-0.2145	1430	16.3258	1336	-3.3556	1242	3.2522	1148	-12.0266
1522	-0.3056	1428	19.0963	1334	-2.9854	1240	3.6714	1146	-11.1085
1520	0.5051	1426	20.1119	1332	-2.3670	1238	4.2938	1144	-10.5140
1518	0.1643	1424	21.5328	1330	-2.1725	1236	5.6777	1142	-10.1519
1516	0.1999	1422	22.5846	1328	-1.9016	1234	7.7232	1140	-9.9639
1514	0.5654	1420	22.2268	1326	-1.4700	1232	9.9689	1138	-9.7198
1512	0.5615	1418	18.9346	1324	-1.0713	1230	12.5688	1136	-9.9236
1510	0.7394	1416	12.5711	1322	-0.3684	1228	16.0504	1134	-6.0464
1508	0.3660	1414	4.6794	1320	-0.1282	1226	17.5717	1132	-2.2521
1506	0.1422	1412	-2.2555	1318	0.2379	1224	17.6534	1130	-5.0291
1504	0.4020	1410	-4.0696	1316	0.1873	1222	16.7176	1128	-3.9516
1502	0.6942	1408	-3.1164	1314	0.1946	1220	13.0029	1126	-2.8830
1500	1.9862	1406	-4.4411	1312	0.5386	1218	8.7042	1124	-2.7579
1498	3.4120	1404	-5.3093	1310	0.0120	1216	2.9390	1122	-2.3813
1496	4.0449	1402	-5.4849	1308	-0.1057	1214	1.9482	1120	-2.1869
1494	4.9178	1400	-5.4568	1306	0.1602	1212	1.4618	1118	-2.0595
1492	4.8534	1398	-4.6313	1304	-0.1083	1210	-0.9826	1116	-1.9249
1490	4.8221	1396	-3.8865	1302	-0.5784	1208	0.5965	1114	-1.9480
1488	4.4800	1394	-1.3533	1300	-0.9478	1206	0.5572	1112	-1.5792

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Table G.2. Regression coefficients for the full NIR dataset (2 of 2).

WL	RC	WL	RC	WL	RC
1110	-0.1275	1016	-0.5311	922	-2.591
1108	0.8645	1014	-0.3494	920	-1.9131
1106	-0.6231	1012	-0.1833	918	-1.6013
1104	-1.2487	1010	-0.5395	916	-2.0317
1102	-1.1449	1008	-0.5954	914	-2.7277
1100	-0.8567	1006	-0.4121	912	-2.38
1098	-0.8082	1004	-0.4807	910	-1.5622
1096	-0.5106	1002	-0.4916	908	-0.618
1094	-1.0062	1000	-0.7185	906	0.7022
1092	-1.1179	998	-1.0221	904	-2.0255
1090	-1.079	996	-1.3275	902	-1.0964
1088	-0.8688	994	-0.7188	900	-1.4065
1086	-0.6718	992	-0.3124	898	-0.6938
1084	0.3063	990	-2.3338	896	-2.179
1082	-0.0791	988	-0.2723	894	-1.3164
1080	-0.8159	986	0.9017	892	-3.1221
1078	-0.8766	984	-1.5189	890	-3.0993
1076	-1.0452	982	-1.5683	888	-4.4129
1074	-0.7039	980	-1.7868	886	-3.399
1072	-0.3824	978	-1.5609	884	-1.9384
1070	-0.3731	976	-1.0277	882	-1.6895
1068	-0.4367	974	-0.8045	880	-2.0093
1066	-0.4305	972	-1.116	922	-2.591
1064	-0.7244	970	-1.3713	920	-1.9131
1062	-0.6991	968	-1.2917	918	-1.6013
1060	-0.8285	966	-1.6372	916	-2.0317
1058	-0.9661	964	-1.995	914	-2.7277
1056	-1.4938	962	-2.2397	912	-2.38
1054	-0.8508	960	-2.2829	910	-1.5622
1052	-0.5131	958	-1.8897	908	-0.618
1050	-0.6556	956	-1.6854	906	0.7022
1048	-0.4716	954	-1.415	904	-2.0255
1046	-0.1145	952	-1.8425	902	-1.0964
1044	-0.0271	950	-1.5285	900	-1.4065
1042	-0.4192	948	-0.1368	898	-0.6938
1040	-0.4727	946	-0.4272	896	-2.179
1038	-0.0747	944	-0.5836	894	-1.3164
1036	-0.3093	942	-0.3785	892	-3.1221
1034	-0.4259	940	-0.6422	890	-3.0993
1032	-0.5598	938	-0.6243	888	-4.4129
1030	-0.4789	936	-0.7231	886	-3.399
1028	-0.5572	934	-0.655	884	-1.9384
1026	-1.0763	932	-0.3613	882	-1.6895
1024	-1.0009	930	-1.0405	880	-2.0093
1022	-0.8915	928	-2.0776		
1020	-1.1405	926	-1.6435		
1018	-0.896	924	-2.2556		

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Table G.3. Regression coefficients for the background removed NIR dataset.

WL	RC	WL	RC	WL	RC	WL	RC	WL	RC	WL	RC
1580	3.3314	1486	6.2903	1392	-3.96	1298	-3.7441	1204	2.8027	1110	-5.0595
1578	2.5497	1484	5.6176	1390	4.8831	1296	-4.3089	1202	-6.4998	1108	-3.7376
1576	2.5233	1482	4.6425	1388	12.187	1294	-4.2788	1200	-10.493	1106	-4.9251
1574	1.8368	1480	4.1982	1386	14.833	1292	-4.1164	1198	-19.684	1104	-5.4721
1572	1.2131	1478	4.1102	1384	12.936	1290	-3.7768	1196	-31.03	1102	-5.4489
1570	1.0378	1476	3.95	1382	8.7414	1288	-3.9572	1194	-32.879	1100	-5.0740
1568	0.5809	1474	4.0626	1380	2.435	1286	-3.6609	1192	-27.205		
1566	0.5659	1472	5.261	1378	-0.2271	1284	-3.6749	1190	-16.541		
1564	-0.366	1470	6.2086	1376	4.0005	1282	-3.6469	1188	-4.3199		
1562	-0.376	1468	7.6575	1374	5.8559	1280	-3.3263	1186	7.4837		
1560	-0.149	1466	8.6741	1372	3.1464	1278	-3.1029	1184	14.463		
1558	-0.316	1464	9.1405	1370	3.4636	1276	-2.9581	1182	14.4592		
1556	-0.047	1462	8.5534	1368	4.0618	1274	-2.9574	1180	9.7704		
1554	-0.174	1460	7.9745	1366	1.2199	1272	-3.0083	1178	0.66		
1552	-0.032	1458	6.4714	1364	-1.5212	1270	-2.7329	1176	-1.5451		
1550	0.7034	1456	5.9775	1362	-2.7471	1268	-2.2938	1174	-0.7723		
1548	-0.023	1454	6.6308	1360	-2.3025	1266	-2.1115	1172	0.529		
1546	-0.363	1452	7.5771	1358	0.7034	1264	-1.6712	1170	1.2388		
1544	-0.56	1450	8.5611	1356	2.0185	1262	-1.7133	1168	0.5765		
1542	-1.255	1448	9.7194	1354	4.2086	1260	-2.0241	1166	-1.3454		
1540	-1.656	1446	10.8809	1352	4.4041	1258	-1.9739	1164	-2.3069		
1538	-1.465	1444	11.596	1350	1.7225	1256	0.6531	1162	-4.4304		
1536	-0.805	1442	12.4513	1348	-2.4652	1254	0.1662	1160	-6.1316		
1534	-0.502	1440	12.7206	1346	-4.7504	1252	0.8742	1158	-8.4626		
1532	-0.142	1438	8.507	1344	-5.378	1250	1.7875	1156	-13.191		
1530	0.1715	1436	7.8705	1342	-5.7316	1248	1.706	1154	-16.3		
1528	0.7294	1434	10.5494	1340	-5.7137	1246	2.4695	1152	-17.718		
1526	0.3766	1432	13.6879	1338	-5.508	1244	2.6887	1150	-16.933		
1524	1.0157	1430	17.6905	1336	-5.3138	1242	3.6392	1148	-14.491		
1522	0.858	1428	21.3099	1334	-4.9801	1240	4.0502	1146	-11.924		
1520	2.0039	1426	22.3839	1332	-4.2896	1238	4.6916	1144	-10.141		
1518	1.4706	1424	23.7074	1330	-4.1576	1236	6.2904	1142	-9.9528		
1516	1.5416	1422	24.1637	1328	-3.9856	1234	8.6109	1140	-10.221		
1514	2.0449	1420	22.843	1326	-3.5155	1232	10.499	1138	-10.182		
1512	2.4452	1418	18.0305	1324	-3.0016	1230	12.983	1136	-11.705		
1510	2.9494	1416	10.063	1322	-2.3881	1228	17.139	1134	-8.0809		
1508	2.4481	1414	1.4881	1320	-2.2755	1226	18.519	1132	-3.8926		
1506	1.8463	1412	-4.0546	1318	-1.7446	1224	17.673	1130	-8.101		
1504	1.6038	1410	-2.3562	1316	-1.9273	1222	16.284	1128	-7.2767		
1502	1.4085	1408	1.1183	1314	-1.9094	1220	11.409	1126	-6.4195		
1500	2.8512	1406	-0.8227	1312	-1.4075	1218	6.0903	1124	-6.7925		
1498	4.3585	1404	-3.9661	1310	-2.0581	1216	-0.2608	1122	-7.0664		
1496	4.9867	1402	-7.2371	1308	-2.3282	1214	-0.0031	1120	-6.8287		
1494	6.2835	1400	-10.73	1306	-1.8988	1212	0.6288	1118	-7.0048		
1492	6.323	1398	-13.164	1304	-2.1541	1210	-1.5	1116	-6.9717		
1490	6.7009	1396	-14.924	1302	-2.7343	1208	2.0361	1114	-7.1193		
1488	6.7556	1394	-12.445	1300	-2.954	1206	3.2958	1112	-6.7291		

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Table G.4. Regression coefficients for the full FTIR dataset (1 of 12). WN – wavenumbers (cm⁻¹).

WN	RC	WN	RC	WN	RC	WN	RC	WN	RC	WN	RC
4000	-6.1835	3953	1.0762	3906	6.9148	3859	9.7721	3812	3.0211	3765	-9.8007
3999	-4.4567	3952	4.1553	3905	10.1909	3858	16.6302	3811	2.5060	3764	-9.7550
3998	-2.9103	3951	7.8616	3904	11.9569	3857	23.6634	3810	0.1491	3763	-9.7981
3997	-1.9536	3950	11.3055	3903	11.4760	3856	27.2886	3809	-4.5108	3762	-9.3508
3996	-2.0272	3949	12.8864	3902	9.3302	3855	24.9689	3808	-8.8205	3761	-6.6788
3995	-3.9067	3948	11.7516	3901	6.9082	3854	18.9148	3807	-8.7160	3760	-1.8317
3994	-6.8556	3947	8.7146	3900	5.4964	3853	13.6616	3806	-3.8806	3759	2.1048
3993	-9.6291	3946	5.6372	3899	5.4236	3852	9.7715	3805	1.9069	3758	2.7005
3992	-10.8084	3945	4.0906	3898	6.0028	3851	5.3881	3804	5.1763	3757	0.8818
3991	-10.4145	3944	4.3641	3897	6.2765	3850	1.0103	3803	5.5267	3756	-1.2536
3990	-8.2735	3943	5.2892	3896	5.8056	3849	-1.5051	3802	4.9688	3755	-2.9969
3989	-5.1964	3942	5.2188	3895	4.8563	3848	-1.2270	3801	5.0368	3754	-4.6380
3988	-2.1054	3941	3.5818	3894	3.8740	3847	1.2091	3800	4.7092	3753	-5.2535
3987	0.3396	3940	1.3432	3893	3.0815	3846	4.1734	3799	2.2776	3752	-2.9011
3986	1.8091	3939	0.0747	3892	2.4752	3845	5.8636	3798	-1.7979	3751	2.5070
3985	1.9660	3938	0.5828	3891	1.9779	3844	5.2969	3797	-5.4370	3750	7.3703
3984	0.9072	3937	2.4495	3890	1.6973	3843	2.8358	3796	-6.6832	3749	9.0732
3983	-0.6811	3936	4.5994	3889	1.7658	3842	-0.4716	3795	-5.4515	3748	8.6108
3982	-1.7011	3935	6.1154	3888	2.3517	3841	-3.1830	3794	-3.1858	3747	7.8351
3981	-1.3983	3934	6.7872	3887	4.2246	3840	-3.7274	3793	-1.4442	3746	8.3481
3980	-0.1486	3933	6.8669	3886	7.8588	3839	-1.4786	3792	-1.0679	3745	11.5165
3979	0.9555	3932	6.6173	3885	11.6480	3838	1.9127	3791	-2.1083	3744	16.0018
3978	1.0215	3931	6.4226	3884	12.8912	3837	3.4915	3790	-3.8309	3743	18.6606
3977	0.0751	3930	6.5027	3883	10.4869	3836	1.6860	3789	-5.3831	3742	18.3168
3976	-1.1647	3929	6.5899	3882	5.8707	3835	-2.6879	3788	-6.3988	3741	16.9094
3975	-1.9764	3928	5.9167	3881	1.6386	3834	-7.6015	3787	-7.1333	3740	16.4950
3974	-1.9804	3927	3.7728	3880	-0.8392	3833	-10.9033	3786	-7.7531	3739	16.8519
3973	-1.1950	3926	0.4171	3879	-2.0521	3832	-11.1727	3785	-7.9269	3738	15.7506
3972	0.0105	3925	-2.7990	3878	-3.0199	3831	-8.6706	3784	-7.3419	3737	12.8030
3971	0.7899	3924	-4.7309	3877	-4.0062	3830	-4.8064	3783	-6.7076	3736	11.7564
3970	0.3019	3923	-5.3644	3876	-4.0524	3829	-1.1738	3782	-6.9639	3735	14.9770
3969	-1.7759	3922	-4.9992	3875	-1.6354	3828	1.4611	3781	-7.9007	3734	18.0442
3968	-4.6621	3921	-3.3992	3874	3.1064	3827	3.3868	3780	-7.9365	3733	16.0889
3967	-7.0179	3920	-0.3335	3873	7.3103	3826	4.9625	3779	-5.7918	3732	10.5061
3966	-8.1437	3919	3.3189	3872	7.9338	3825	5.7906	3778	-2.1300	3731	5.2751
3965	-8.3716	3918	5.8097	3871	5.6707	3824	4.9232	3777	1.0331	3730	1.6999
3964	-8.5745	3917	5.8011	3870	4.2529	3823	2.9960	3776	2.5191	3729	-1.4032
3963	-9.1468	3916	3.6036	3869	4.9301	3822	2.7260	3775	2.5962	3728	-4.8476
3962	-9.5532	3915	0.6816	3868	4.7922	3821	4.7720	3774	2.0018	3727	-7.5693
3961	-9.2125	3914	-1.5418	3867	1.4490	3820	5.8554	3773	0.9990	3726	-7.8452
3960	-8.1603	3913	-2.3276	3866	-3.3428	3819	3.1025	3772	-0.5125	3725	-5.1510
3959	-7.1342	3912	-1.8298	3865	-5.6886	3818	-2.4990	3771	-2.1152	3724	-0.6133
3958	-6.4725	3911	-0.8788	3864	-4.0240	3817	-6.8328	3770	-3.3786	3723	4.0751
3957	-5.9229	3910	-0.1985	3863	-0.9382	3816	-6.4686	3769	-4.4653	3722	7.3387
3956	-4.9539	3909	0.3258	3862	0.9826	3815	-2.6786	3768	-5.9655	3721	8.2467
3955	-3.3637	3908	1.4072	3861	2.2705	3814	0.8133	3767	-7.8523	3720	7.1005
3954	-1.3342	3907	3.6268	3860	4.8510	3813	2.5366	3766	-9.3291	3719	5.3285

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Table G.5. Regression coefficients for the full FTIR dataset (2 of 12).

WN	RC	WN	RC	WN	RC	WN	RC	WN	RC	WN	RC
3718	4.5907	3671	2.6637	3624	3.0301	3577	0.4171	3530	3.9073	3483	9.4922
3717	5.8089	3670	0.9860	3623	2.5063	3576	-0.2798	3529	3.7709	3482	7.2087
3716	8.3950	3669	-0.9708	3622	1.2061	3575	0.8791	3528	4.7192	3481	6.5031
3715	10.7960	3668	-3.5557	3621	-0.8664	3574	3.8541	3527	4.8282	3480	6.9586
3714	11.4182	3667	-6.2318	3620	-2.4675	3573	7.8262	3526	3.0227	3479	7.0925
3713	9.3320	3666	-8.1481	3619	-1.8339	3572	11.7702	3525	0.2979	3478	6.0577
3712	5.0045	3665	-8.9008	3618	1.5546	3571	15.0095	3524	-1.3967	3477	4.1698
3711	0.6769	3664	-8.3836	3617	6.6593	3570	17.3179	3523	-1.1661	3476	2.1192
3710	-1.4731	3663	-6.6081	3616	11.6506	3569	18.7033	3522	-0.3297	3475	0.1565
3709	-1.3717	3662	-3.8067	3615	14.5156	3568	18.7424	3521	-1.1147	3474	-1.7337
3708	-0.1843	3661	-0.5417	3614	13.8804	3567	16.9366	3520	-4.5798	3473	-3.3752
3707	0.7491	3660	2.3723	3613	10.1584	3566	14.1584	3519	-9.6615	3472	-4.2850
3706	0.3193	3659	3.9737	3612	5.0509	3565	12.0746	3518	-13.8735	3471	-4.2080
3705	-1.7822	3658	3.7159	3611	-0.1278	3564	11.4520	3517	-15.1536	3470	-3.1854
3704	-4.4701	3657	2.3436	3610	-4.6691	3563	12.0072	3516	-13.1749	3469	-1.6920
3703	-5.7603	3656	1.7487	3609	-7.5247	3562	12.8428	3515	-9.2481	3468	-0.5697
3702	-4.4944	3655	2.7669	3608	-7.6407	3561	13.1078	3514	-4.8445	3467	-0.4631
3701	-1.4039	3654	4.3835	3607	-5.7318	3560	12.2290	3513	-0.8481	3466	-1.2882
3700	1.5827	3653	5.2964	3606	-3.8447	3559	9.6719	3512	2.1379	3465	-2.2547
3699	3.1433	3652	5.6569	3605	-3.1699	3558	5.3089	3511	3.2444	3464	-2.6379
3698	3.2331	3651	6.7158	3604	-3.1680	3557	0.0984	3510	1.4626	3463	-2.5500
3697	2.7658	3650	7.5282	3603	-2.3104	3556	-4.1945	3509	-2.7848	3462	-2.3836
3696	2.5933	3649	5.5621	3602	0.4592	3555	-5.8252	3508	-7.3972	3461	-1.9749
3695	2.4677	3648	2.0520	3601	4.5328	3554	-4.0836	3507	-10.0725	3460	-0.8510
3694	1.6430	3647	-0.6220	3600	7.5311	3553	0.1252	3506	-9.7321	3459	0.6968
3693	0.1406	3646	-2.2120	3599	7.8251	3552	4.6846	3505	-6.6661	3458	1.4690
3692	-0.5633	3645	-3.6939	3598	6.0376	3551	7.6338	3504	-1.8471	3457	0.7094
3691	1.3231	3644	-5.8622	3597	4.3482	3550	7.8754	3503	3.6676	3456	-0.8820
3690	5.2840	3643	-8.2004	3596	4.3401	3549	5.4111	3502	8.9440	3455	-1.9205
3689	8.1522	3642	-9.2394	3595	5.7528	3548	1.2700	3501	12.9614	3454	-1.9154
3688	8.3947	3641	-8.3359	3594	6.8789	3547	-2.3209	3500	14.9258	3453	-1.4752
3687	7.1072	3640	-6.2894	3593	6.4371	3546	-2.9923	3499	14.3798	3452	-1.4972
3686	5.3774	3639	-4.2562	3592	4.7110	3545	-0.5194	3498	11.2874	3451	-2.3887
3685	3.5919	3638	-2.9137	3591	2.9124	3544	2.6765	3497	6.1674	3450	-4.2945
3684	1.9447	3637	-2.1782	3590	2.3910	3543	3.9555	3496	0.2868	3449	-6.8497
3683	0.5894	3636	-1.3793	3589	4.0274	3542	2.6325	3495	-4.6865	3448	-8.8943
3682	-0.3798	3635	0.4464	3588	7.1029	3541	0.0519	3494	-7.2493	3447	-8.9920
3681	-0.6754	3634	3.7093	3587	9.2623	3540	-1.9356	3493	-7.1648	3446	-6.9293
3680	0.3542	3633	6.9899	3586	8.9491	3539	-2.2480	3492	-5.4945	3445	-3.8988
3679	2.3504	3632	7.8059	3585	6.9854	3538	-1.1044	3491	-3.7320	3444	-1.2514
3678	3.5315	3631	4.6331	3584	5.2886	3537	0.9027	3490	-2.6092	3443	0.4876
3677	3.0714	3630	-0.1492	3583	4.8840	3536	3.4992	3489	-1.5658	3442	1.3355
3676	2.6740	3629	-1.8424	3582	5.4600	3535	6.4665	3488	0.6059	3441	1.2867
3675	3.8344	3628	0.2513	3581	6.0987	3534	8.9864	3487	4.4294	3440	0.4913
3674	5.3805	3627	2.6005	3580	5.8488	3533	9.8366	3486	8.7858	3439	-0.5733
3673	5.6106	3626	3.4054	3579	4.4324	3532	8.5178	3485	11.6569	3438	-1.4094
3672	4.3998	3625	3.3144	3578	2.3132	3531	5.8923	3484	11.7043	3437	-2.0500

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Table G.6. Regression coefficients for the full FTIR dataset (3 of 12).

WN	RC	WN	RC	WN	RC	WN	RC	WN	RC	WN	RC
3436	-2.5513	3389	-1.3672	3342	2.1929	3295	-3.3527	3248	-2.2986	3201	-0.8762
3435	-2.3683	3388	-2.1884	3341	-1.2785	3294	-3.0000	3247	-1.8267	3200	1.3689
3434	-0.9448	3387	-3.4634	3340	-4.4140	3293	-2.8285	3246	-2.3508	3199	2.0595
3433	0.9979	3386	-5.7294	3339	-6.0424	3292	-2.6607	3245	-2.9898	3198	0.7892
3432	1.7037	3385	-8.4073	3338	-5.7321	3291	-1.6856	3244	-2.4705	3197	-1.8581
3431	0.1710	3384	-10.4052	3337	-3.7076	3290	0.3836	3243	0.0115	3196	-4.6672
3430	-2.3120	3383	-11.0631	3336	-0.6174	3289	2.9046	3242	4.1397	3195	-6.3760
3429	-3.7890	3382	-10.5229	3335	2.6337	3288	4.9249	3241	8.5196	3194	-6.2147
3428	-3.9177	3381	-9.3083	3334	4.8856	3287	5.9405	3240	11.1060	3193	-4.1232
3427	-4.0639	3380	-7.6337	3333	5.3425	3286	5.5464	3239	10.3508	3192	-1.0605
3426	-4.9619	3379	-5.3914	3332	4.1485	3285	3.2196	3238	6.4125	3191	1.3569
3425	-5.3740	3378	-2.6378	3331	2.5513	3284	-0.8889	3237	1.2269	3190	1.9322
3424	-3.7902	3377	0.0492	3330	2.0091	3283	-5.1924	3236	-2.8886	3189	0.7878
3423	-0.7186	3376	1.8651	3329	3.1844	3282	-7.5647	3235	-4.4709	3188	-1.0199
3422	1.4292	3375	2.4260	3328	5.5919	3281	-7.1749	3234	-3.4841	3187	-2.5735
3421	1.1331	3374	2.0108	3327	7.8348	3280	-5.1301	3233	-1.0473	3186	-3.5469
3420	-0.5562	3373	1.4171	3326	8.3420	3279	-2.8505	3232	1.3631	3185	-3.7324
3419	-1.6006	3372	1.1553	3325	6.4323	3278	-0.6225	3231	2.5894	3184	-2.8441
3418	-1.4373	3371	1.1620	3324	2.9566	3277	1.7275	3230	2.5624	3183	-1.1293
3417	-1.1805	3370	1.0017	3323	-0.2282	3276	3.6947	3229	1.8118	3182	0.3850
3416	-1.9863	3369	0.5730	3322	-1.6767	3275	4.2407	3228	0.6986	3181	0.9340
3415	-3.6702	3368	0.1342	3321	-1.3202	3274	3.0995	3227	-0.9844	3180	0.9090
3414	-5.1487	3367	-0.0571	3320	-0.2292	3273	1.1633	3226	-3.0430	3179	1.1825
3413	-5.3901	3366	-0.3863	3319	0.4797	3272	-0.2702	3225	-4.3589	3178	1.9460
3412	-4.4488	3365	-1.3455	3318	0.3152	3271	-0.3016	3224	-3.6959	3177	2.5987
3411	-3.3539	3364	-2.6053	3317	-0.7417	3270	1.3099	3223	-1.2137	3176	2.7163
3410	-3.2491	3363	-3.3673	3316	-2.2091	3269	3.9580	3222	1.4058	3175	2.4894
3409	-4.1185	3362	-3.4905	3315	-3.3342	3268	6.0823	3221	2.5241	3174	2.3475
3408	-4.6616	3361	-4.0427	3314	-3.5618	3267	6.1595	3220	1.9877	3173	2.3848
3407	-3.8035	3360	-5.9346	3313	-3.1311	3266	4.1091	3219	0.8029	3172	2.4266
3406	-2.1766	3359	-8.5269	3312	-2.7999	3265	1.4813	3218	0.0480	3171	2.1244
3405	-1.6719	3358	-9.9677	3311	-2.5609	3264	-0.2032	3217	0.0059	3170	1.1462
3404	-3.1549	3357	-9.2037	3310	-1.6950	3263	-1.0354	3216	0.1784	3169	-0.8153
3403	-5.2882	3356	-6.9612	3309	0.0187	3262	-2.1994	3215	-0.1747	3168	-3.5667
3402	-6.0278	3355	-4.7960	3308	1.0767	3261	-4.1453	3214	-1.6295	3167	-6.2483
3401	-4.6860	3354	-3.4375	3307	-0.3290	3260	-5.8600	3213	-4.0219	3166	-7.8877
3400	-2.2369	3353	-2.6203	3306	-4.0024	3259	-5.9389	3212	-6.4395	3165	-8.1138
3399	0.0901	3352	-1.8057	3305	-7.2963	3258	-4.0255	3211	-7.7757	3164	-7.2541
3398	1.8539	3351	-0.8968	3304	-7.3470	3257	-0.9325	3210	-7.5895	3163	-6.0097
3397	3.1873	3350	0.0128	3303	-3.9406	3256	2.1401	3209	-6.4369	3162	-4.9002
3396	4.2518	3349	0.9534	3302	0.5218	3255	4.1254	3208	-5.4156	3161	-4.2561
3395	5.0014	3348	1.9790	3301	3.3682	3254	4.2532	3207	-5.2831	3160	-4.0475
3394	5.3239	3347	3.0246	3300	3.6446	3253	2.3796	3206	-6.0268	3159	-3.8918
3393	4.9910	3346	4.1027	3299	2.0186	3252	-0.6424	3205	-6.9131	3158	-3.3311
3392	3.7267	3345	5.0903	3298	-0.2773	3251	-3.2641	3204	-7.0680	3157	-1.8521
3391	1.7808	3344	5.5153	3297	-2.2594	3250	-4.2136	3203	-5.9840	3156	0.3714
3390	-0.1509	3343	4.6645	3296	-3.3004	3249	-3.5341	3202	-3.6842	3155	2.4953

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Table G.7. Regression coefficients for the full FTIR dataset (4 of 12).

WN	RC	WN	RC	WN	RC	WN	RC	WN	RC	WN	RC
3154	3.5219	3107	8.9402	3060	-4.7686	3013	-7.1828	2966	21.6699	2919	21.2297
3153	3.1837	3106	8.2064	3059	-3.5545	3012	-7.9285	2965	24.1397	2918	21.4687
3152	2.1886	3105	5.8621	3058	-3.2960	3011	-7.8996	2964	25.9564	2917	24.0471
3151	1.2799	3104	3.1274	3057	-4.2081	3010	-7.2819	2963	27.3157	2916	28.0158
3150	0.5907	3103	1.3955	3056	-5.4378	3009	-7.0747	2962	28.4979	2915	31.3314
3149	-0.2886	3102	1.2891	3055	-5.6454	3008	-7.8614	2961	30.0800	2914	33.0287
3148	-1.5815	3101	2.2108	3054	-4.7593	3007	-8.9450	2960	32.3322	2913	33.5930
3147	-3.0550	3100	3.0795	3053	-3.8483	3006	-9.3224	2959	34.5509	2912	33.4505
3146	-4.2972	3099	3.2534	3052	-3.8185	3005	-8.6837	2958	34.7306	2911	32.5781
3145	-4.6247	3098	2.7043	3051	-4.5764	3004	-7.6050	2957	30.8662	2910	31.3523
3144	-3.2968	3097	1.8581	3050	-5.7438	3003	-6.6447	2956	22.7253	2909	30.5210
3143	-0.0922	3096	1.1484	3049	-7.1957	3002	-6.3766	2955	12.0619	2908	30.1400
3142	3.9002	3095	0.8159	3048	-8.6982	3001	-7.3334	2954	1.5161	2907	29.2044
3141	6.7551	3094	0.7951	3047	-9.3104	3000	-9.6738	2953	-7.3650	2906	26.9939
3140	7.1447	3093	0.8293	3046	-8.3569	2999	-12.7858	2952	-14.5041	2905	24.4191
3139	5.2839	3092	0.8761	3045	-6.3991	2998	-15.5683	2951	-20.8711	2904	23.2427
3138	2.5200	3091	0.9898	3044	-4.8712	2997	-16.9631	2950	-27.6833	2903	24.2011
3137	0.1720	3090	1.2382	3043	-4.7168	2996	-16.4679	2949	-35.2891	2902	26.0090
3136	-1.1399	3089	1.4053	3042	-5.7090	2995	-14.0782	2948	-42.6344	2901	26.6023
3135	-1.4569	3088	1.1602	3041	-7.0744	2994	-10.5934	2947	-47.7379	2900	24.9560
3134	-1.4719	3087	0.2010	3040	-8.1709	2993	-7.5042	2946	-49.3507	2899	21.9048
3133	-1.8018	3086	-1.3267	3039	-8.5445	2992	-6.2080	2945	-47.9882	2898	19.0196
3132	-2.4321	3085	-2.9286	3038	-7.8002	2991	-6.7703	2944	-45.2106	2897	17.1167
3131	-2.5930	3084	-4.2419	3037	-6.3078	2990	-8.0465	2943	-41.9885	2896	15.7994
3130	-1.6599	3083	-5.2984	3036	-5.2920	2989	-8.7792	2942	-38.2016	2895	14.3177
3129	-0.1730	3082	-6.4200	3035	-5.9594	2988	-8.5424	2941	-33.5274	2894	12.3375
3128	0.6563	3081	-7.7302	3034	-8.2811	2987	-7.8343	2940	-28.1445	2893	9.7088
3127	0.0904	3080	-8.9594	3033	-10.8459	2986	-7.1430	2939	-22.4619	2892	6.2424
3126	-1.2836	3079	-9.7150	3032	-12.2182	2985	-6.9135	2938	-16.7036	2891	1.9515
3125	-2.2858	3078	-9.9148	3031	-12.2445	2984	-7.2513	2937	-11.0908	2890	-2.2741
3124	-2.3871	3077	-9.6205	3030	-11.8361	2983	-8.1045	2936	-5.9776	2889	-5.1515
3123	-1.9460	3076	-8.9802	3029	-11.6352	2982	-9.4406	2935	-1.6658	2888	-6.0760
3122	-1.4428	3075	-8.3086	3028	-11.6364	2981	-11.2445	2934	1.7607	2887	-5.7371
3121	-0.7880	3074	-8.1146	3027	-11.6746	2980	-13.3343	2933	4.4373	2886	-5.2209
3120	0.2843	3073	-8.5452	3026	-11.7757	2979	-15.3738	2932	6.3412	2885	-4.8497
3119	1.5276	3072	-9.1867	3025	-11.8493	2978	-16.7256	2931	7.4589	2884	-4.2176
3118	1.9022	3071	-9.2322	3024	-11.4461	2977	-16.9568	2930	7.9171	2883	-2.8990
3117	0.5949	3070	-8.4641	3023	-10.5528	2976	-15.9082	2929	8.0119	2882	-0.9880
3116	-2.0230	3069	-7.3902	3022	-9.9990	2975	-13.8171	2928	8.3573	2881	0.9401
3115	-4.3133	3068	-6.9174	3021	-10.7290	2974	-11.1781	2927	9.4481	2880	2.2381
3114	-4.6891	3067	-7.5309	3020	-12.4434	2973	-8.4632	2926	11.3065	2879	2.6467
3113	-2.8583	3066	-8.9489	3019	-13.6757	2972	-5.7369	2925	13.2996	2878	2.5016
3112	0.1059	3065	-10.1438	3018	-13.2627	2971	-2.3918	2924	14.9396	2877	2.4255
3111	2.8663	3064	-10.2403	3017	-11.2357	2970	2.1653	2923	16.6981	2876	2.5860
3110	4.9599	3063	-9.2205	3016	-8.7653	2969	7.7457	2922	19.0290	2875	2.4806
3109	6.6378	3062	-7.7310	3015	-6.9586	2968	13.4359	2921	21.1772	2874	1.7686
3108	8.1405	3061	-6.2218	3014	-6.5150	2967	18.1940	2920	21.8357	2873	0.7683

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Table G.8. Regression coefficients for the full FTIR dataset (5 of 12).

WN	RC	WN	RC	WN	RC	WN	RC	WN	RC	WN	RC
2872	-0.0639	2825	-5.9305	2778	-0.7008	2731	-1.5319	2684	3.1141	2637	-0.9530
2871	-1.0738	2824	-5.4519	2777	0.4229	2730	-2.7608	2683	2.2036	2636	-0.1822
2870	-2.9392	2823	-4.3566	2776	1.4027	2729	-3.4249	2682	1.2495	2635	0.3034
2869	-5.6808	2822	-2.8204	2775	1.4775	2728	-3.1443	2681	0.7479	2634	0.6154
2868	-8.3968	2821	-1.2146	2774	0.9365	2727	-2.2806	2680	0.5506	2633	0.9763
2867	-10.3275	2820	0.1774	2773	0.5153	2726	-1.6974	2679	0.3650	2632	1.5439
2866	-11.4988	2819	1.4840	2772	0.5705	2725	-1.9353	2678	0.1253	2631	2.2036
2865	-12.2934	2818	2.9072	2771	0.7654	2724	-2.5831	2677	0.0113	2630	2.7206
2864	-12.6730	2817	4.2391	2770	0.5579	2723	-2.5918	2676	0.0035	2629	2.8522
2863	-12.4794	2816	5.0570	2769	-0.0864	2722	-1.3418	2675	-0.1008	2628	2.5632
2862	-11.9118	2815	4.7336	2768	-0.8139	2721	0.5207	2674	-0.3484	2627	1.8113
2861	-11.5176	2814	3.2527	2767	-0.9807	2720	1.8113	2673	-0.5325	2626	0.6936
2860	-11.4119	2813	1.1665	2766	-0.2249	2719	1.9752	2672	-0.4388	2625	-0.5270
2859	-11.1697	2812	-0.5839	2765	1.1059	2718	1.5610	2671	-0.3991	2624	-1.3052
2858	-10.2817	2811	-1.3502	2764	2.1551	2717	1.2503	2670	-0.9694	2623	-1.3100
2857	-8.5261	2810	-1.0341	2763	2.3838	2716	1.2049	2669	-2.2104	2622	-0.4474
2856	-5.7216	2809	-0.2193	2762	1.8639	2715	1.2606	2668	-3.4166	2621	0.8711
2855	-1.7960	2808	0.6953	2761	1.1023	2714	1.3756	2667	-3.6238	2620	1.9530
2854	2.8761	2807	1.5582	2760	0.4869	2713	1.6537	2666	-2.5869	2619	2.1596
2853	7.4229	2806	2.3769	2759	0.0766	2712	1.9827	2665	-0.8629	2618	1.3024
2852	10.9007	2805	3.1252	2758	-0.1075	2711	2.0239	2664	0.7047	2617	0.0497
2851	12.8448	2804	3.6150	2757	0.0314	2710	1.6367	2663	1.4663	2616	-0.6721
2850	13.3074	2803	3.6279	2756	0.5263	2709	1.0658	2662	1.1538	2615	-0.5455
2849	12.7372	2802	3.2289	2755	1.2818	2708	0.9086	2661	0.0308	2614	-0.1349
2848	11.3177	2801	2.7357	2754	2.0359	2707	1.6709	2660	-1.2420	2613	-0.1491
2847	9.0799	2800	2.6680	2753	2.5968	2706	3.3624	2659	-1.8814	2612	-0.5626
2846	5.9994	2799	3.2478	2752	2.8193	2705	5.1067	2658	-1.5485	2611	-0.7509
2845	2.3437	2798	4.1508	2751	2.6378	2704	5.7923	2657	-0.6508	2610	-0.3319
2844	-1.2717	2797	4.7582	2750	2.1287	2703	5.1093	2656	0.0432	2609	0.4693
2843	-4.2855	2796	4.8077	2749	1.5782	2702	4.1084	2655	0.0436	2608	1.0039
2842	-6.7145	2795	4.5144	2748	1.1391	2701	3.9215	2654	-0.4516	2607	0.8231
2841	-8.9603	2794	4.0225	2747	0.8341	2700	4.5752	2653	-0.9396	2606	0.0710
2840	-11.1614	2793	3.2745	2746	0.5834	2699	4.8660	2652	-1.2060	2605	-0.4417
2839	-13.1069	2792	2.0597	2745	0.6215	2698	3.9281	2651	-1.4548	2604	-0.1934
2838	-14.4986	2791	0.4162	2744	1.2551	2697	2.2039	2650	-1.9547	2603	0.3444
2837	-15.2755	2790	-1.3611	2743	2.2542	2696	0.7774	2649	-2.5914	2602	-0.1042
2836	-15.3628	2789	-2.8991	2742	2.6772	2695	0.2430	2648	-2.8284	2601	-2.0138
2835	-14.5869	2788	-3.7571	2741	1.8232	2694	0.2649	2647	-2.2936	2600	-4.0536
2834	-12.9690	2787	-3.5605	2740	0.0336	2693	0.2747	2646	-1.0546	2599	-4.2235
2833	-10.9900	2786	-2.3267	2739	-1.4525	2692	-0.1316	2645	0.3383	2598	-2.1799
2832	-9.3736	2785	-0.6312	2738	-1.8214	2691	-0.9698	2644	1.1709	2597	0.2273
2831	-8.4076	2784	0.9150	2737	-1.2954	2690	-1.9333	2643	1.0931	2596	0.9389
2830	-7.8846	2783	1.9113	2736	-0.6979	2689	-2.4376	2642	0.2084	2595	-0.2938
2829	-7.3743	2782	2.0920	2735	-0.3420	2688	-1.8357	2641	-0.9957	2594	-1.8151
2828	-6.7977	2781	1.3614	2734	-0.1300	2687	-0.1457	2640	-1.9018	2593	-2.0606
2827	-6.3152	2780	0.0319	2733	-0.0689	2686	1.8752	2639	-2.1612	2592	-0.8215
2826	-6.0804	2779	-0.9131	2732	-0.4922	2685	3.1361	2638	-1.7424	2591	1.0784

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Table G.9. Regression coefficients for the full FTIR dataset (6 of 12).

WN	RC	WN	RC	WN	RC	WN	RC	WN	RC	WN	RC
2590	2.9225	2543	6.6729	2496	-2.3665	2449	2.9706	2402	3.5747	2355	-7.9184
2589	4.2600	2542	6.4648	2495	-1.0415	2448	3.1379	2401	4.3038	2354	-6.4128
2588	4.6836	2541	4.4665	2494	0.0624	2447	2.5866	2400	2.6453	2353	-4.0863
2587	3.6947	2540	1.7362	2493	0.3484	2446	2.0676	2399	-0.3229	2352	-4.5838
2586	1.4786	2539	-0.2563	2492	-0.2273	2445	1.7728	2398	-2.9996	2351	-9.1061
2585	-0.6843	2538	-1.1976	2491	-1.1443	2444	1.3918	2397	-4.5581	2350	-14.6650
2584	-1.3202	2537	-1.9358	2490	-1.9163	2443	0.7501	2396	-5.0439	2349	-17.3777
2583	-0.1533	2536	-2.5895	2489	-2.4343	2442	0.1586	2395	-4.7341	2348	-15.8955
2582	1.5936	2535	-2.0528	2488	-2.7245	2441	-0.2889	2394	-3.8792	2347	-11.4782
2581	2.3275	2534	0.2136	2487	-2.7174	2440	-0.7349	2393	-2.6960	2346	-7.1897
2580	1.6193	2533	2.7238	2486	-2.6194	2439	-1.2492	2392	-1.5146	2345	-5.6952
2579	0.3576	2532	3.1734	2485	-2.6917	2438	-1.5768	2391	-0.6837	2344	-7.0020
2578	-0.4840	2531	0.6368	2484	-2.7059	2437	-1.4695	2390	-0.4216	2343	-7.6979
2577	-0.8547	2530	-3.5984	2483	-1.7167	2436	-0.9621	2389	-0.8714	2342	-5.2565
2576	-1.3703	2529	-7.0620	2482	0.5523	2435	0.0824	2388	-2.0179	2341	-1.6768
2575	-2.1309	2528	-8.0226	2481	2.9916	2434	1.7673	2387	-3.6284	2340	-0.0603
2574	-2.2267	2527	-6.4299	2480	3.9493	2433	3.5140	2386	-5.5775	2339	-1.4386
2573	-0.6590	2526	-3.6702	2479	2.8738	2432	4.0295	2385	-7.8922	2338	-4.3556
2572	2.2393	2525	-1.6161	2478	0.4573	2431	2.5822	2384	-10.4305	2337	-7.2616
2571	4.5557	2524	-1.3568	2477	-2.3247	2430	0.0433	2383	-12.5909	2336	-9.2365
2570	4.3950	2523	-2.8415	2476	-4.7470	2429	-2.1302	2382	-13.6169	2335	-10.0156
2569	1.7809	2522	-4.9902	2475	-6.1193	2428	-3.4471	2381	-13.1328	2334	-9.3543
2568	-1.0537	2521	-6.1604	2474	-5.7765	2427	-4.4611	2380	-11.5346	2333	-8.1997
2567	-2.0223	2520	-5.0039	2473	-3.4826	2426	-5.3790	2379	-9.5911	2332	-8.3053
2566	-1.2016	2519	-1.8460	2472	0.0165	2425	-5.4964	2378	-8.0369	2331	-10.8008
2565	-0.5264	2518	1.3258	2471	3.3795	2424	-4.1357	2377	-7.3411	2330	-14.1308
2564	-1.2771	2517	2.4158	2470	5.0524	2423	-1.5244	2376	-7.7780	2329	-16.1452
2563	-2.6652	2516	1.2431	2469	4.1013	2422	1.3781	2375	-9.3857	2328	-16.1344
2562	-3.1732	2515	-0.7180	2468	0.9763	2421	3.5141	2374	-11.6558	2327	-14.7836
2561	-2.4992	2514	-1.8918	2467	-2.5880	2420	4.1934	2373	-13.2924	2326	-12.9964
2560	-1.7530	2513	-1.8353	2466	-4.6616	2419	2.9019	2372	-12.8612	2325	-11.0004
2559	-1.9859	2512	-0.7511	2465	-4.4341	2418	-0.1450	2371	-10.0203	2324	-8.6041
2558	-2.8253	2511	0.9984	2464	-2.2785	2417	-3.6818	2370	-6.2874	2323	-5.4020
2557	-3.3549	2510	2.5350	2463	0.8028	2416	-5.9406	2369	-3.7496	2322	-1.4594
2556	-3.3515	2509	2.4511	2462	3.7029	2415	-5.9750	2368	-3.1334	2321	1.5519
2555	-3.3584	2508	0.3359	2461	5.3825	2414	-4.2347	2367	-3.1418	2320	1.7733
2554	-3.5878	2507	-2.5298	2460	5.4106	2413	-2.1503	2366	-2.3877	2319	-1.4697
2553	-3.5652	2506	-4.1696	2459	4.2179	2412	-0.7692	2365	-1.2634	2318	-6.2202
2552	-3.2649	2505	-3.8141	2458	2.6237	2411	-0.2377	2364	-1.7908	2317	-9.8440
2551	-3.6163	2504	-2.2034	2457	0.9306	2410	-0.0490	2363	-5.2278	2316	-10.6010
2550	-5.2468	2503	-0.5856	2456	-0.8455	2409	0.1828	2362	-10.4955	2315	-8.9260
2549	-7.0131	2502	0.1417	2455	-2.4977	2408	0.3040	2361	-14.6649	2314	-6.4681
2548	-6.8969	2501	-0.2467	2454	-3.4181	2407	-0.1544	2360	-14.8749	2313	-4.5940
2547	-4.1691	2500	-1.4468	2453	-3.2307	2406	-1.2292	2359	-10.9773	2312	-3.5418
2546	-0.3015	2499	-2.7491	2452	-1.9941	2405	-1.9868	2358	-6.6785	2311	-2.7082
2545	3.0582	2498	-3.4606	2451	-0.1469	2404	-1.2714	2357	-5.3968	2310	-1.5838
2544	5.3804	2497	-3.3054	2450	1.7381	2403	1.0818	2356	-6.8514	2309	-0.3076

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Table G.10. Regression coefficients for the full FTIR dataset (7 of 12).

WN	RC	WN	RC	WN	RC	WN	RC	WN	RC	WN	RC
2308	0.3857	2261	-9.0799	2214	-11.0215	2167	8.1160	2120	-0.9879	2073	-1.0360
2307	-0.1519	2260	-8.1287	2213	-12.1933	2166	1.1547	2119	-0.5426	2072	-3.2273
2306	-2.3561	2259	-6.1987	2212	-12.7849	2165	-4.5577	2118	0.4472	2071	-4.0510
2305	-5.7361	2258	-4.8192	2211	-12.5153	2164	-5.2565	2117	0.5774	2070	-4.1335
2304	-8.7034	2257	-4.4096	2210	-10.2800	2163	-1.6776	2116	-0.8059	2069	-4.2992
2303	-9.3735	2256	-4.3894	2209	-5.9502	2162	2.2836	2115	-2.8043	2068	-4.6400
2302	-7.3837	2255	-3.9616	2208	-1.8797	2161	2.6332	2114	-3.8318	2067	-4.3422
2301	-4.4857	2254	-2.7135	2207	-0.6660	2160	-2.5797	2113	-3.6674	2066	-2.5962
2300	-2.7712	2253	-1.2508	2206	-2.1113	2159	-11.7909	2112	-3.2479	2065	0.4932
2299	-2.7256	2252	-0.6757	2205	-3.4267	2158	-19.9772	2111	-3.3444	2064	3.5224
2298	-3.2054	2251	-0.8542	2204	-2.9037	2157	-21.9195	2110	-3.7904	2063	4.7237
2297	-3.1719	2250	-0.1621	2203	-1.9001	2156	-16.6798	2109	-4.1549	2062	3.3591
2296	-2.4597	2249	2.2727	2202	-2.1937	2155	-8.1991	2108	-4.0515	2061	0.4259
2295	-1.4202	2248	5.0749	2201	-3.0690	2154	-1.4627	2107	-3.0488	2060	-2.0821
2294	-0.3885	2247	5.9853	2200	-2.1868	2153	1.2805	2106	-0.8486	2059	-2.9495
2293	-0.1286	2246	4.5520	2199	1.1585	2152	0.7618	2105	1.9727	2058	-2.5613
2292	-1.3971	2245	1.9765	2198	4.7865	2151	-1.2228	2104	4.0248	2057	-2.0749
2291	-3.9353	2244	-1.1199	2197	6.4360	2150	-3.1057	2103	4.2756	2056	-1.9257
2290	-6.3293	2243	-5.0704	2196	6.0841	2149	-3.3536	2102	3.2928	2055	-1.8129
2289	-7.0829	2242	-9.4978	2195	5.3481	2148	-0.8506	2101	2.4342	2054	-1.4943
2288	-5.6351	2241	-12.3994	2194	4.9966	2147	3.8925	2100	2.2766	2053	-1.0529
2287	-2.5162	2240	-12.0071	2193	4.3738	2146	8.6681	2099	2.1232	2052	-0.1303
2286	1.0714	2239	-8.4210	2192	2.9786	2145	11.1458	2098	1.1767	2051	2.0621
2285	3.4589	2238	-3.1259	2191	1.5523	2144	10.6006	2097	-0.4381	2050	5.3681
2284	3.5632	2237	1.9931	2190	1.1074	2143	8.3410	2096	-1.8543	2049	8.0925
2283	2.0521	2236	5.0265	2189	1.6327	2142	6.2780	2095	-2.3362	2048	8.4541
2282	0.8547	2235	4.5398	2188	2.4710	2141	5.4868	2094	-1.8615	2047	6.6773
2281	1.1120	2234	1.2046	2187	3.0595	2140	5.3413	2093	-0.9445	2046	4.4779
2280	2.1652	2233	-1.9555	2186	2.9358	2139	4.5247	2092	-0.2642	2045	2.7240
2279	2.6079	2232	-2.3085	2185	1.0143	2138	2.6722	2091	-0.3531	2044	0.7468
2278	1.8332	2231	-0.1948	2184	-3.1783	2137	1.0320	2090	-1.1234	2043	-2.1163
2277	0.0348	2230	1.6911	2183	-7.7504	2136	0.4561	2089	-1.7747	2042	-5.1646
2276	-2.2506	2229	1.3214	2182	-9.0830	2135	-0.0435	2088	-1.3230	2041	-6.6433
2275	-4.0186	2228	-0.8214	2181	-5.7511	2134	-2.0711	2087	0.4200	2040	-5.2601
2274	-3.8744	2227	-3.0298	2180	-0.5940	2133	-4.8804	2086	2.7179	2039	-1.1907
2273	-1.5796	2226	-4.1914	2179	2.1816	2132	-5.6255	2085	4.7382	2038	3.7693
2272	1.2057	2225	-4.1244	2178	1.5631	2131	-2.6538	2084	6.2601	2037	7.0867
2271	2.2773	2224	-2.9639	2177	0.1423	2130	2.1171	2083	7.5929	2036	7.0601
2270	1.0925	2223	-0.9752	2176	0.2054	2129	4.8156	2082	8.4730	2035	4.2179
2269	-0.7108	2222	1.3435	2175	0.8608	2128	3.4017	2081	8.0873	2034	0.6083
2268	-1.0361	2221	3.0353	2174	-0.2214	2127	-0.7344	2080	6.0365	2033	-2.1771
2267	0.7441	2220	3.4558	2173	-3.4531	2126	-4.6650	2079	3.4347	2032	-3.7975
2266	3.3170	2219	2.6787	2172	-6.2205	2125	-6.2043	2078	2.1499	2031	-4.4438
2265	4.2642	2218	0.9254	2171	-5.2706	2124	-5.1529	2077	2.8099	2030	-3.7486
2264	1.9498	2217	-1.7772	2170	0.2552	2123	-2.8902	2076	4.0916	2029	-1.4832
2263	-2.8475	2216	-5.2606	2169	7.3358	2122	-1.1765	2075	4.0181	2028	1.6633
2262	-7.3122	2215	-8.6714	2168	10.9009	2121	-0.8202	2074	1.9257	2027	4.1072

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Table G.11. Regression coefficients for the full FTIR dataset (8 of 12).

WN	RC	WN	RC	WN	RC	WN	RC	WN	RC	WN	RC
2026	4.1829	1979	-2.3363	1932	1.4011	1885	-3.8328	1838	0.2094	1791	-3.1610
2025	1.3947	1978	2.4972	1931	1.3022	1884	-3.3513	1837	-1.0939	1790	-2.8096
2024	-2.7386	1977	6.6901	1930	-0.1854	1883	-2.8518	1836	-2.1800	1789	-2.4846
2023	-5.4392	1976	8.6586	1929	-1.8781	1882	-2.6170	1835	-2.6641	1788	-2.1959
2022	-5.1234	1975	9.2998	1928	-2.4147	1881	-2.6032	1834	-2.5663	1787	-1.5088
2021	-3.3980	1974	10.3403	1927	-1.6385	1880	-2.2788	1833	-1.9957	1786	-0.4152
2020	-3.2981	1973	11.6499	1926	-0.6489	1879	-1.1106	1832	-1.1314	1785	0.6098
2019	-5.9923	1972	11.4190	1925	-0.2425	1878	0.4600	1831	-0.2306	1784	1.0872
2018	-9.5717	1971	8.8159	1924	-0.2449	1877	1.1421	1830	0.5344	1783	1.0471
2017	-11.4041	1970	5.0478	1923	-0.0274	1876	0.1663	1829	0.9068	1782	0.5882
2016	-10.8219	1969	2.1222	1922	0.4424	1875	-1.7871	1828	0.7778	1781	-0.3383
2015	-8.5594	1968	0.8891	1921	0.9000	1874	-3.2419	1827	0.1325	1780	-1.4381
2014	-5.0546	1967	1.0653	1920	1.5028	1873	-3.3313	1826	-0.8749	1779	-2.0673
2013	-0.5923	1966	2.0373	1919	2.4542	1872	-2.4200	1825	-1.7487	1778	-1.9252
2012	3.8420	1965	3.0304	1918	3.1791	1871	-1.3800	1824	-2.0711	1777	-1.1758
2011	7.0077	1964	2.9694	1917	2.9477	1870	-0.8773	1823	-2.0498	1776	-0.0789
2010	8.4460	1963	1.4791	1916	2.0571	1869	-0.8100	1822	-2.2413	1775	1.2176
2009	8.2081	1962	-0.2371	1915	1.6064	1868	-0.4577	1821	-2.7393	1774	2.4572
2008	6.4008	1961	-0.1615	1914	2.3001	1867	0.4493	1820	-3.0794	1773	3.0829
2007	4.0054	1960	1.9792	1913	3.5385	1866	1.3108	1819	-2.7157	1772	3.0430
2006	3.0184	1959	4.3540	1912	3.9977	1865	1.4057	1818	-1.6784	1771	3.2081
2005	4.1799	1958	5.3293	1911	2.7013	1864	0.4515	1817	-0.6224	1770	3.7411
2004	5.3732	1957	5.5530	1910	-0.0263	1863	-1.2947	1816	-0.2240	1769	3.8006
2003	3.7072	1956	6.7785	1909	-2.5435	1862	-3.1764	1815	-0.3963	1768	2.8339
2002	-0.7168	1955	9.1310	1908	-3.5088	1861	-4.5937	1814	-0.4959	1767	1.2786
2001	-4.8318	1954	10.4619	1907	-2.9328	1860	-5.3578	1813	-0.3079	1766	0.1526
2000	-6.3973	1953	8.4788	1906	-1.7779	1859	-5.4409	1812	-0.3505	1765	-0.1570
1999	-6.4201	1952	3.2255	1905	-0.9342	1858	-4.7931	1811	-1.1234	1764	0.1147
1998	-6.7772	1951	-3.0213	1904	-0.7304	1857	-3.5239	1810	-2.0428	1763	0.4483
1997	-6.9340	1950	-7.4667	1903	-1.1508	1856	-1.9595	1809	-1.8642	1762	0.5102
1996	-4.5064	1949	-8.5617	1902	-2.1939	1855	-0.5047	1808	-0.2020	1761	0.3320
1995	1.0132	1948	-6.4744	1901	-3.7064	1854	0.5358	1807	1.8928	1760	0.0740
1994	7.0143	1947	-2.5131	1900	-5.2913	1853	1.0579	1806	3.1951	1759	0.0101
1993	9.9078	1946	1.2897	1899	-6.2241	1852	1.2068	1805	3.2227	1758	0.2259
1992	8.7852	1945	2.6714	1898	-5.9650	1851	1.2326	1804	2.3999	1757	0.4513
1991	6.1439	1944	0.0899	1897	-4.6366	1850	1.2273	1803	1.3066	1756	0.3087
1990	4.6359	1943	-5.6535	1896	-3.2034	1849	1.0315	1802	0.3335	1755	-0.1599
1989	4.7428	1942	-10.6421	1895	-2.8740	1848	0.5438	1801	-0.2790	1754	-0.5560
1988	5.4670	1941	-11.4723	1894	-3.9462	1847	-0.0819	1800	-0.5702	1753	-0.6614
1987	5.8183	1940	-8.4659	1893	-5.4413	1846	-0.6781	1799	-0.8771	1752	-0.5495
1986	5.4215	1939	-4.3295	1892	-6.0978	1845	-1.1554	1798	-1.4390	1751	-0.2592
1985	4.2093	1938	-1.4233	1891	-5.5428	1844	-1.3375	1797	-1.9539	1750	-0.0277
1984	2.2619	1937	-0.4222	1890	-4.3775	1843	-1.0615	1796	-1.9121	1749	-0.0738
1983	-0.2966	1936	-0.6417	1889	-3.6486	1842	-0.3519	1795	-1.2982	1748	-0.3863
1982	-3.0937	1935	-0.9754	1888	-3.6821	1841	0.5111	1794	-0.9323	1747	-0.6856
1981	-5.2103	1934	-0.6683	1887	-3.9723	1840	1.1376	1793	-1.6322	1746	-1.0021
1980	-5.2301	1933	0.3805	1886	-4.0657	1839	1.0780	1792	-2.8099	1745	-1.6716

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Table G.12. Regression coefficients for the full FTIR dataset (9 of 12).

WN	RC	WN	RC	WN	RC	WN	RC	WN	RC	WN	RC
1744	-2.5753	1697	-0.9602	1650	1.5000	1603	-6.3808	1556	0.9651	1509	-4.4043
1743	-3.1612	1696	-0.1865	1649	0.9403	1602	-6.8408	1555	1.1219	1508	-6.7127
1742	-3.0133	1695	-0.1149	1648	0.0923	1601	-6.3800	1554	0.9296	1507	-7.5359
1741	-2.6710	1694	-0.4274	1647	-0.8907	1600	-5.2991	1553	0.9975	1506	-6.7860
1740	-2.8969	1693	-0.4322	1646	-1.0435	1599	-4.2971	1552	1.0317	1505	-7.2610
1739	-3.6049	1692	-0.0687	1645	-0.5049	1598	-3.9164	1551	0.7116	1504	-8.2912
1738	-3.9971	1691	0.4473	1644	-0.1315	1597	-4.2329	1550	-0.2036	1503	-8.5993
1737	-3.5032	1690	0.7030	1643	-0.1169	1596	-4.8503	1549	-1.2054	1502	-8.0394
1736	-2.4274	1689	0.5158	1642	-0.3735	1595	-5.1338	1548	-1.8171	1501	-7.1307
1735	-1.3601	1688	0.0542	1641	-0.7440	1594	-4.7202	1547	-2.0033	1500	-6.6278
1734	-0.5518	1687	-0.4837	1640	-1.0299	1593	-3.8435	1546	-2.1616	1499	-6.6925
1733	-0.2249	1686	-1.4033	1639	-1.0306	1592	-3.0964	1545	-2.6787	1498	-6.8214
1732	-0.6120	1685	-3.1396	1638	-0.6344	1591	-2.8833	1544	-3.7188	1497	-6.3743
1731	-1.5206	1684	-3.5480	1637	0.1805	1590	-3.1470	1543	-4.7847	1496	-5.6095
1730	-2.4647	1683	-1.2736	1636	1.0879	1589	-3.5864	1542	-4.7187	1495	-5.3318
1729	-3.0432	1682	1.3301	1635	1.2276	1588	-3.8985	1541	-1.1932	1494	-5.5327
1728	-3.2423	1681	2.4119	1634	0.4629	1587	-3.8111	1540	3.8142	1493	-5.8659
1727	-3.2518	1680	1.9571	1633	-0.4037	1586	-3.2849	1539	4.6308	1492	-6.3332
1726	-3.2085	1679	0.6355	1632	-0.8532	1585	-2.4515	1538	2.5115	1491	-7.1937
1725	-3.1787	1678	-0.3611	1631	-0.7687	1584	-1.6328	1537	0.2602	1490	-8.1186
1724	-3.0774	1677	-0.6370	1630	-0.5719	1583	-1.0490	1536	-1.2999	1489	-8.1775
1723	-2.7336	1676	-0.4077	1629	-0.6868	1582	-0.6393	1535	-2.3169	1488	-7.5371
1722	-2.0779	1675	-0.0493	1628	-1.0959	1581	-0.3618	1534	-2.8236	1487	-6.9877
1721	-1.1240	1674	0.5416	1627	-1.4395	1580	-0.2246	1533	-2.4619	1486	-6.7180
1720	0.0596	1673	1.4756	1626	-1.5415	1579	-0.3208	1532	-1.6920	1485	-6.6733
1719	1.3105	1672	2.5280	1625	-1.7442	1578	-0.9829	1531	-1.2984	1484	-6.7314
1718	2.5603	1671	2.9707	1624	-2.3200	1577	-2.1700	1530	-1.1643	1483	-6.7184
1717	3.5723	1670	2.1772	1623	-2.8410	1576	-2.9987	1529	-0.7920	1482	-6.5480
1716	3.6284	1669	0.6895	1622	-2.8116	1575	-2.9382	1528	-0.1573	1481	-6.3268
1715	2.8909	1668	-0.3411	1621	-2.4624	1574	-2.5233	1527	-0.0344	1480	-6.1104
1714	2.0260	1667	-0.5990	1620	-2.2290	1573	-1.9596	1526	-1.0753	1479	-5.8946
1713	1.3000	1666	-0.1589	1619	-2.3492	1572	-1.1174	1525	-2.5122	1478	-5.5870
1712	0.5219	1665	0.6740	1618	-2.9150	1571	-0.1132	1524	-2.9942	1477	-5.3566
1711	-0.3385	1664	1.2225	1617	-3.4989	1570	0.5100	1523	-1.9812	1476	-5.3845
1710	-1.1897	1663	0.8830	1616	-3.2281	1569	0.2304	1522	-0.2134	1475	-5.5834
1709	-1.7920	1662	0.0585	1615	-2.3896	1568	-0.4738	1521	0.7803	1474	-4.9643
1708	-2.0026	1661	-0.4063	1614	-1.8282	1567	-0.7697	1520	0.7102	1473	-2.0263
1707	-1.8448	1660	-0.5886	1613	-1.8403	1566	-0.3403	1519	0.3040	1472	2.1433
1706	-1.4766	1659	-0.9227	1612	-2.3094	1565	0.6043	1518	-0.1897	1471	4.9565
1705	-0.8546	1658	-1.3494	1611	-2.9648	1564	1.3692	1517	-0.6669	1470	6.5821
1704	0.1316	1657	-1.3146	1610	-3.5047	1563	1.7749	1516	-0.9517	1469	8.3637
1703	1.5344	1656	-0.2402	1609	-3.8905	1562	1.6912	1515	-1.1496	1468	10.7277
1702	3.0544	1655	1.9031	1608	-4.2092	1561	0.8111	1514	-1.3593	1467	13.7924
1701	3.3114	1654	3.9880	1607	-4.4239	1560	-2.8833	1513	-1.5931	1466	17.3322
1700	1.4508	1653	4.5598	1606	-4.5024	1559	-6.5247	1512	-1.7904	1465	20.4816
1699	-0.7918	1652	3.6172	1605	-4.7620	1558	-3.6557	1511	-2.1397	1464	21.7285
1698	-1.5255	1651	2.3822	1604	-5.4750	1557	-0.1176	1510	-2.8221	1463	20.8915

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Table G.13. Regression coefficients for the full FTIR dataset (10 of 12).

WN	RC	WN	RC	WN	RC	WN	RC	WN	RC	WN	RC
1462	19.0029	1415	-0.7413	1368	7.7514	1321	-1.2580	1274	-1.6496	1227	-2.5552
1461	16.9921	1414	-1.0794	1367	8.2088	1320	-1.2764	1273	-1.5336	1226	-1.9761
1460	15.0396	1413	-1.7694	1366	7.1152	1319	-1.2055	1272	-1.2267	1225	-1.2104
1459	12.5192	1412	-2.5548	1365	5.0480	1318	-1.1866	1271	-0.8223	1224	-0.6719
1458	7.1570	1411	-3.0420	1364	2.9519	1317	-1.1566	1270	-0.4250	1223	-0.4929
1457	-1.1951	1410	-2.9673	1363	1.9676	1316	-0.9700	1269	-0.3982	1222	-0.6176
1456	-7.4820	1409	-2.2729	1362	2.2604	1315	-0.5860	1268	-0.7916	1221	-0.9446
1455	-10.8578	1408	-1.1841	1361	2.7173	1314	-0.3557	1267	-1.3962	1220	-1.2976
1454	-13.5545	1407	-0.1055	1360	2.4983	1313	-0.5560	1266	-1.7814	1219	-1.5306
1453	-16.4438	1406	0.4603	1359	1.7657	1312	-1.1649	1265	-1.7329	1218	-1.5750
1452	-19.5053	1405	0.3946	1358	1.0728	1311	-1.8354	1264	-1.3156	1217	-1.5096
1451	-22.3099	1404	0.0894	1357	0.8389	1310	-2.1798	1263	-0.8070	1216	-1.3193
1450	-24.4785	1403	-0.0415	1356	1.2556	1309	-2.1029	1262	-0.4418	1215	-1.0267
1449	-25.9974	1402	0.0864	1355	2.2167	1308	-1.7914	1261	-0.4041	1214	-0.7398
1448	-26.6510	1401	0.2454	1354	3.3125	1307	-1.5858	1260	-0.8233	1213	-0.5720
1447	-26.4405	1400	0.3333	1353	3.9620	1306	-1.6568	1259	-1.5028	1212	-0.5561
1446	-25.7771	1399	0.3239	1352	3.8806	1305	-1.8126	1258	-1.9071	1211	-0.4569
1445	-25.0156	1398	0.3328	1351	3.3337	1304	-1.7407	1257	-1.5579	1210	-0.1971
1444	-24.0323	1397	0.3223	1350	2.7397	1303	-1.3825	1256	-0.7208	1209	0.0901
1443	-22.6298	1396	0.1516	1349	2.2215	1302	-1.0390	1255	-0.0982	1208	0.2021
1442	-20.8776	1395	-0.3126	1348	1.5953	1301	-0.9779	1254	-0.2296	1207	0.1681
1441	-19.1039	1394	-0.9789	1347	0.6934	1300	-1.1023	1253	-0.8544	1206	0.1842
1440	-17.4824	1393	-1.5104	1346	-0.2428	1299	-1.0396	1252	-1.3543	1205	0.3394
1439	-15.9226	1392	-1.5866	1345	-0.8816	1298	-0.6293	1251	-1.4122	1204	0.4979
1438	-14.1001	1391	-1.0408	1344	-0.9475	1297	0.0190	1250	-1.1174	1203	0.6445
1437	-11.6158	1390	-0.0230	1343	-0.5745	1296	0.6062	1249	-0.7052	1202	0.7264
1436	-8.7871	1389	1.2538	1342	-0.0227	1295	0.9438	1248	-0.2607	1201	0.7034
1435	-6.8089	1388	2.6204	1341	0.3676	1294	1.0637	1247	0.0255	1200	0.4758
1434	-5.8841	1387	4.0341	1340	0.3964	1293	0.9108	1246	-0.0001	1199	-0.0114
1433	-5.4439	1386	5.1970	1339	0.3367	1292	0.5035	1245	-0.3852	1198	-0.6336
1432	-5.2480	1385	5.8437	1338	0.6124	1291	-0.0949	1244	-1.0079	1197	-1.2737
1431	-5.3104	1384	6.1102	1337	1.2582	1290	-0.6167	1243	-1.5187	1196	-1.8800
1430	-5.3522	1383	6.4383	1336	1.9276	1289	-0.8145	1242	-1.6850	1195	-2.5041
1429	-5.0521	1382	7.0084	1335	2.2544	1288	-0.7006	1241	-1.4474	1194	-3.0295
1428	-4.5321	1381	7.7058	1334	2.0700	1287	-0.5836	1240	-0.8470	1193	-3.1846
1427	-4.2036	1380	7.9119	1333	1.3548	1286	-0.7238	1239	-0.2508	1192	-2.8880
1426	-4.2402	1379	7.0326	1332	0.3031	1285	-1.0640	1238	-0.0582	1191	-2.2697
1425	-4.4809	1378	5.0939	1331	-0.7527	1284	-1.3402	1237	-0.3545	1190	-1.6318
1424	-4.5862	1377	2.7532	1330	-1.4774	1283	-1.2603	1236	-0.8740	1189	-1.1115
1423	-4.1750	1376	0.5296	1329	-1.7049	1282	-0.8517	1235	-1.1895	1188	-0.7066
1422	-3.2255	1375	-1.4242	1328	-1.5591	1281	-0.3844	1234	-1.0678	1187	-0.4282
1421	-1.8448	1374	-2.5667	1327	-1.3280	1280	-0.2016	1233	-0.6850	1186	-0.4261
1420	-0.4916	1373	-2.3493	1326	-1.1577	1279	-0.3803	1232	-0.2642	1185	-0.6111
1419	0.0633	1372	-0.9370	1325	-1.0133	1278	-0.7570	1231	-0.1958	1184	-0.7691
1418	-0.2426	1371	1.0973	1324	-0.9226	1277	-1.1531	1230	-0.7379	1183	-0.7292
1417	-0.6145	1370	3.5158	1323	-0.9371	1276	-1.4481	1229	-1.6823	1182	-0.6658
1416	-0.6896	1369	5.9557	1322	-1.0951	1275	-1.6139	1228	-2.4552	1181	-0.9031

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Table G.14. Regression coefficients for the full FTIR dataset (11 of 12).

WN	RC	WN	RC	WN	RC	WN	RC	WN	RC	WN	RC
1180	-1.3445	1133	0.2029	1086	-0.4315	1039	-3.6875	992	-3.3402	945	-2.7109
1179	-1.6279	1132	0.7298	1085	-0.4299	1038	-3.3824	991	-3.8634	944	-1.8859
1178	-1.5093	1131	1.3758	1084	-0.8319	1037	-2.9854	990	-4.1109	943	-1.0685
1177	-1.1833	1130	2.1939	1083	-1.3288	1036	-2.5055	989	-3.9450	942	-0.7283
1176	-0.9419	1129	2.9250	1082	-1.7078	1035	-2.1849	988	-3.5619	941	-0.9630
1175	-0.7317	1128	3.1849	1081	-1.9424	1034	-2.4165	987	-3.1930	940	-1.5030
1174	-0.3285	1127	2.7572	1080	-2.1378	1033	-3.2452	986	-2.9502	939	-2.1019
1173	0.2822	1126	1.8078	1079	-2.2906	1032	-4.2439	985	-2.7248	938	-2.5348
1172	0.9417	1125	0.8140	1078	-2.3995	1031	-5.0227	984	-2.4688	937	-2.7246
1171	1.4980	1124	0.1937	1077	-2.4038	1030	-5.5437	983	-2.0242	936	-2.5343
1170	1.9910	1123	0.0313	1076	-2.2798	1029	-5.8643	982	-1.3294	935	-1.9411
1169	2.4106	1122	-0.0423	1075	-1.9254	1028	-5.6964	981	-0.5904	934	-1.2089
1168	2.5260	1121	-0.4156	1074	-1.4475	1027	-4.7520	980	-0.2556	933	-0.6450
1167	2.2036	1120	-1.1673	1073	-1.1993	1026	-3.2573	979	-0.6568	932	-0.3328
1166	1.5723	1119	-1.8931	1072	-1.3993	1025	-1.8689	978	-1.7350	931	-0.1721
1165	0.9543	1118	-2.2116	1071	-1.8570	1024	-1.1015	977	-2.9874	930	-0.1600
1164	0.6036	1117	-2.0282	1070	-2.1809	1023	-0.9152	976	-3.5901	929	-0.4972
1163	0.5784	1116	-1.4795	1069	-2.1169	1022	-1.1615	975	-2.8999	928	-1.2149
1162	0.7150	1115	-0.7099	1068	-1.8010	1021	-1.7388	974	-0.9674	927	-2.0327
1161	0.8250	1114	0.1214	1067	-1.4593	1020	-2.5603	973	1.3098	926	-2.5337
1160	0.9594	1113	0.7811	1066	-1.4281	1019	-3.3076	972	2.7333	925	-2.5224
1159	1.2675	1112	1.0888	1065	-1.9359	1018	-3.5703	971	2.9130	924	-2.1178
1158	1.8921	1111	0.9782	1064	-2.8633	1017	-3.3035	970	2.3872	923	-1.4428
1157	2.7143	1110	0.5377	1063	-3.5389	1016	-2.7499	969	1.8331	922	-0.6458
1156	3.3587	1109	-0.2379	1062	-3.1598	1015	-2.2518	968	1.3169	921	0.0049
1155	3.6370	1108	-1.2352	1061	-1.7220	1014	-1.8386	967	0.4068	920	0.1426
1154	3.6935	1107	-2.0333	1060	-0.3061	1013	-1.3281	966	-0.9578	919	-0.3168
1153	3.7746	1106	-2.2624	1059	0.1678	1012	-0.6909	965	-2.1714	918	-0.8608
1152	3.8360	1105	-1.8770	1058	-0.3349	1011	-0.1563	964	-2.6946	917	-0.6780
1151	3.6533	1104	-1.3174	1057	-1.0119	1010	0.0027	963	-2.6383	916	0.2923
1150	3.2469	1103	-0.9425	1056	-1.3929	1009	-0.3952	962	-2.4249	915	1.2849
1149	2.9283	1102	-0.7654	1055	-1.4984	1008	-1.2811	961	-2.2681	914	1.2627
1148	2.9338	1101	-0.6675	1054	-1.5754	1007	-2.3878	960	-2.0094	913	-0.0435
1147	3.0662	1100	-0.7484	1053	-1.6978	1006	-3.3757	959	-1.5700	912	-1.7344
1146	2.9645	1099	-1.1544	1052	-1.7857	1005	-3.7996	958	-1.1291	911	-2.6226
1145	2.5958	1098	-1.8033	1051	-1.8387	1004	-3.4911	957	-0.8419	910	-2.2191
1144	2.1834	1097	-2.4781	1050	-1.6922	1003	-2.6118	956	-0.7831	909	-1.1166
1143	1.8718	1096	-3.0958	1049	-1.3522	1002	-1.6327	955	-0.8182	908	-0.3634
1142	1.5951	1095	-3.6555	1048	-1.0007	1001	-1.0145	954	-0.9960	907	-0.4430
1141	1.2812	1094	-4.1881	1047	-0.9240	1000	-0.8593	953	-1.3378	906	-1.1103
1140	1.0927	1093	-4.5777	1046	-0.9891	999	-1.0854	952	-1.6886	905	-1.9325
1139	1.0351	1092	-4.7093	1045	-0.9572	998	-1.5683	951	-1.8837	904	-2.5541
1138	0.9486	1091	-4.4878	1044	-0.9238	997	-2.1423	950	-1.8951	903	-2.6647
1137	0.5601	1090	-3.9055	1043	-1.3172	996	-2.6202	949	-1.9541	902	-2.0276
1136	0.0193	1089	-2.9975	1042	-2.2616	995	-2.8285	948	-2.2779	901	-0.6769
1135	-0.3031	1088	-1.9508	1041	-3.2785	994	-2.8171	947	-2.7728	900	0.8113
1134	-0.2217	1087	-1.0015	1040	-3.7551	993	-2.9371	946	-3.0399	899	1.6462

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Table G.15. Regression coefficients for the full FTIR dataset (12 of 12).

WN	RC	WN	RC	WN	RC	WN	RC	WN	RC	WN	RC
898	1.5959	851	-3.4283	804	-9.1304	757	-1.2994	710	-0.8218	663	0.4702
897	1.0413	850	-3.8056	803	-9.0034	756	-2.0069	709	-0.6016	662	-0.2565
896	0.3689	849	-4.5310	802	-8.3207	755	-3.1067	708	-1.3504	661	-0.3778
895	-0.2710	848	-5.4485	801	-6.9308	754	-4.3580	707	-2.9750	660	0.6756
894	-0.9832	847	-6.1249	800	-5.5733	753	-5.5439	706	-4.9373	659	1.8910
893	-1.7749	846	-6.0937	799	-4.7150	752	-6.4943	705	-6.6238	658	2.3363
892	-2.5338	845	-5.2298	798	-3.9409	751	-7.1542	704	-7.5909	657	2.9079
891	-3.0920	844	-3.9729	797	-2.7595	750	-7.6251	703	-7.5869	656	4.2169
890	-3.2491	843	-3.0854	796	-1.5275	749	-7.8988	702	-6.8385	655	7.5178
889	-3.0946	842	-3.0283	795	-1.1595	748	-7.8063	701	-6.0538	654	9.4357
888	-2.9833	841	-3.5616	794	-2.1880	747	-7.3238	700	-6.0059	653	7.9253
887	-3.4026	840	-3.9822	793	-4.2041	746	-6.7758	699	-6.7243	652	4.2872
886	-4.4942	839	-3.8299	792	-6.3332	745	-6.5382	698	-7.1927	651	1.0591
885	-5.7880	838	-3.1622	791	-7.8163	744	-6.6488	697	-6.1986	650	-0.2172
884	-6.4612	837	-2.5269	790	-8.2171	743	-6.8903	696	-3.6030		
883	-5.9528	836	-2.4797	789	-7.6205	742	-7.1790	695	-0.4856		
882	-4.4276	835	-3.2078	788	-6.4223	741	-7.4928	694	1.6980		
881	-2.8471	834	-4.4563	787	-5.1442	740	-7.7535	693	2.3651		
880	-2.3727	833	-5.4992	786	-4.2209	739	-7.8550	692	1.9798		
879	-3.2697	832	-5.8596	785	-4.1203	738	-7.7799	691	1.2930		
878	-4.5897	831	-5.4687	784	-5.0907	737	-7.5617	690	0.5075		
877	-5.0126	830	-4.7470	783	-6.7178	736	-7.0058	689	-0.7109		
876	-4.0483	829	-4.1831	782	-7.9034	735	-5.8514	688	-2.3655		
875	-2.5302	828	-3.9957	781	-7.6886	734	-4.2481	687	-3.5387		
874	-1.6259	827	-4.2396	780	-6.2695	733	-2.6246	686	-3.1840		
873	-1.8927	826	-4.9471	779	-4.6291	732	-1.4613	685	-1.5070		
872	-2.8884	825	-5.8863	778	-3.5250	731	-0.7208	684	-0.1590		
871	-3.8285	824	-6.8333	777	-3.0114	730	-0.2285	683	-0.5216		
870	-4.0912	823	-7.6564	776	-3.0048	729	0.1380	682	-2.0759		
869	-3.6400	822	-8.4385	775	-3.8320	728	0.3555	681	-3.0425		
868	-2.9343	821	-9.0115	774	-5.4790	727	0.6519	680	-2.2618		
867	-2.5652	820	-9.0937	773	-7.1942	726	1.2043	679	-0.3861		
866	-2.7999	819	-8.7047	772	-7.8122	725	1.7815	678	1.3660		
865	-3.4592	818	-8.2616	771	-6.7214	724	1.6702	677	2.5555		
864	-4.2285	817	-8.2425	770	-4.4220	723	0.4542	676	3.3598		
863	-4.8125	816	-8.7767	769	-2.1908	722	-1.4782	675	3.6544		
862	-4.9121	815	-9.9399	768	-1.2661	721	-3.0115	674	3.0054		
861	-4.3579	814	-11.8012	767	-2.0520	720	-3.4064	673	1.5771		
860	-3.1678	813	-14.1969	766	-3.8880	719	-2.8062	672	0.1654		
859	-1.9152	812	-16.3092	765	-5.4561	718	-1.8047	671	-0.4191		
858	-1.1631	811	-17.2539	764	-6.0141	717	-0.8816	670	0.1035		
857	-1.0977	810	-16.9162	763	-5.7378	716	-0.2825	669	1.6799		
856	-1.5056	809	-15.8905	762	-5.2326	715	-0.1102	668	3.1914		
855	-2.0230	808	-14.6349	761	-4.5724	714	-0.5222	667	3.1126		
854	-2.5329	807	-13.0210	760	-3.5474	713	-1.2180	666	2.1757		
853	-2.9444	806	-11.1143	759	-2.2619	712	-1.6370	665	1.5448		
852	-3.2295	805	-9.6518	758	-1.3597	711	-1.4022	664	1.1512		

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Table G.16. Regression coefficients for the background removed FTIR dataset (1 of 3).

WN	RC	WN	RC	WN	RC	WN	RC	WN	RC
3000	-32.7730	2953	-71.9920	2906	34.9943	2859	-62.2674	2812	-9.9425
2999	-55.6363	2952	-58.4951	2905	20.4065	2858	-82.6008	2811	-16.3033
2998	-74.0058	2951	-40.1271	2904	15.1139	2857	-93.0899	2810	-13.8821
2997	-80.4928	2950	-28.7993	2903	25.3676	2856	-91.6906	2809	-7.8804
2996	-74.8198	2949	-31.0325	2902	42.8584	2855	-81.8488	2808	-0.5829
2995	-59.0928	2948	-44.0219	2901	53.7557	2854	-69.2412	2807	8.5132
2994	-37.3857	2947	-56.5198	2900	51.5669	2853	-57.1613	2806	18.9239
2993	-16.1417	2946	-59.0057	2899	42.3949	2852	-45.3876	2805	27.9267
2992	-3.2484	2945	-51.6761	2898	36.1521	2851	-33.2441	2804	32.0206
2991	-0.6423	2944	-41.9101	2897	36.3774	2850	-23.0122	2803	30.1680
2990	-3.5207	2943	-34.6934	2896	38.9325	2849	-16.7925	2802	24.4915
2989	-5.5405	2942	-28.5169	2895	38.8565	2848	-16.0331	2801	18.2835
2988	-4.0897	2941	-20.9427	2894	35.3666	2847	-19.1290	2800	15.4133
2987	0.2537	2940	-12.2965	2893	28.6895	2846	-23.3324	1520	19.6826
2986	8.6342	2939	-2.9257	2892	18.0839	2845	-25.3840	1519	21.5022
2985	19.4972	2938	9.3338	2891	2.9787	2844	-22.9941	1518	21.6575
2984	27.8730	2937	25.3544	2890	-12.3682	2843	-16.8441	1517	18.7445
2983	27.6095	2936	41.0329	2889	-22.5322	2842	-12.2801	1516	13.8024
2982	16.8239	2935	50.3575	2888	-25.2131	2841	-14.7791	1515	9.6597
2981	-0.2093	2934	50.2117	2887	-23.1408	2840	-24.2961	1514	7.6724
2980	-16.7339	2933	43.4875	2886	-18.7940	2839	-35.2012	1513	7.4457
2979	-29.3058	2932	33.5230	2885	-11.6788	2838	-41.6952	1512	8.1438
2978	-36.9420	2931	21.9041	2884	-0.4053	2837	-42.7844	1511	7.7199
2977	-39.9651	2930	8.8316	2883	14.3397	2836	-40.0964	1510	5.0567
2976	-38.7794	2929	-4.2553	2882	29.7150	2835	-34.6794	1509	-2.0209
2975	-34.2530	2928	-13.0860	2881	40.5185	2834	-26.7363	1508	-11.0946
2974	-29.0214	2927	-14.2845	2880	40.7787	2833	-18.8055	1507	-14.2946
2973	-25.7485	2926	-7.8778	2879	28.4966	2832	-15.7129	1506	-14.9769
2972	-24.9004	2925	2.1393	2878	9.7231	2831	-20.1512	1505	-22.9551
2971	-23.3161	2924	13.8841	2877	-4.9707	2830	-29.5464	1504	-31.5599
2970	-17.5805	2923	30.9746	2876	-10.7548	2829	-37.2429	1503	-33.4088
2969	-7.8192	2922	53.7486	2875	-11.9424	2828	-39.2012	1502	-28.0250
2968	3.3606	2921	71.3819	2874	-14.0129	2827	-36.3176	1501	-20.3002
2967	12.5115	2920	70.6056	2873	-16.4221	2826	-32.4696	1500	-17.2093
2966	17.8011	2919	52.7935	2872	-15.8550	2825	-29.4178	1499	-20.9956
2965	17.5861	2918	36.3858	2871	-13.8881	2824	-25.0477	1498	-26.6233
2964	10.3825	2917	36.4499	2870	-14.9175	2823	-16.6123	1497	-25.0688
2963	-1.5224	2916	49.2103	2869	-19.4184	2822	-5.4791	1496	-16.1917
2962	-10.3727	2915	61.4368	2868	-22.1714	2821	4.6392	1495	-9.9476
2961	-7.3001	2914	66.1071	2867	-19.6594	2820	11.3053	1494	-10.1697
2960	8.9649	2913	65.5661	2866	-13.9997	2819	16.2991	1493	-14.5627
2959	28.9879	2912	61.6841	2865	-9.2105	2818	23.1097	1492	-21.1458
2958	36.8769	2911	53.9605	2864	-6.3906	2817	31.6656	1491	-28.5336
2957	22.2063	2910	45.7536	2863	-5.6397	2816	38.3349	1490	-32.2816
2956	-10.8980	2909	43.2904	2862	-8.6944	2815	36.4087	1489	-28.1334
2955	-47.2268	2908	46.2338	2861	-19.4267	2814	23.8679	1488	-20.3969
2954	-69.7145	2907	45.7201	2860	-38.7041	2813	5.3839	1487	-14.7462

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Table G.17. Regression coefficients for the background removed FTIR dataset (2 of 3).

WN	RC	WN	RC	WN	RC	WN	RC	WN	RC
1486	-11.6813	1439	-42.5552	1392	8.3056	1345	-0.6373	859	-7.6318
1485	-10.7259	1438	-31.1708	1391	9.8587	1344	-1.1976	858	2.0565
1484	-10.6559	1437	-16.5606	1390	14.3090	1343	1.3682	857	8.3685
1483	-9.8275	1436	-3.9190	1389	19.8182	1342	6.0136	856	10.4620
1482	-6.9241	1435	1.1318	1388	24.0321	1341	9.9174	855	9.5202
1481	-2.9845	1434	0.4760	1387	26.8487	1340	10.3942	854	5.9046
1480	0.6942	1433	-1.1235	1386	27.4947	900	23.7659	853	0.4677
1479	3.5725	1432	-2.6370	1385	25.6227	899	29.2395	852	-5.0569
1478	6.0524	1431	-5.4052	1384	22.6685	898	27.8788	851	-8.3953
1477	6.5002	1430	-8.0389	1383	21.4932	897	22.2559	850	-9.4066
1476	4.0860	1429	-7.9769	1382	23.0820	896	14.9738	849	-10.3051
1475	-0.2201	1428	-5.7910	1381	26.3666	895	8.1979	848	-13.2124
1474	-1.1078	1427	-4.4143	1380	27.8475	894	3.0881	847	-16.4570
1473	7.7020	1426	-5.3496	1379	24.1674	893	-0.0094	846	-15.3982
1472	16.8915	1425	-7.5714	1378	16.1258	892	-2.3845	845	-8.2330
1471	14.1578	1424	-9.0730	1377	8.0267	891	-4.8876	844	-0.1324
1470	5.5452	1423	-7.3450	1376	3.6538	890	-6.0519	843	1.6387
1469	-0.6958	1422	-2.2015	1375	3.0060	889	-4.8641	842	-4.5745
1468	-1.9488	1421	5.6640	1374	5.4538	888	-3.3786	841	-12.6751
1467	2.8037	1420	13.4062	1373	10.2473	887	-5.7417	840	-15.4868
1466	13.1924	1419	16.2924	1372	15.3440	886	-13.7908	839	-11.6037
1465	25.6373	1418	14.2179	1371	18.3097	885	-24.5750	838	-4.6054
1464	32.8458	1417	11.5420	1370	19.6548	884	-32.1915	837	0.5123
1463	32.9722	1416	10.4608	1369	20.5361	883	-31.6254	836	1.2298
1462	29.9933	1415	9.4531	1368	22.4161	882	-22.4603	835	-2.1602
1461	28.4293	1414	6.4652	1367	25.1427	881	-10.2033	834	-7.5384
1460	28.9522	1413	0.9743	1366	27.4564	880	-4.2536	833	-11.6956
1459	29.2993	1412	-5.1042	1365	29.4493	879	-8.7830	832	-13.6781
1458	20.0694	1411	-8.9281	1364	31.3387	878	-18.0129	831	-13.6507
1457	-3.1784	1410	-8.7857	1363	32.8007	877	-21.5005	830	-12.5849
1456	-24.1419	1409	-4.3271	1362	32.1113	876	-14.2858	829	-10.8846
1455	-36.6039	1408	2.8744	1361	27.3366	875	-2.3446	828	-9.0333
1454	-45.4908	1407	10.0322	1360	19.2921	874	5.1744	827	-8.5865
1453	-51.6971	1406	13.5051	1359	11.4231	873	3.9361	826	-10.7159
1452	-55.9560	1405	12.3279	1358	6.3123	872	-1.9928	825	-13.9833
1451	-59.0745	1404	9.1643	1357	5.2690	871	-6.2528	824	-16.5362
1450	-61.4323	1403	7.2873	1356	8.6042	870	-5.4142	823	-18.2702
1449	-63.9039	1402	7.8326	1355	15.7472	869	-1.8883	822	-21.2981
1448	-65.4342	1401	9.4120	1354	24.0051	868	-0.0828	821	-25.5687
1447	-64.9138	1400	11.4107	1353	29.1684	867	-1.7353	820	-28.2369
1446	-63.1573	1399	13.0501	1352	28.4781	866	-5.0059	819	-26.7366
1445	-61.9923	1398	14.0665	1351	23.5397	865	-7.7001	818	-21.7792
1444	-61.4618	1397	14.3442	1350	17.8014	864	-10.7211	817	-17.5008
1443	-60.6021	1396	14.5158	1349	13.6259	863	-15.7828	816	-17.7765
1442	-58.3371	1395	14.4418	1348	10.4887	862	-21.1264	815	-24.6744
1441	-54.8342	1394	12.9137	1347	6.8235	861	-22.7351	814	-37.0476
1440	-49.9334	1393	10.0997	1346	2.7206	860	-17.4116	813	-52.2307

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Table G.18. Regression coefficients for the background removed FTIR dataset (3 of 3).

WN	RC	WN	RC	WN	RC	WN	RC
812	-65.2990	765	-18.7542	718	1.8000	671	14.5247
811	-71.9556	764	-17.7726	717	10.2348	670	24.5244
810	-70.9468	763	-13.7327	716	14.2784	669	35.7275
809	-65.0284	762	-11.7906	715	12.9117	668	44.8419
808	-57.7155	761	-9.9002	714	6.6897	667	45.0394
807	-50.1438	760	-3.9529	713	-0.4657	666	34.6827
806	-43.1125	759	5.4709	712	-4.2174	665	24.7291
805	-39.3254	758	13.4812	711	-3.0706	664	21.0352
804	-39.2996	757	17.2545	710	0.6355	663	19.1069
803	-38.9595	756	16.9755	709	3.5391	662	15.5845
802	-32.9745	755	13.1673	708	2.1925	661	11.7913
801	-22.2313	754	5.0370	707	-4.5328	660	13.4589
800	-12.5294	753	-5.9337	706	-14.9445	659	16.3932
799	-6.9850	752	-16.4927	705	-24.8262	658	16.5595
798	-2.1092	751	-23.9157	704	-29.5762	657	20.5669
797	5.5332	750	-27.7685	703	-26.4909	656	34.4830
796	12.4095	749	-28.0108	702	-17.7010	655	64.8428
795	11.8365	748	-24.0564	701	-9.5372	654	86.7388
794	2.1769	747	-17.3359	700	-9.2107	653	84.0673
793	-10.8464	746	-11.7806	699	-18.0663	652	61.1729
792	-20.4999	745	-10.9916	698	-28.0591	651	35.6903
791	-24.4325	744	-15.2530	697	-27.6531	650	18.7678
790	-23.3913	743	-21.4697	696	-13.4701		
789	-19.4041	742	-26.2953	695	6.5418		
788	-13.1416	741	-28.1282	694	20.4598		
787	-4.9227	740	-27.5686	693	23.2145		
786	3.9980	739	-26.4035	692	18.3984		
785	8.8346	738	-26.3553	691	11.7090		
784	5.1437	737	-27.3134	690	4.9763		
783	-5.8411	736	-27.6314	689	-3.8501		
782	-16.1458	735	-25.4336	688	-15.5376		
781	-18.4170	734	-20.8509	687	-25.2348		
780	-13.5574	733	-14.8390	686	-25.3517		
779	-6.7435	732	-9.8196	685	-14.9083		
778	-0.9132	731	-7.0801	684	-3.4964		
777	3.6545	730	-7.3440	683	-1.2204		
776	4.9545	729	-9.5386	682	-6.4300		
775	-1.2661	728	-10.8479	681	-8.2361		
774	-13.4606	727	-6.5779	680	-0.3073		
773	-23.6091	726	5.0208	679	11.1024		
772	-24.0031	725	18.9505	678	17.2373		
771	-13.5994	724	25.2873	677	17.4590		
770	1.4129	723	18.2848	676	16.2930		
769	12.3455	722	2.0144	675	15.3975		
768	12.6303	721	-11.6657	674	12.8463		
767	2.3521	720	-14.7114	673	9.6030		
766	-11.3681	719	-8.2186	672	9.1670		

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Table G.19. Regression intercepts (*C*) corresponding to the coefficients presented in this appendix.

Spectra Type	Number of Regression Components	Background Sections Removed	Intercept
NIR	7	No	-62.81
		Yes	-41.66
FTIR	7	No	-17.99
		Yes	-9.54

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APPENDIX H

Derivatives for the ESD and SAFT-BACK Equations of State

In order to predict the speed of sound, multiple derivatives of each equation of state are needed. In the case of the ESD, the required derivatives are:

$$\left(\frac{\partial V}{\partial P}\right)_T, \left(\frac{\partial P}{\partial T}\right)_V, \left(\frac{\partial V}{\partial T}\right)_P, \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

And for the SAFT-BACK equation:

$$\left(\frac{\partial A}{\partial V}\right)_T, \left(\frac{\partial V}{\partial P}\right)_T, \left(\frac{\partial P}{\partial T}\right)_V, \left(\frac{\partial V}{\partial T}\right)_P, \left(\frac{\partial^2 A^{res}}{\partial T^2}\right)_V$$

Note that the $(\partial V/\partial T)_P$ derivative would require implicit differentiation. Instead, the triple product rule is used such that:

$$\left(\frac{\partial V}{\partial T}\right)_P = -\frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_T} \quad (\text{H.1})$$

This also allows us to eliminate one required derivative for the SAFT-BACK equation.

The derivatives for the ESD equation are:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2} - \frac{4.2qbRT + 3.99qb^2RT + 3.8VbRT + 3.61b^2RT}{(V^2 - 1.9bV)^2} + \frac{19VqYbRT + 16.85775qY^2b^2RT}{(V^2 + 1.7745YbV)^2} \quad (\text{H.2})$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} + \frac{2.1qbR + 1.9bR}{V^2 - 1.9bV} + \frac{\varepsilon e^{\varepsilon/kT} \left(\frac{9.5RTbq}{V^2 + 1.7745YbV} - \frac{16.85775RTVYb^2q}{(V^2 + 1.7745YbV)^2} \right)}{T^2k} - \frac{9.5RTbq}{V^2 + 1.7745YbV} \quad (\text{H.3})$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\frac{R}{P} + \frac{1.9Rb}{P(V - 1.9b)} + \frac{2.1Rbq}{P(V - 1.9b)} - \frac{9.5RYbq}{P(V + 1.7745Yb)} + \frac{38RVb\varepsilon q e^{\varepsilon/kT}}{PTk(4V^2 + 14.196VYb + 12.5954Y^2b^2)}}{\frac{1.9RTb}{P(V - 1.9b)^2} + \frac{2.1RTbq}{P(V - 1.9b)^2} - \frac{9.5RTYbq}{P(V + 1.7745Yb)^2} + 1} \quad (\text{H.4})$$

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V = \frac{-38000Re^{\varepsilon/kT}b\varepsilon^2q(2V + 3.549Yb - 7.098be^{\varepsilon/kT})}{T^3k^2(2V + 3.549Yb)^3} \quad (\text{H.5})$$

Equation (H.2) is the inverse of what is required, but it is an easier derivative to perform.

The derivatives for the SAFT-BACK equation are more complicated. In order to make these derivatives easier, the chain rule is used. Also, the derivatives are sometimes done with respect to density rather than molar volume, depending on what property is needed and what will make the process easier.

First, the derivative of the Helmholtz energy (A) is taken with respect to density to find the compressibility factor (Z), such that:

$$Z = \rho \left(\frac{\partial \left(\frac{A}{RT} \right)}{\partial \rho} \right)_{N,T} = \eta \left(\frac{\partial \left(\frac{A}{RT} \right)}{\partial \eta} \right)_{N,T} \quad (\text{H.6})$$

Each term is evaluated individually:

$$Z^{hcb} = m \left[\frac{(1 + 3\alpha)\eta + (3\alpha^2 - 3\alpha - 2)\eta^2 + (1 - \alpha^2)\eta^3}{(1 - \eta)^3} \right] \quad (\text{H.7})$$

$$Z^{chain,hcb} = \frac{(1 - m)\eta}{(1 - \eta)} \left[1 + \frac{3\alpha(1 + \alpha)}{(1 + 3\alpha)(1 - \eta)^2 g^{hcb}(d)} + \frac{4\alpha^2\eta}{(1 + 3\alpha)(1 - \eta)^3 g^{hcb}(d)} \right] \quad (\text{H.8})$$

$$Z^{dis} = m \sum_i \sum_j j D_{ij} \left[\frac{u}{kT} \right]^i \left[\frac{\eta}{\tau} \right]^j \quad (\text{H.9})$$

$$Z^{chain,dis} = \lambda \left[\frac{A^{chain,hcb}}{A^{hcb}} Z^{dis} + \frac{A^{dis}}{A^{hcb}} Z^{chain,hcb} - \frac{A^{chain,hcb} A^{dis}}{(A^{hcb})^2} Z^{hcb} \right] \quad (\text{H.10})$$

$$Z^{ideal} = 1 \quad (\text{H.11})$$

$$\begin{aligned}
P &= \frac{RT}{V} [Z^{ideal} + Z^{hcb} + Z^{chain,hcb} + Z^{dis} + Z^{chain,dis}] \\
&= \frac{\eta RT}{b} [Z^{ideal} + Z^{hcb} + Z^{chain,hcb} + Z^{dis} + Z^{chain,dis}]
\end{aligned}
\tag{H.12}$$

Just like with the ESD, it is easier to evaluate $(\partial P/\partial V)_T$ instead of $(\partial V/\partial P)_T$. In addition, the chain rule is used, since η is also dependent on V . Each derivative is first evaluated with respect to η , then multiplied by the derivative of η with respect to V .

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial P}{\partial \eta}\right)_T \left(\frac{\partial \eta}{\partial V}\right)_T
\tag{H.13}$$

$$\begin{aligned}
\left(\frac{dP^{hcb}}{dV}\right)_T &= \frac{-RTm}{V^2} \left[\frac{(1+3\alpha)\eta + (3\alpha^2 - 3\alpha - 2)\eta^2 + (1-\alpha^2)\eta^3}{(1-\eta)^3} \right. \\
&\quad + \eta \left[\frac{3[(1+3\alpha)\eta + (3\alpha^2 - 3\alpha - 2)\eta^2 + (1-\alpha^2)\eta^3]}{(1-\eta)^4} \right. \\
&\quad \left. \left. + \frac{(1+3\alpha) + 2(3\alpha^2 - 3\alpha - 2)\eta + 3(1-\alpha^2)\eta^2}{(1-\eta)^3} \right] \right]
\end{aligned}
\tag{H.14}$$

$$\begin{aligned}
\left(\frac{dP^{chain,hcb}}{dV}\right)_T &= \frac{-RT(1-m)}{V^2} \left[\frac{2\eta - \eta^2}{(1-\eta)^2} \right] \left[1 + \frac{3\alpha(1+\alpha)}{(1+3\alpha)(1-\eta)^2 g^{hcb}(d)} + \frac{4\alpha^2\eta}{(1+3\alpha)(1-\eta)^3 g^{hcb}(d)} \right] \\
&\quad - \frac{RT\eta^2(1-m)}{V^2(1-\eta)} \frac{\alpha}{(1+3\alpha)(1-\eta)^2 g^{hcb}(d)} \left[\frac{6(1+3\alpha) + 4\alpha}{1-\eta} \right] \\
&\quad - \frac{3\alpha(1+3\alpha)}{g^{hcb}(d)} \left[\frac{g^{hcb}(d)}{1-\eta} + \frac{3\alpha(1+\alpha)}{(1+3\alpha)(1-\eta)^3} + \frac{4\alpha^2\eta}{(1+3\alpha)(1-\eta)^4} \right] + \frac{12\alpha\eta}{(1-\eta)^2} \\
&\quad - \frac{4\alpha\eta \left[\frac{g^{hcb}(d)}{1-\eta} + \frac{3\alpha(1+\alpha)}{(1+3\alpha)(1-\eta)^3} + \frac{4\alpha^2\eta}{(1+3\alpha)(1-\eta)^4} \right]}{(1-\eta)g^{hcb}(d)} \Bigg]
\end{aligned} \tag{H.15}$$

$$\left(\frac{dP^{dis}}{dV}\right)_T = \frac{-RTm}{V} \sum_i \sum_j (j + j^2) D_{ij} \left[\frac{u}{kT} \right]^i \left[\frac{\eta}{\tau} \right]^j \tag{H.16}$$

$$\begin{aligned}
\left(\frac{dP^{chain,dis}}{dV}\right)_T &= \frac{-\lambda b}{V^2} \left[\frac{P^{dis}}{\frac{A^{hcb}}{RT}} \frac{Z^{chain,hcb}}{\eta} + \frac{\frac{A^{chain,hcb}}{RT}}{\frac{A^{hcb}}{RT}} \left(\frac{\partial P^{dis}}{\partial \eta} \right)_T - \frac{\frac{A^{chain,hcb}}{RT} P^{dis}}{\left(\frac{A^{hcb}}{RT} \right)^2} \frac{Z^{hcb}}{\eta} + \frac{P^{chain,hcb}}{\frac{A^{hcb}}{RT}} \frac{Z^{dis}}{\eta} \right. \\
&\quad + \frac{\frac{A^{dis}}{RT}}{\frac{A^{hcb}}{RT}} \left(\frac{\partial P^{chain,hcb}}{\partial \eta} \right)_T - \frac{\frac{A^{dis}}{RT} P^{chain,hcb}}{\left(\frac{A^{hcb}}{RT} \right)^2} \frac{Z^{hcb}}{\eta} - \frac{\frac{A^{dis}}{RT} P^{hcb}}{\left(\frac{A^{hcb}}{RT} \right)^2} \frac{Z^{chain,hcb}}{\eta} - \frac{\frac{A^{chain,hcb}}{RT} P^{hcb}}{\left(\frac{A^{hcb}}{RT} \right)^2} \frac{Z^{dis}}{\eta} \\
&\quad \left. - \frac{\frac{A^{chain,hcb}}{RT} \frac{A^{dis}}{RT}}{\left(\frac{A^{hcb}}{RT} \right)^2} \left(\frac{\partial P^{hcb}}{\partial \eta} \right)_T + \frac{2 \frac{A^{chain,hcb}}{RT} \frac{A^{dis}}{RT} P^{hcb}}{\left(\frac{A^{hcb}}{RT} \right)^3} \frac{Z^{hcb}}{\eta} \right]
\end{aligned} \tag{H.17}$$

$$\left(\frac{dP^{ideal}}{dV}\right)_T = \frac{-RT}{V^2} \quad (\text{H.18})$$

$$\left(\frac{dP}{dV}\right)_T = \left(\frac{dP^{ideal}}{dV}\right)_T + \left(\frac{dP^{hcb}}{dV}\right)_T + \left(\frac{dP^{chain,hcb}}{dV}\right)_T + \left(\frac{dP^{dis}}{dV}\right)_T + \left(\frac{dP^{chain,dis}}{dV}\right)_T \quad (\text{H.19})$$

The next derivative is evaluated using the chain rule again, but this time with respect to T .

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial P}{\partial \eta}\right)_V \left(\frac{\partial \eta}{\partial T}\right)_V \quad (\text{H.20})$$

$$\left(\frac{\partial \eta}{\partial T}\right)_V = \frac{0.36 \left(\frac{\pi N_{AV} m d^3}{6V}\right) \left(\frac{-3u^0}{k}\right) \sigma^3}{T^2} \exp\left(\frac{-3u^0}{kT}\right) \left(1 - 0.12 \exp\left(\frac{-3u^0}{kT}\right)\right)^2 \quad (\text{H.21})$$

$$\begin{aligned} \left(\frac{dP^{hcb}}{d\eta}\right)_V = \frac{RTm}{b} & \left[\frac{(1 + 3\alpha)\eta + (3\alpha^2 - 3\alpha - 2)\eta^2 + (1 - \alpha^2)\eta^3}{(1 - \eta)^3} \right. \\ & + \eta \left[\frac{3[(1 + 3\alpha)\eta + (3\alpha^2 - 3\alpha - 2)\eta^2 + (1 - \alpha^2)\eta^3]}{(1 - \eta)^4} \right. \\ & \left. \left. + \frac{(1 + 3\alpha) + 2(3\alpha^2 - 3\alpha - 2)\eta + 3(1 - \alpha^2)\eta^2}{(1 - \eta)^3} \right] \right] \quad (\text{H.22}) \end{aligned}$$

$$\begin{aligned}
& \left(\frac{dP^{chain,hcb}}{d\eta} \right)_v \\
&= \frac{RT(1-m)}{b} \left[\frac{2\eta - \eta^2}{(1-\eta)^2} \right] \left[1 + \frac{3\alpha(1+\alpha)}{(1+3\alpha)(1-\eta)^2 g^{hcb}(d)} + \frac{4\alpha^2\eta}{(1+3\alpha)(1-\eta)^3 g^{hcb}(d)} \right] \\
&+ \frac{RT\eta^2(1-m)}{b(1-\eta)} \frac{\alpha}{(1+3\alpha)(1-\eta)^2 g^{hcb}(d)} \left[\frac{6(1+3\alpha) + 4\alpha}{1-\eta} \right. \\
&- \frac{3\alpha(1+3\alpha) \left[\frac{g^{hcb}(d)}{1-\eta} + \frac{3\alpha(1+\alpha)}{(1+3\alpha)(1-\eta)^3} + \frac{4\alpha^2\eta}{(1+3\alpha)(1-\eta)^4} \right]}{g^{hcb}(d)} + \frac{12\alpha\eta}{(1-\eta)^2} \\
&- \left. \frac{4\alpha\eta \left[\frac{g^{hcb}(d)}{1-\eta} + \frac{3\alpha(1+\alpha)}{(1+3\alpha)(1-\eta)^3} + \frac{4\alpha^2\eta}{(1+3\alpha)(1-\eta)^4} \right]}{(1-\eta)g^{hcb}(d)} \right]
\end{aligned} \tag{H.23}$$

$$\left(\frac{dP^{dis}}{d\eta} \right)_v = \frac{RTm}{b} \sum_i \sum_j (j + j^2) D_{ij} \left[\frac{u}{kT} \right]^i \left[\frac{\eta}{\tau} \right]^j \tag{H.24}$$

$$\begin{aligned}
& \left(\frac{dP^{chain,dis}}{d\eta} \right)_V \\
&= \lambda \left[\frac{P^{dis}}{\frac{A^{hcb}}{RT}} \left(\frac{\partial \left(\frac{A^{chain,hcb}}{RT} \right)}{\partial \eta} \right)_V + \frac{\frac{A^{chain,hcb}}{RT}}{\frac{A^{hcb}}{RT}} \left(\frac{\partial P^{dis}}{\partial \eta} \right)_V - \frac{\frac{A^{chain,hcb}}{RT} P^{dis}}{\left(\frac{A^{hcb}}{RT} \right)^2} \left(\frac{\partial \left(\frac{A^{hcb}}{RT} \right)}{\partial \eta} \right)_V \right. \\
&+ \frac{P^{chain,hcb}}{\frac{A^{hcb}}{RT}} \left(\frac{\partial \left(\frac{A^{dis}}{RT} \right)}{\partial \eta} \right)_V + \frac{\frac{A^{dis}}{RT}}{\frac{A^{hcb}}{RT}} \left(\frac{\partial P^{chain,hcb}}{\partial \eta} \right)_V - \frac{\frac{A^{dis}}{RT} P^{chain,hcb}}{\left(\frac{A^{hcb}}{RT} \right)^2} \left(\frac{\partial \left(\frac{A^{hcb}}{RT} \right)}{\partial \eta} \right)_V \\
&- \frac{\frac{A^{dis}}{RT} P^{hcb}}{\left(\frac{A^{hcb}}{RT} \right)^2} \left(\frac{\partial \left(\frac{A^{chain,hcb}}{RT} \right)}{\partial \eta} \right)_V - \frac{\frac{A^{chain,hcb}}{RT} P^{hcb}}{\left(\frac{A^{hcb}}{RT} \right)^2} \left(\frac{\partial \left(\frac{A^{dis}}{RT} \right)}{\partial \eta} \right)_V - \frac{\frac{A^{chain,hcb}}{RT} \frac{A^{dis}}{RT}}{\left(\frac{A^{hcb}}{RT} \right)^2} \left(\frac{\partial P^{hcb}}{\partial \eta} \right)_V \\
&\left. + \frac{2 \frac{A^{chain,hcb}}{RT} \frac{A^{dis}}{RT} P^{hcb}}{\left(\frac{A^{hcb}}{RT} \right)^3} \left(\frac{\partial \left(\frac{A^{hcb}}{RT} \right)}{\partial \eta} \right)_V \right] \quad (H.25)
\end{aligned}$$

$$\left(\frac{dP^{ideal}}{dT} \right)_V = \frac{R}{V} \quad (H.26)$$

$$\left(\frac{dP}{dT} \right)_V = \left(\frac{dP^{ideal}}{dT} \right)_V + \left[\left(\frac{dP^{hcb}}{d\eta} \right)_V + \left(\frac{dP^{chain,hcb}}{d\eta} \right)_V + \left(\frac{dP^{dis}}{d\eta} \right)_V + \left(\frac{dP^{chain,dis}}{d\eta} \right)_V \right] \left(\frac{\partial \eta}{\partial T} \right)_V \quad (H.27)$$

The final series of derivatives are used to correct the ideal gas phase heat capacity. The chain rule is used multiple times throughout these derivatives.

$$\left(\frac{\partial^2 A}{\partial T^2} \right)_V = 2R \left(\frac{\partial \left(\frac{A}{RT} \right)}{\partial T} \right)_V + RT \left(\frac{\partial^2 \left(\frac{A}{RT} \right)}{\partial T^2} \right)_V \quad (H.28)$$

$$\left(\frac{\partial\left(\frac{A}{RT}\right)}{\partial T}\right)_v = \left(\frac{\partial\left(\frac{A}{RT}\right)}{\partial \eta}\right)_v \left(\frac{\partial \eta}{\partial T}\right)_v \quad (\text{H.29})$$

$$\left(\frac{\partial^2\left(\frac{A}{RT}\right)}{\partial T^2}\right)_v = \frac{\partial}{\partial T} \left[\left(\frac{\partial\left(\frac{A}{RT}\right)}{\partial \eta}\right)_v \left(\frac{\partial \eta}{\partial T}\right)_v \right] = \left(\frac{\partial\left(\frac{A}{RT}\right)}{\partial \eta}\right)_v \left(\frac{\partial^2 \eta}{\partial T^2}\right)_v + \left(\frac{\partial^2\left(\frac{A}{RT}\right)}{\partial \eta^2}\right)_v \left(\frac{\partial \eta}{\partial T}\right)_v^2 \quad (\text{H.30})$$

$$\begin{aligned} \left(\frac{\partial^2 \eta}{\partial T^2}\right)_v &= \frac{-0.72 \left(\frac{\pi N_{AV} m d^3}{6V}\right) \left(\frac{-3u^0}{k}\right) \sigma^3}{T^3} \exp\left(\frac{-3u^0}{kT}\right) \left(1 - 0.12 \exp\left(\frac{-3u^0}{kT}\right)\right)^2 \\ &\quad - \frac{0.36 \left(\frac{\pi N_{AV} m d^3}{6V}\right) \left(\frac{-3u^0}{k}\right)^2 \sigma^3}{T^4} \exp\left(\frac{-3u^0}{kT}\right) \left(1 - 0.12 \exp\left(\frac{-3u^0}{kT}\right)\right)^2 \\ &\quad + \frac{0.0864 \left(\frac{\pi N_{AV} m d^3}{6V}\right) \left(\frac{-3u^0}{k}\right)^2 \sigma^3}{T^4} \exp\left(\frac{-6u^0}{kT}\right) \left(1 - 0.12 \exp\left(\frac{-3u^0}{kT}\right)\right) \end{aligned} \quad (\text{H.31})$$

$$\left(\frac{\partial\left(\frac{A^{hcb}}{RT}\right)}{\partial \eta}\right)_v = m \left[\frac{1 + 3\alpha + (3\alpha^2 - 3\alpha - 2)\eta + (1 - \alpha^2)\eta^2}{(1 - \eta)^3} \right] \quad (\text{H.32})$$

$$\left(\frac{\partial\left(\frac{A^{chain,hcb}}{RT}\right)}{\partial \eta}\right)_v = \frac{(1 - m)}{(1 - \eta)} \left[1 + \frac{3\alpha(1 + \alpha)}{(1 + 3\alpha)(1 - \eta)^2 g^{hcb}(d)} + \frac{4\alpha^2 \eta}{(1 + 3\alpha)(1 - \eta)^3 g^{hcb}(d)} \right] \quad (\text{H.33})$$

$$\left(\frac{\partial\left(\frac{A^{dis}}{RT}\right)}{\partial \eta}\right)_v = m \sum_i \sum_j j D_{ij} \eta^{j-1} \left[\frac{u}{kT}\right]^i \left[\frac{1}{\tau}\right]^j \quad (\text{H.34})$$

$$\left(\frac{\partial\left(\frac{A^{chain,dis}}{RT}\right)}{\partial\eta}\right)_v = \lambda \left[\frac{\frac{A^{chain,hcb}}{RT}}{\frac{A^{hcb}}{RT}} \left(\frac{\partial\left(\frac{A^{dis}}{RT}\right)}{\partial\eta}\right)_v + \frac{\frac{A^{dis}}{RT}}{\frac{A^{hcb}}{RT}} \left(\frac{\partial\left(\frac{A^{chain,hcb}}{RT}\right)}{\partial\eta}\right)_v - \frac{\frac{A^{chain,hcb}}{RT} \frac{A^{dis}}{RT}}{\left(\frac{A^{hcb}}{RT}\right)^2} \left(\frac{\partial\left(\frac{A^{hcb}}{RT}\right)}{\partial\eta}\right)_v \right] \quad (\text{H.35})$$

$$\left(\frac{\partial^2\left(\frac{A^{hcb}}{RT}\right)}{\partial\eta^2}\right)_v = m \left[\frac{1 + 6\alpha + 3\alpha^2 + (4\alpha^2 - 6\alpha - 2)\eta + (1 - \alpha^2)\eta^2}{(1 - \eta)^4} \right] \quad (\text{H.36})$$

$$\frac{\partial(g^{hcb}(d))}{\partial\eta} = \frac{1}{1 - \eta} \left[g^{hcb}(d) + \frac{3\alpha(1 + \alpha)}{(1 + 3\alpha)(1 - \eta)^2} + \frac{4\alpha^2\eta}{(1 + 3\alpha)(1 - \eta)^3} \right] \quad (\text{H.37})$$

$$\begin{aligned} \left(\frac{\partial^2\left(\frac{A^{chain,hcb}}{RT}\right)}{\partial\eta^2}\right)_v \\ = \frac{1}{1 - \eta} \left(\frac{\partial\left(\frac{A^{chain,hcb}}{RT}\right)}{\partial\eta}\right)_v + \frac{(1 - m)\alpha}{(1 + 3\alpha)(1 - \eta)^3 g^{hcb}(d)} \end{aligned} \quad (\text{H.38})$$

$$\begin{aligned} \cdot \left[\frac{6 + 10\alpha}{1 - \eta} + \frac{12\alpha\eta}{(1 - \eta)^2} - \frac{3(1 + \alpha)}{g^{hcb}(d)} \frac{\partial(g^{hcb}(d))}{\partial\eta} - \frac{4\alpha\eta}{(1 - \eta)g^{hcb}(d)} \frac{\partial(g^{hcb}(d))}{\partial\eta} \right] \\ \left(\frac{\partial^2\left(\frac{A^{dis}}{RT}\right)}{\partial\eta^2}\right)_v = m \sum_i \sum_j \frac{j(j - 1)D_{i,j}}{\eta^2} \left(\frac{u}{kT}\right)^i \left(\frac{\eta}{\tau}\right)^j \end{aligned} \quad (\text{H.39})$$

$$\begin{aligned}
\left(\frac{\partial^2 \left(\frac{A^{dis}}{RT} \right)}{\partial T^2} \right)_v &= 2R \left(\frac{\partial \left(\frac{A^{dis}}{RT} \right)}{\partial \eta} \right)_v \left(\frac{\partial \eta}{\partial T} \right)_v - \frac{Rm}{T} \sum_i \sum_j i D_{i,j} \left(\frac{u}{kT} \right)^i \left(\frac{\eta}{T} \right)^j \frac{1 + 2 \frac{\epsilon}{kT}}{1 + \frac{\epsilon}{kT}} \\
&\quad - 2Rm \left(\frac{\partial \eta}{\partial T} \right)_v \sum_i \sum_j \frac{ij D_{i,j}}{\eta} \left(\frac{u}{kT} \right)^i \left(\frac{\eta}{T} \right)^j \frac{1 + 2 \frac{\epsilon}{kT}}{1 + \frac{\epsilon}{kT}} + \frac{Rm}{T} \sum_i \sum_j D_{i,j} i^2 \left(\frac{u}{kT} \right)^i \left(\frac{\eta}{T} \right)^j \frac{\left(1 + 2 \frac{\epsilon}{kT} \right)^2}{\left(1 + \frac{\epsilon}{kT} \right)^2} \quad (H.40) \\
&\quad + \frac{Rm}{T^2} \sum_i \sum_j \frac{i D_{i,j}}{\left(1 + \frac{\epsilon}{kT} \right)^2} \left(\frac{u}{kT} \right)^i \left(\frac{\eta}{T} \right)^j + RT \left[\left(\frac{\partial^2 \left(\frac{A^{dis}}{RT} \right)}{\partial \eta^2} \right)_v \left(\frac{\partial \eta}{\partial T} \right)_v + \left(\frac{\partial \left(\frac{A^{dis}}{RT} \right)}{\partial \eta} \right)_v \left(\frac{\partial^2 \eta}{\partial T^2} \right)_v \right]
\end{aligned}$$

$$\begin{aligned}
&\left(\frac{\partial^2 \left(\frac{A^{chain,dis}}{RT} \right)}{\partial T^2} \right)_v \\
&= \lambda \left[\frac{2}{A^{hcb}} \left(\frac{\partial \left(\frac{A^{dis}}{RT} \right)}{\partial T} \right)_v \left(\frac{\partial \left(\frac{A^{chain,hcb}}{RT} \right)}{\partial T} \right)_v - \frac{2A^{dis}}{(A^{hcb})^2} \left(\frac{\partial \left(\frac{A^{chain,hcb}}{RT} \right)}{\partial T} \right)_v \left(\frac{\partial \left(\frac{A^{hcb}}{RT} \right)}{\partial T} \right)_v \right. \\
&\quad - \frac{2A^{chain,hcb}}{(A^{hcb})^2} \left(\frac{\partial \left(\frac{A^{dis}}{RT} \right)}{\partial T} \right)_v \left(\frac{\partial \left(\frac{A^{hcb}}{RT} \right)}{\partial T} \right)_v + \frac{A^{dis}}{A^{hcb}} \left(\frac{\partial^2 \left(\frac{A^{chain,hcb}}{RT} \right)}{\partial \eta^2} \right)_v \\
&\quad + \frac{A^{chain,hcb}}{A^{hcb}} \left(\frac{\partial^2 \left(\frac{A^{dis}}{RT} \right)}{\partial \eta^2} \right)_v - \frac{A^{chain,hcb} A^{dis}}{(A^{hcb})^2} \left(\frac{\partial^2 \left(\frac{A^{hcb}}{RT} \right)}{\partial \eta^2} \right)_v \\
&\quad \left. + \frac{2A^{chain,hcb} A^{dis}}{(A^{hcb})^3} \left(\frac{\partial^2 \left(\frac{A^{hcb}}{RT} \right)}{\partial \eta^2} \right)_v^2 \right] \quad (H.41)
\end{aligned}$$

REFERENCES

REFERENCES

- [1] Chiu C.-W., Schumacher L.G., Suppes G.J., Impact of cold flow improvers on soybean biodiesel blend, *Biomass and Bioenergy*, 27 (2004) 485-91.
- [2] Bhale P.V., Deshpande N.V., Thombre S.B., Improving low temperature properties of biodiesel fuel, *Renewable Energy*, 34 (2009) 794-800.
- [3] Knothe G., Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters, *Fuel Processing Technology*, 86 (2005) 1059-70.
- [4] Military Specification; Turbine Fuel, Aviation, Grades JP-4, JP-5, and JP-5/JP-8 ST. Department of Defense; Report no.:MIL-T-5624R.
- [5] Dunn R.O., Improving the Cold Flow Properties of Biodiesel by Fractionation, In: *Soybean - Applications and Technology*, (T.-B. Ng, editor). InTech, Rijeka, Croatia, 2011, Ch. 12.
- [6] Bist S., Tao B.Y., Mohtar S.A., inventor; Purdue Research Foundation, assignee. Method for Preparation, Use and Separation of Fatty Acid Esters. United States US 60/547,992. 2007
- [7] Pinzi S., Garcia I.L., Lopez-Gimenez F.J., Luque de Castro M.D., Dorado G., Dorado M.P., The Ideal Vegetable Oil-based Biodiesel Composition: A Review of Social, Economical and Technical Implications, *Energy & Fuels*, 23 (2009) 2325-41.
- [8] Korres D.M., Karonis D., Lois E., Linck M.B., Gupta A.K., Aviation fuel JP-5 and biodiesel on a diesel engine, *Fuel*, 87 (2008) 70-8.
- [9] Park J.-Y., Kim D.-K., Lee J.-P., Park S.-C., Kim Y.-J., Lee J.-S., Blending effects of biodiesels on oxidation stability and low temperature flow properties, *Bioresource Technology*, 99 (2008) 1196-203.
- [10] Naik S.N., Goud V.V., Rout P.K., Dalai A.K., Production of first and second generation biofuels: A comprehensive review, *Renewable and Sustainable Energy Reviews*, 14 (2010) 578-97.
- [11] Ko C., Park S., Jeon J.-K., Suh D., Jeong K.-E., Park Y.-K., Upgrading of biofuel by the catalytic deoxygenation of biomass, *Korean Journal of Chemical Engineering*, 29 (2012) 1657-65.
- [12] Komvokis V.G., Karakoulia S., Iliopoulou E.F., Papapetrou M.C., Vasalos I.A., Lappas A.A., et al., Upgrading of Fischer-Tropsch synthesis bio-waxes via catalytic cracking: Effect of acidity, porosity and metal modification of zeolitic and mesoporous aluminosilicate catalysts, *Catalysis Today*, 196 (2012) 42-55.
- [13] Poling B.E., Prausnitz J.M., O'Connell J.P., *Properties of Gases and Liquids*, Fifth ed., McGraw-Hill, New York, NY, 2000.

- [14] Huber M.L., Lemmon E.W., Bruno T.J., Surrogate Mixture Models for the Thermophysical Properties of Aviation Fuel Jet-A, *Energy and Fuels*, 24 (2010) 3565–71.
- [15] Windom B., Huber M.L., Bruno T.J., Lown A., Lira C.T., Measurements and Modeling Study on a High-Aromatic Diesel Fuel, *Energy and Fuels*, 26 (2012) 1787-97.
- [16] Chen W., Zhao Z., Zhang X., Wang L., Thermodynamic phase equilibria of wax precipitation in crude oils, *Fluid Phase Equilibria*, 255 (2007) 31-6.
- [17] Coutinho J.A.P., Dauphin C., Daridon J.L., Measurements and modelling of wax formation in diesel fuels, *Fuel*, 79 (2000) 607-16.
- [18] Mirante F.I.C., Coutinho J.A.P., Cloud point prediction of fuels and fuel blends, *Fluid Phase Equilibria*, 180 (2001) 247-55.
- [19] Esmaeilzadeh F., Kaljahi J.F., Ghanaei E., Investigation of different activity coefficient models in thermodynamic modeling of wax precipitation, *Fluid Phase Equilibria*, 248 (2006) 7-18.
- [20] Hansen J.H., Fredenslund A., Pedersen K.S., Ronningsen H.P., A Thermodynamic Model for Predicting Wax Formation in Crude Oils, *AIChE Journal*, 34 (1988) 1937-42.
- [21] Escobar-Remolina J.C.M., Prediction of Characteristics of Wax Precipitation in Synthetic Mixtures and Fluids of Petroleum: A New Model, *Fluid Phase Equilibria*, 240 (2006) 197-203.
- [22] Coto B., Coutinho J.A.P., Martos C., Robustillo M.D., Espada J.J., Pena J.L., Assessment and Improvement of n-Paraffin Distribution Obtained by HTGC To Predict Accurately Crude Oil Cold Properties, *Energy & Fuels*, 25 (2011) 1153-60.
- [23] Ra Y., Reitz R.D., A vaporization model for discrete multi-component fuel sprays, *International Journal of Multiphase Flow*, 35 (2009) 101-17.
- [24] Ramirez L. H.P., Hadj-Ali K., Dievart P., Moreac G., Dagaut P., Kinetics of Oxidation of Commercial and Surrogate Diesel Fuels in a Jet-Stirred Reactor: Experimental and Modeling Studies, *Energy and Fuels*, 24 (2010) 1668-76.
- [25] Cookson D.J., Iliopoulos P., Smith B.E., Composition Property Relations for Jet and Diesel Fuels of Variable Boiling Range, *Fuel*, 74 (1995) 70-8.
- [26] Ghosh P., Jaffe S.B., Detailed Composition-Based Model for Predicting the Cetane Number of Diesel Fuels, *Industrial & Engineering Chemistry Research*, 45 (2006) 346-51.
- [27] Fodor G.E., Kohl K.B., Analysis of Middle Distillate Fuels by Midband Infrared Spectroscopy, *Energy & Fuels*, 7 (1993) 598-601.
- [28] Fodor G.E., Kohl K.B., Mason R.L., Analysis of Gasolines by FT-IR Spectroscopy, *Analytical Chemistry*, 68 (1996) 23-30.

- [29] Fodor G.E., Mason R.A., Hutzler S.A., Estimation of Middle Distillate Fuel Properties by FT-IR, *Applied Spectroscopy*, 53 (1999) 1292-8.
- [30] Fodor G.E., Analysis of Petroleum Fuels by Midband Infrared Spectroscopy, SAE Technical Paper 941019, (1994).
- [31] DeFries T.H., Kastrup R.V., Indritz D., Prediction of cetane number by group additivity and carbon-13 Nuclear Magnetic Resonance, *Industrial & Engineering Chemistry Research*, 26 (1987) 188-93.
- [32] Androulakis I.P., Weisel M.D., Hsu C.S., Qian K., Green L.A., Farrell J.T., et al., An Integrated Approach for Creating Model Diesel Fuels, *Energy & Fuels*, 19 (2005) 111-9.
- [33] Lestz S.J., LePera M.E., Technology Demonstration of U.S. Army Ground Materiel Operating on Aviation Kerosene Fuel, SAE Technical Paper 920193, (1992).
- [34] Pickett L.M., Hoogterp L., Fundamental Spray and Combustion Measurements of JP-8 at Diesel Conditions, *SAE Int. J. Commer. Veh.*, 1 (2008) 108-18.
- [35] Murphy L., Rothamer D., Effects of Cetane Number on Jet Fuel Combustion in a Heavy-Duty Compression Ignition Engine at High Load, SAE Technical Paper 2011-01-0335, (2011).
- [36] Outcalt S.L., Laesecke A., Fortin T.J., Density and speed of sound measurements of 1- and 2-butanol, *Journal of Molecular Liquids*, 151 (2010) 50-9.
- [37] Outcalt S., Laesecke A., Freund M.B., Density and Speed of Sound Measurements of Jet A and S-8 Aviation Turbine Fuels, *Energy & Fuels*, 23 (2009) 1626-33.
- [38] Payri R., Salvador F.J., Gimeno J., Bracho G., The effect of temperature and pressure on thermodynamic properties of diesel and biodiesel fuels, *Fuel*, 90 (2011) 1172-80.
- [39] Jain D.V.S., North A.M., Pethrick R.A., Adiabatic compressibility of binary liquid mixtures, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 70 (1974) 1292-8.
- [40] Fort R.J., Moore W.R., Adiabatic compressibilities of binary liquid mixtures, *Transactions of the Faraday Society*, 61 (1965) 2102-11.
- [41] Glinski J., Additivity of Sound Velocity in Binary Liquid Mixtures, *Journal of Solution Chemistry*, 31 (2002) 59-70.
- [42] de Villiers A.J., Schwarz C.E., Burger A.J., Kontogeorgis G.M., Evaluation of the PC-SAFT, SAFT and CPA equations of state in predicting derivative properties of selected non-polar and hydrogen-bonding compounds, *Fluid Phase Equilibria*, 338 (2013) 1-15.

- [43] Liang X., Maribo-Mogensen B., Thomsen K., Yan W., Kontogeorgis G.M., Approach to Improve Speed of Sound Calculation within PC-SAFT Framework, *Industrial & Engineering Chemistry Research*, 51 (2012) 14903-14.
- [44] Llovell F., Vega L.F., Prediction of Thermodynamic Derivative Properties of Pure Fluids through the Soft-SAFT Equation of State, *The Journal of Physical Chemistry B*, 110 (2006) 11427-37.
- [45] Maghari A., Sadeghi M.S., Prediction of sound velocity and heat capacities of n-alkanes from the modified SAFT-BACK equation of state, *Fluid Phase Equilibria*, 252 (2007) 152-61.
- [46] Salimi M., Bahramian A., The Prediction of the Speed of Sound in Hydrocarbon Liquids and Gases: The Peng-Robinson Equation of State Versus SAFT-BACK, *Petroleum Science and Technology*, 32 (2014) 409-17.
- [47] McDougal J.N., Rogers J.V., Local and systemic toxicity of JP-8 from cutaneous exposures, *Toxicology Letters*, 149 (2004) 301-8.
- [48] Edwards T., Liquid Fuels and Propellants for Aerospace Propulsion: 1903-2003, *Journal of Propulsion and Power*, 19 (2003) 1089-107.
- [49] Lane J., Biofuels Mandates Around the World [Internet]. *Biofuels Digest*; [updated 2011 July 21; cited 2012 June 15]. Available from: <http://www.biofuelsdigest.com/bdigest/2011/07/21/biofuels-mandates-around-the-world/>
- [50] Werpy T.A., Holladay J.E., White J.F. Top Value Added Chemicals From Biomass: I. Results of Screening for Potential Candidates from Sugars and Synthesis Gas. Golden (CO): National Renewable Energy Laboratory; 2004 Nov. Report No.: PNNL-14808. Contract No.: AC05-76RL01830. Sponsored by Department of Energy.
- [51] Ott L.S., Smith B.L., Bruno T.J., Composition-Explicit Distillation Curves of Mixtures of Diesel Fuel with Biomass-Derived Glycol Ester Oxygenates: A Fuel Design Tool for Decreased Particulate Emissions *Energy & Fuels*, 22 (2008) 2518-26.
- [52] Smith B.L., Ott L.S., Bruno T.J., Composition-Explicit Distillation Curves of Diesel Fuel with Glycol Ether and Glycol Ester Oxygenates: Fuel Analysis Metrology to Enable Decreased Particulate Emissions, *Environmental Science & Technology*, 42 (2008) 7682-9.
- [53] Linstrom P.J., Mallard W.G., editors. NIST Chemistry Webbook. National Institute of Standards and Technology, Gaithersburg, MD, [updated 2013 July 15; cited 2012 October 8]. Available from: <http://webbook.nist.gov/chemistry/>
- [54] Rowley R.L., Wilding W.V., Oscarson J.L., Giles N.F., DIPPR Data Compilation of Pure Chemical Properties. Design Institute for Physical Properties, AIChE, New York, NY, 2011,

- [55] Kolah A.K., Asthana N.S., Vu D.T., Lira C.T., Miller D.J., Reaction Kinetics for the Heterogeneously Catalyzed Esterification of Succinic Acid with Ethanol, *Industrial & Engineering Chemistry Research*, 47 (2008) 5313-7.
- [56] Zhang C., Yang H., Yang F., Ma Y., Current Progress on Butyric Acid Production by Fermentation, *Current Microbiology*, 59 (2009) 656-63.
- [57] Gaertner C.A., Serrano-Ruiz J.C., Braden D.J., Dumesic J.A., Catalytic coupling of carboxylic acids by ketonization as a processing step in biomass conversion, *Journal of Catalysis*, 266 (2009) 71-8.
- [58] Murkute A.D., Jackson J.E., Miller D.J., Supported mesoporous solid base catalysts for condensation of carboxylic acids, *Journal of Catalysis*, 278 (2011) 189-99.
- [59] Pappu V.K.S., Kanyi V., Santhanakrishnan A., Lira C.T., Miller D.J., Butyric acid esterification kinetics over Amberlyst solid acid catalysts: The effect of alcohol carbon chain length, *Bioresource Technology*, 130 (2013) 793-7.
- [60] Kurtz E.M., Kuhel D., Anderson J.E., Mueller S.A., A Comparison of Combustion and Emissions of Diesel Fuels and Oxygenated Fuels in a Modern DI Diesel Engine, *SAE Int. J. Fuels Lubr.*, 5 (2012) 1199-215.
- [61] Murphy M.J., Taylor J.D., McCormick R.L. Compendium of Experimental Cetane Number Data. 2004. Report No.: NREL/SR-540-36805; Other: KAF-9-29764-23. Contract No.: OSTI ID: 1086353. Sponsored by NREL.
- [62] Kim S.M., Lee M.E., Choi J.-W., Suh D.J., Suh Y.-W., Conversion of biomass-derived butanal into gasoline-range branched hydrocarbon over Pd-supported catalysts, *Catalysis Communications*, 16 (2011) 108-13.
- [63] Reynolds J.C., Last D.J., McGillen M., Nijs A., Horn A.B., Percival C., et al., Structural Analysis of Oligomeric Molecules Formed from the Reaction Products of Oleic Acid Ozonolysis, *Environmental Science & Technology*, 40 (2006) 6674-81.
- [64] Fortin T.J., Assessment of Variability in the Thermophysical Properties of Rocket Propellant RP-1, *Energy & Fuels*, 26 (2012) 4383-94.
- [65] Manzini G., Crescenzi V., Thermodynamics of Nonpolar Mixtures Exhibiting Liquid-Liquid Phase Equilibria. Aliphatic and Aromatic Esters with Alkanes, *The Journal of Physical Chemistry*, 81 (1977) 431-4.
- [66] Reaxys. Version 1.7.8, Elsevier, 2012, RRN: 1786221, (accessed: 12/2012)
- [67] Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., et al., *Gaussian 03*, Revision C.02, (2004).
- [68] Ochterski J., Thermochemistry in Gaussian [Internet]. Gaussian, Inc.; [updated 9/18/2012; cited 3/11/2013]. Available from: http://www.gaussian.com/g_whitepap/thermo.htm

- [69] Elliott J.R., Lira C.T., Introductory Chemical Engineering Thermodynamics, Second ed., Prentice Hall, Upper Saddle River, NJ, 2012.
- [70] Bruno T.J., Ott L.S., Smith B.L., Lovestead T.M., Complex Fluid Analysis with the Advanced Distillation Curve Approach, *Analytical Chemistry*, 82 (2009) 777-83.
- [71] Dirand M., Bouroukba M., Chavallier V., Petitjean D., Behar E., Ruffier-Meray V., Normal Alkanes, Multialkane Synthetic Model Mixtures, and Real Petroleum Waxes: Crystallographic Structures, Thermodynamic Properties, and Crystallization, *Journal of Chemical Engineering Data*, 47 (2002) 115-43.
- [72] Segudovic N., Tomic T., Skrobonja L., Kontic L., Local round robin test for determination of aromatics in diesel fuels by HPLC, *Journal of Separation Sciences*, 27 (2004) 65-70.
- [73] Striebich R.C., Shafer L.M., West Z.J., Adams R.K., Zabarnick S., Hydrocarbon Group-Type Analysis of Current and Future Aviation Fuels: Comparing ASTM D2425 to GCxGC. In: IASH 2011, the 12TH International Conference on Stability, Handling, and Use of Liquid Fuels, International Association for Stability, Handling, and Use of Liquid Fuels, Sarasota, Florida, USA, 2011.
- [74] Striebich R.C., Shafer L.M., Adams R.K., West Z.J., DeWitt M.J., Zabarnick S., Hydrocarbon Group-Type Analysis of Petroleum-Derived and Synthetic Fuels Using Two-Dimensional Gas Chromatography, *Energy & Fuels*, 28 (2014) 5696-706.
- [75] Young S., Correction of boiling points of liquids from observed to normal pressures, *Proceedings of the Chemical Society, London*, 81 (1902) 777.
- [76] Ott L.S., Smith B.L., Bruno T.J., Experimental test of the Sydney Young equation for the presentation of distillation curves, *The Journal of Chemical Thermodynamics*, 40 (2008) 1352-7.
- [77] Won K.W., Thermodynamic calculation of cloud point temperatures and wax phase compositions of refined hydrocarbon mixtures, *Fluid Phase Equilibria*, 53 (1989) 377-96.
- [78] Lira-Galeana C., Firoozabadi A., Prausnitz J.M., Thermodynamics of wax precipitation in petroleum mixtures, *AIChE Journal*, 42 (1996) 239-48.
- [79] Coutinho J.A.P., Andersen S.I., Stenby E.H., Evaluation of activity coefficient models in prediction of alkane solid-liquid equilibria, *Fluid Phase Equilibria*, 103 (1995) 23-39.
- [80] Bruno T.J., Ott L.S., Lovestead T.M., Huber M.L., Relating Complex Fluid Composition and Thermophysical Properties with the Advanced Distillation Curve Approach, *Chemical Engineering & Technology*, 33 (2010) 363-76.
- [81] Owens E.C., LePera M.E., Lestz S.J., Use of Aviation Turbine Fuel JP-8 as the Single Fuel on the Battlefield, *SAE Technical Paper 892071*, (1989).

- [82] Ladommatos N., Goacher J., Equations for predicting the cetane number of diesel fuels from their physical properties, *Fuel*, 74 (1995) 1083-93.
- [83] Gulder O.L., Burton G.F., Whyte R.B., NRCC Cetane Index - 1: An Improved Cetane Number Predictor, SAE Technical Paper 861519, (1986).
- [84] Gulder O.L., Glavincevski B., Burton G.F., Ignition Quality Rating Methods for Diesel Fuels - A Critical Appraisal, SAE Technical Paper 852080, (1985).
- [85] Steere D.E., Development of the Canadian General Standards Board (CGBS) Cetane Index, SAE Technical Paper 841344, (1984).
- [86] Ingham M.C., Bert J.A., Painter L.J., Improved Predictive Equations for Cetane Number, SAE Technical Paper 860250, (1986).
- [87] Burley H.A., Rosebrock T.L., Automotive Diesel Engines-Fuel Composition vs Particulates, SAE Technical Paper 790923, (1979).
- [88] O'Connor C.T., Forrester R.D., Scurrall M.S., Cetane number determination of synthetic diesel fuels, *Fuel*, 71 (1992) 1323-7.
- [89] Saldana D.A., Starck L., Mougin P., Rousseau B., Pidol L., Jeuland N., et al., Flash Point and Cetane Number Predictions for Fuel Compounds Using Quantitative Structure Property Relationship (QSPR) Methods, *Energy & Fuels*, 25 (2011) 3900-8.
- [90] Kapur G.S., Ecker A., Meusinger R., Establishing Quantitative Structure-Property Relationships (QSPR) of Diesel Samples by Proton-NMR & Multiple Linear Regression (MLR) Analysis, *Energy & Fuels*, 15 (2001) 943-8.
- [91] Smolenskii E.A., Bavykin V.M., Ryzhov A.N., Slovokhotova O.L., Chuvaeva I.V., Lapidus A.L., Cetane numbers of hydrocarbons: calculations using optimal topological indices, *Russian Chemical Bulletin*, 57 (2008) 461-7.
- [92] Creton B., Dartiguelongue C., de Bruin T., Toulhoat H., Prediction of the Cetane Number of Diesel Compounds Using the Quantitative Structure Property Relationship, *Energy & Fuels*, 24 (2010) 5396-403.
- [93] Simpson M.B., Near-Infrared Spectroscopy for Process Analytical Technology: Theory, Technology and Implementation, In: *Process Analytical Technology: Spectroscopic Tools and Implementation Strategies for the Chemical and Pharmaceutical Industries*, (K.A. Bakeev, editor). John Wiley & Sons, Ltd, Chichester, UK, 2010, 5, 107-55.
- [94] Cooper J.B., Larkin C.M., Schmitigal J., Morris R.E., Abdelkader M.F., Rapid Analysis of Jet Fuel Using a Handheld Near-Infrared (NIR) Analyzer, *Applied Spectroscopy*, 65 (2011) 187-92.

- [95] Santos Jr V.O., Oliveira F.C.C., Lima D.G., Petry A.C., Garcia E., Suarez P.A.Z., et al., A comparative study of diesel analysis by FTIR, FTNIR and FT-Raman spectroscopy using PLS and artificial neural network analysis, *Analytica Chimica Acta*, 547 (2005) 188-96.
- [96] Balabin R.M., Safieva R.Z., Lomakina E.I., Gasoline classification using near infrared (NIR) spectroscopy data: Comparison of multivariate techniques, *Analytica Chimica Acta*, 671 (2010) 27-35.
- [97] Fernanda Pimentel M., Ribeiro G.M.G.S., da Cruz R.S., Stragevitch L., Pacheco Filho J.G.A., Teixeira L.S.G., Determination of biodiesel content when blended with mineral diesel fuel using infrared spectroscopy and multivariate calibration, *Microchemical Journal*, 82 (2006) 201-6.
- [98] Socrates G., *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, Third ed., John Wiley and Sons, Ltd., Chichester, West Sussex, England, 2004.
- [99] R Core Team. (2013) R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. Available from: <http://www.R-project.org/>.
- [100] Boehman A.L., Morris D., Szybist J., Esen E., The Impact of the Bulk Modulus of Diesel Fuels on Fuel Injection Timing, *Energy & Fuels*, 18 (2004) 1877-82.
- [101] Lapuerta M., Agudelo J.R., Prorok M., Boehman A.L., Bulk Modulus of Compressibility of Diesel/Biodiesel/HVO Blends, *Energy & Fuels*, 26 (2012) 1336-43.
- [102] Kostas J., Honnery D., Soria J., Kastengren A., Liu Z., Powell C.F., et al., Effect of nozzle transients and compressibility on the penetration of fuel sprays, *Applied Physics Letters*, 95 (2009) 024101.
- [103] Tyrer D., CCXXXVI.-Adiabatic and isothermal compressibilities of liquids between one and two atmospheres' pressure, *Journal of the Chemical Society, Transactions*, 105 (1914) 2534-53.
- [104] Liebenberg D.H., Mills R.L., Bronson J.C., High-pressure apparatus for simultaneous adiabatic and isothermal compressibility measurements: Data on argon to 13 kbar, *Journal of Applied Physics*, 45 (1974) 741-7.
- [105] Kleppa O.J., Ultrasonic Velocities of Sound in Some Metallic Liquids. Adiabatic and Isothermal Compressibilities of Liquid Metals at Their Melting Points, *The Journal of Chemical Physics*, 18 (1950) 1331-6.
- [106] Dzida M., Jezak S., Sumara J., Zarska M., Goralski P., High pressure physicochemical properties of biodiesel components used for spray characteristics in diesel injection systems, *Fuel*, 111 (2013) 165-71.
- [107] Wang Z., Nur A., Ultrasonic velocities in pure hydrocarbons and mixtures, *The Journal of the Acoustical Society of America*, 89 (1991) 2725-30.

- [108] Berryman J.G., Analysis of ultrasonic velocities in hydrocarbon mixtures, *The Journal of the Acoustical Society of America*, 93 (1993) 2666-8.
- [109] Yousefi F., Moghadasi J., Papari M.M., Campo A., Extension of Tao-Mason Equation of State to Mixtures: Results for PVTx Properties of Refrigerants Fluid Mixtures, *Industrial & Engineering Chemistry Research*, 48 (2009) 5079-84.
- [110] Yousefi F., Karimi H., Papari M.M., Extension of Tao-Mason Equation of State to Heavy n-Alkanes, *Chinese Journal of Chemical Engineering*, 21 (2013) 894-900.
- [111] Tao F.-M., Mason E.A., Statistical-mechanical equation of state for nonpolar fluids: Prediction of phase boundaries, *The Journal of Chemical Physics*, 100 (1994) 9075-87.
- [112] Moosavi M., Prediction of thermodynamic properties of long chain 1-carboxylic acids and esters using a group contribution equation, *Fluid Phase Equilibria*, 316 (2012) 122-31.
- [113] Moosavi M., Extension of GCM-GMA equation to long chain primary, secondary and tertiary alcohols, primary and secondary amines, and ketones using group contribution method, *Fluid Phase Equilibria*, 310 (2011) 63-73.
- [114] Mansouri S.S., Farsi A., Shadravan V., Ghader S., Density calculation of liquid organic compounds using a simple equation of state up to high pressures, *Journal of Molecular Liquids*, 160 (2011) 94-102.
- [115] Kunz O., Wagner W., The GERG-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures: An Expansion of GERG-2004, *Journal of Chemical & Engineering Data*, 57 (2012) 3032-91.
- [116] Lemmon E.W., Huber M.L., McLinden M.O., NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 9.1, National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, (2013).
- [117] Dias A.M.A., Llovel F., Coutinho J.A.P., Marrucho I.M., Vega L.F., Thermodynamic characterization of pure perfluoroalkanes, including interfacial and second order derivative properties, using the crossover soft-SAFT EoS, *Fluid Phase Equilibria*, 286 (2009) 134-43.
- [118] Chen J., Mi J.-g., Equation of state extended from SAFT with improved results for non-polar fluids across the critical point, *Fluid Phase Equilibria*, 186 (2001) 165-84.
- [119] Maghari A., ZiaMajidi F., Prediction of thermodynamic properties of pure ionic liquids through extended SAFT-BACK equation of state, *Fluid Phase Equilibria*, 356 (2013) 109-16.
- [120] Maghari A., Hamzehloo M., Second-order thermodynamic derivative properties of binary mixtures of n-alkanes through the SAFT-CP equation of state, *Fluid Phase Equilibria*, 302 (2011) 195-201.

- [121] Chapman W.G., Gubbins K.E., Jackson G., Radosz M., SAFT: Equation-of-state solution model for associating fluids, *Fluid Phase Equilibria*, 52 (1989) 31-8.
- [122] Chen S.S., Kreglewski A., Applications of the Augmented van der Waals Theory of Fluids.: I. Pure Fluids, *Berichte der Bunsengesellschaft für physikalische Chemie*, 81 (1977) 1048-52.
- [123] Lemmon E.W., McLinden M.O., Friend D.G., "Thermophysical Properties of Fluid Systems", In: NIST Chemistry WebBook, NIST Standard Reference Database Number 69, (P.J. Linstrom, W.G. Mallard, editor). National Institute of Standards and Technology, Gaithersburg MD, 20899, <http://webbook.nist.gov>, June 2014.
- [124] Privat R., Gani R., Jaubert J.-N., Are safe results obtained when the PC-SAFT equation of state is applied to ordinary pure chemicals?, *Fluid Phase Equilibria*, 295 (2010) 76-92.
- [125] Privat R., Conte E., Jaubert J.-N., Gani R., Are safe results obtained when SAFT equations are applied to ordinary chemicals? Part 2: Study of solid-liquid equilibria in binary systems, *Fluid Phase Equilibria*, 318 (2012) 61-76.