2014

Chemical Characterization Of Aviation Fuels By Gas Chromatography-Mass Spectrometry

Thomas Francois Gardler
North Carolina Agricultural and Technical State University

Recommended Citation

Gardler, Thomas Francois, "Chemical Characterization Of Aviation Fuels By Gas Chromatography-Mass Spectrometry" (2014). *Theses*. 222.
https://digital.library.ncat.edu/theses/222

Chemical Characterization of Aviation Fuels by Gas Chromatography-Mass Spectrometry

Thomas F. Gardler

North Carolina A&T State University

A thesis submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department: Chemical, Biological, and Bio-Engineering

Major: Chemical Engineering

Major Professor: Dr. Vinayak N. Kabadi

Greensboro, North Carolina

2014

The Graduate School
North Carolina Agricultural and Technical State University
This is to certify that the Master's Thesis of

Thomas F. Gardler

Has met the thesis requirements of
North Carolina Agricultural and Technical State University

Greensboro, North Carolina
2014

Approved by:

Dr. Vinayak N. Kabadi
Major Professor

Dr. Shamsuddin Ilias
Committee Member

Dr. Jianzhong Lou
Committee Member

Dr. Stephen B. Knisley
Department Chair

Dr. Sanjiv Sarin
Dean, The Graduate School

BIOGRAPHICAL SKETCH

Thomas F. Gardler came to North Carolina A&T State University in the summer of 2009 after receiving his Bachelor's of Science in Chemistry from the University of North Carolina at Chapel Hill. His strong chemistry background made him a good fit for the chemical characterization project Dr. Vinayak N. Kabadi was working on for the NASA-funded Center for Aviation Safety.

During his research, Thomas presented his research to a review board from NASA on multiple occasions and participated in collaborations with researchers from the NASA Glenn Research Center in order to procure and test actual fuel samples.

In the summer of 2013, Thomas received a job offer from ZINK Imaging, Inc. and began working there as he finished his thesis work. He is presently the Environmental/Safety Engineer and Analytical Chemist for the manufacturing site stationed in North Carolina.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

This research proposes that analysis of greater depth can be performed on fuels to help understand their composition better than what is currently performed. At present, there is a disconnect between the groups that use fuels and the groups that make fuels—neither side knows precisely what the other wants. By having a better understanding of a fuel's chemical makeup, correlations between different components and different properties may be found. Using this knowledge, fuels could be made exactly how an end-user would need them. This could reduce waste of undesirable fuel as well as drive us away from fossil fuel dependence since synthetic generation of these fuels will likely be more beneficial when we fully understand how different components of fuel affect its different properties.

Using these ideas, I have developed a method to characterize the different hydrocarbon types present in an aviation fuel as well as attempt to determine the degree of branching in its paraffinic components. As paraffins typically make up the majority of most fuels, this takes a great step toward better understanding the makeup of an aviation fuel.

This method, while similar to ASTM methods that characterize the hydrocarbon types present in different cuts of fuel, refines those methodologies for aviation fuel specifically and expands upon them with branching determinations. Understanding the branching present in hydrocarbons will provide a better understanding of the combustion properties and other physical properties including things like volatility. All of this together means that this facet of information will better allow for prediction of fuel properties from knowledge of fuel composition. This would save time manually testing things like freezing point, heats of combustion, and so forth.

In this paper I walk through the way in which this method was formed and the method is applied in the characterization of a JP-8 aviation fuel sample. While this analysis will show that the proposed branching determination does not work, I believe that the trends do exist in the mass spectral data by which to perform this determination.

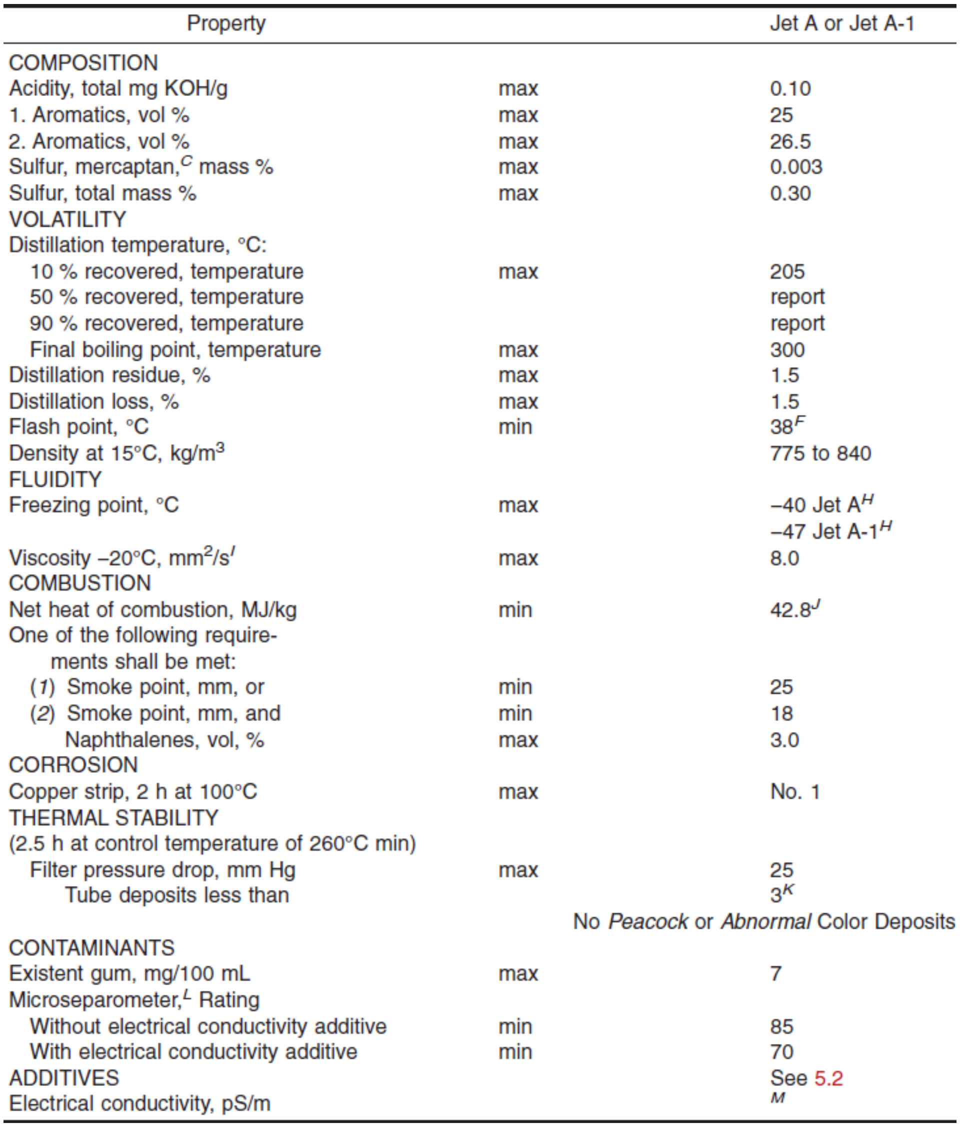
CHAPTER 1

Introduction

1.1 Aviation Fuels

Standard aviation fuel is a blend of many compounds typically consisting of paraffins, cycloparaffins, and aromatics.[1] Paraffins are hydrocarbon chains consisting of just carbon and hydrogen without double or triple bonds. Cycloparaffins are paraffinic in the sense that they contain only carbon and hydrogen and do not contain double or triple bonds, but cycloparaffins include a ring of five or six carbons named a cyclopentyl (five-membered hydrocarbon ring) or cyclohexyl (six-membered hydrocarbon ring) group as part of their structure. Aromatics are hydrocarbons that contain a conjugated aromatic ring. This aromatic ring is characterized by the alternation of double and single bonds in a hydrocarbon ring. The most notable aromatic compound is benzene: a six-membered ring with three single bonds and three double bonds between its six carbons. The double bonds in benzene are actually free to move through the compound offering great stability since each bond in benzene is at some time a double bond. This makes the bond strengths closer to one-and-a-half bonds for each. The aromatics being investigated in this work will be alkylbenzenes: paraffinic hydrocarbon chains that include a benzene ring (or benzyl group) as part of their structure. These aromatic groups in aviation fuel are typically present as less than 25% of the fuel.[1]

For commercial purposes, Jet A or Jet A-1 fuel is typically used.[1] These classifications are used to define the specific parameters required for the fuel. The specific information used in this classification cover a multitude of properties including total allowed acidity in the fuel, volatility parameters, thermal stability, and contaminants as outlined in ASTM D1655 and shown in Figure 1.1.[2]



Property		Jet A or Jet A-1
COMPOSITION		
Acidity, total mg KOH/g	max	0.10
1. Aromatics, vol %	max	25
2. Aromatics, vol %	max	26.5
Sulfur, mercaptan,^{C} mass %	max	0.003
Sulfur, total mass %	max	0.30
VOLATILITY		
Distillation temperature, °C:		
10 % recovered, temperature	max	205
50 % recovered, temperature		report
90 % recovered, temperature		report
Final boiling point, temperature	max	300
Distillation residue, %	max	1.5
Distillation loss, %	max	1.5
Flash point, °C	min	38^F
Density at 15°C, kg/m^3		775 to 840
FLUIDITY		
Freezing point, °C	max	−40 Jet A^H −47 Jet A-1^H
Viscosity −20°C, mm^2/s^I	max	8.0
COMBUSTION		
Net heat of combustion, MJ/kg	min	42.8^J
One of the following requirements shall be met:		
(*1*) Smoke point, mm, or	min	25
(*2*) Smoke point, mm, and	min	18
Naphthalenes, vol, %	max	3.0
CORROSION		
Copper strip, 2 h at 100°C	max	No. 1
THERMAL STABILITY		
(2.5 h at control temperature of 260°C min)		
Filter pressure drop, mm Hg	max	25
Tube deposits less than		3^K
		No *Peacock* or *Abnormal* Color Deposits
CONTAMINANTS		
Existent gum, mg/100 mL	max	7
Microseparometer,^{L} Rating		
Without electrical conductivity additive	min	85
With electrical conductivity additive	min	70
ADDITIVES		See 5.2
Electrical conductivity, pS/m		^{M}

Figure 1.1. Fuel specifications for Jet A or Jet A-1 from ASTM D1655.[3]

Of important note for this work are the distillation parameters. The distillation parameters were used in determining which compounds to include in the database. ASTM D1655 states that 10% or less of the mixture should be recovered at 205°C and that the final boiling point of the mixture should be no higher than 300°C.

From the distillation requirements above, a lower carbon number limit of C_{10} was originally selected due to the fact that decane ($C_{10}H_{22}$) has a boiling point of about 174°C.[3] Decane was selected because it provided space for the 10% recovery allowed at 205°C.

Similarly, an upper carbon number limit of C_{18} was selected because octadecane ($C_{18}H_{38}$) has a boiling point of 316°C.[3] Despite the fact that octadecane exceeds the 300°C final boiling point requirement, it was selected as the upper limit because going up to octadecane would encompass any compounds that might be in that volatility regime of the fuel.

1.2 Gas Chromatography

Gas chromatography is a separation method which separates compounds in a mixture by volatility. The gas chromatograph (GC) runs a small injection of sample through a column, pushing the sample through with a carrier gas. The analytical method being used after the gas chromatographic separation determines many of the specifics of the GC equipment being used. For mass spectrometric analysis, as is used in this research, injection sizes are typically 1μL to 10μL, the column is a capillary column, and the carrier gas is helium.

How quickly a particular compound moves through the GC column is determined by how much time it spends in the gas phase. Even at temperatures below their boiling points, compounds will have some amount in the gas phase over the liquid phase. As it moves along the column, this gas phase will condense into the liquid phase and more liquid will evaporate into the gas phase.

The capillary column is housed in an oven which can regulate the temperature to a desired level. This allows for control of the volatility of the compounds. As the oven temperature passes the boiling point of compounds and they move completely into the gas phase, they will all move at the same speed of the carrier gas. As the oven temperature increases, but remains under a compound's boiling point, its speed will increase because its molecules will spend more time in the gas phase.

For instance, hexane, heptane, and octane have boiling points of 69°C, 98°C, and 125°C respectively. If a mixture of these three hydrocarbons is made and run through the GC with the oven set at 85°C, then hexane will elute first since it will boil and completely enter the gas phase upon entering the column. Heptane will elute second since its boiling point is closer to 85°C than that of octane, causing more of its molecules to be in the gas phase at any given time. For another example, consider the same three compounds in the mixture, but assume that the oven temperature is set at 110°C. Now, both hexane and heptane will boil immediately, causing them to elute at the same time and octane will follow after.

The GC oven can also be run under a temperature program, adjusting the temperature as the run progresses. If the temperature is left isothermal at 85°C, as in the first example above, then all compounds will elute and be separated, but octane will take a few minutes to do so. In a three compound mixture like this, that is not a great issue, but if the compounds went up to octadecane, which has a boiling point of 316°C,[3] then it would take a long time to elute octadecane under isothermal conditions. To speed up this process, the temperature can be set at 70°C and held there for a couple minutes in order to elute hexane and give a small separation of the other compounds. Then, the temperature can be ramped up to 200°C at 5°C per minute. This increase in temperature over time helps less volatile compounds, like octadecane, to elute from the column more quickly without causing other compounds to overlap eachother in elution time.

1.3 Mass Spectrometry

Mass spectrometry is an analytical technique that is able to identify specific compounds based on mass fragments observed. This analytical method typically follows some sort of separating technique such as gas chromatography or liquid chromatography. After separation by gas chromatography for example, compounds elute from the capillary column and enter the mass spectrometer (MS). In the MS, compounds are vaporized because of the near vacuum condition of the MS (around 10^{-5} Torr is typical).

In an electron ionization (EI) MS, such as the one used in this research, these compounds are then ionized through bombardment with electrons. This causes an electron of the compound to be knocked loose, giving the compound a net +1 charge. This ion then moves toward the mass analyzer or fragments with one piece of the overall compound holding the charge before moving toward the mass analyzer.

The most common mass analyzer, and the one used in this research, is a quadrupole mass analyzer.[4] Either as a whole compound or as a fragment, the charge-carrying ion will then move through the quadrupole towards the detector. The quadrupole is a set of four metal rods aligned in parallel along the length of the MS. One pair of opposite rods is connected to a positive DC source, the other pair to a negative DC source.[4] Additionally, AC voltages that are 180° out of phase are applied to the two pairs of rods. The application of both AC and DC voltages are the key to high selectivity of the MS.[4] By adjusting these voltages the MS is able to allow only compounds of a particular mass and charge through at a time so that, when detected, the signal is applied to the correct mass-to-charge ratio.[4]

Without the DC voltage, ions will converge toward the center during the positive cycle of the AC voltage and diverge toward the rods during the negative cycle.[4] If the positively-charged ion reaches and contacts the rod, the ion would immediately lose its positive charge and would no longer be pulled along the quadrupole.[4] This movement toward the rods is dictated by two factors: the ion's mass and its charge. The greater an ion's mass, the slower it will move and the lighter an ion is the faster it moves. Additionally, the greater an ion's charge the faster it will move and the smaller its charge the slower it will move. These two factors comprise the mass-to-charge (m/z) ratio—the parameter by which the MS characterizes fragments and, therefore, compounds.

In the case above, by overlaying a positive DC voltage on the AC voltage, heavier ions can be kept in place because the constant positive DC voltage will have a greater effect on the large positive ions than the constantly alternating AC voltage.[4] This creates a high-pass mass filter that will remove ions with a m/z ratio that is too low.

For the other pair of rods, a negative DC voltage is applied over the AC voltage. This causes heavier positively-charged ions, essentially unaffected by the alternating AC voltage, to constantly move towards the rods until they are neutralized.[4] This makes the second pair of rods a low-pass mass filter which will remove ions above a certain m/z ratio.[4]

By adjusting the applied voltages described above, the MS is able to accurately detect ions of a particular m/z ratio. From the detected m/z ratios, it is possible to identify specific compounds from the pattern of fragmentation. Mass spectrometric databases are available that include spectra for a variety of compounds. Using these databases, a compound can be identified by comparing relative abundance of different m/z ratios detected. As will be discussed later, similar types of compounds present similar m/z ratios, but the specific abundances of each act as a fingerprint for identification.

CHAPTER 2

Literature Review

2.1 Fuels Research

One major facet of fuels research revolves around the desire to better understand what is in a given fuel. This information will potentially be all that is necessary to determine all the physical properties of a fuel from its distillation curve and initial freezing point all the way to the total amount of energy that can be derived from the fuel. In order to make these leaps, first a reliable and encompassing method of characterizing the fuel must be developed.

One of these areas of research is determining fraction of hydrocarbon types in petroleum fuel.[5] This can be done in a number of ways including elution chromatography, liquid chromatography, mass spectrometry, and super-critical fluid chromatography.[5] Hydrocarbon type determination is an important first step in the overall characterization process because understanding the different hydrocarbon types present, whether they are paraffins, cycloparaffins, alkylbenzenes, indanes, tetralins, etcetera, will yield good initial information on physical properties. This is due to the different physical properties observed for the different hydrocarbon types.

More recently, this same hydrocarbon type analysis has been performed using nuclear magnetic resonance (NMR) spectroscopy.[5] The major benefit of NMR spectroscopy over the other analytical methods is its speed.[5] When compared to the accuracy of mass spectrometric techniques, NMR spectroscopy was shown to be superior at analyzing aromatic fractions when sulfur is present in the fuel.[5] Since petroleum fuels are extracted from the earth, all manner of impurities are possible in the fuel, including sulfur. As petroleum becomes increasingly scarce, less and less pure petroleum will be extracted, increasing the likelihood of impurities like sulfur.

As a result, this NMR characterization will be beneficial in the future as a way to accurately characterize these fuels until alternative fuels become more reliably made and used. The NMR spectroscopy method works similarly to the mass spectrometry methods in that certain peaks seen in the spectrum correspond to different hydrocarbon types.[5]

Beyond the use of petroleum fuels, however, the accuracy of NMR analysis in the presence of sulfur will be significantly less important. Alternative fuels will not contain the same impurities that petroleum fuel does, and, therefore, will not have the same analytical issues for aromatics presently seen.

2.2 Alternative Fuels

Given the growing scarcity and cost of conventional petroleum fuels, the field of alternative fuels research is a major one. Incorporation of alternative fuels, even if not a complete replacement outright, would help reduce the need for petroleum-based fuels. A couple of the larger fields of research into alternative fuels are using fuels generated through the Fischer-Tropsch method [6,7,8] and using fuels obtained from biomass.[9,10]

2.2.1 Fischer-Tropsch Fuel Generation. The Fischer-Tropsch (F-T) method of fuel generation utilizes what is known as synthesis gas to generate hydrocarbons of a desired size.[6,7,8] Synthesis gas is a combination of hydrogen (H_2) and carbon monoxide (CO) and it is converted to hydrocarbons through F-T synthesis.[6]

The F-T synthesis method was developed by Franz Fischer and Hans Tropsch back in the 1920s.[6] It involves a step-wise addition of carbon atoms taken from the CO gas and stabilization of these carbons using hydrogen atoms from the H_2 gas.[6] This process must take place in the presence of a catalyst to facilitate this reaction and hydrocarbon chain growth.[6]

This process has the ability to generate both paraffins (saturated hydrocarbons with chemical formula of C_nH_{2n+2}) and olefins (unsaturated hydrocarbons which include a double bond and have a chemical formula of C_nH_{2n}).[6] This generation of specific compounds reduces the amount of poly-aromatic hydrocarbons (PAH) present in the fuel as well as eliminates the sulfur-containing impurities that can form sulfur oxides when combusted.[6] Poly-aromatic hydrocarbons include indanes and tetralins which contain multiple hydrocarbon rings with at least one of these rings containing a conjugated double bond system. These hydrocarbons are extremely stable and may not fully combust when burned resulting in particulate emissions when the fuel is used.[6] As a result, F-T fuels can also reduce the amount of particulate matter generated in fuel consumption. Further, the F-T process generates hydrocarbons over a wide range from very light gaseous hydrocarbons to gasoline and kerosene to diesel. This versatility makes F-T synthesis very desirable and also contributes to its long-standing use as a fuel generation method that has been around since the 1920s. It can generate all the different fuel types commonly used both for personal and for commercial and industrial use. This does, however, add a distillation step in order to separate the different products.

Research into the F-T process, and fuel generation using it, continue today.[9] Since the F-T synthesis requires a catalyst to make the reaction work, there is obviously research into developing better, more efficient, and more customized catalysts for this synthesis process.[7,8] Additionally, process improvements are also a great field of interest. For instance, synthesis gas often undergoes a water-gas-shift reaction in order to increase its hydrogen content.[6,8] This reaction produces CO_2 as a by-product and, at the end of the process, this CO_2 is released to the atmosphere.[6,8] Unfortunately, this CO_2 production is much greater than the CO_2 production associated with processing petroleum to create the same fuel.[8] This is obviously problematic when we are, as a society, trying to constantly reduce our carbon footprint and minimize greenhouse gas production. Research into process improvement has shown that use of a catalytic dehydrogenation (CDH) step, instead of the water-gas-shift reaction, can significantly reduce, if not completely eliminate, this CO_2 release.[8] This CDH step would be performed in process to dehydrogenate the lighter products of the F-T process in order to generate the necessary additional H_2.

2.2.2 Fuel Generation from Biomass. Traditionally, almost all aviation fuel has been derived from crude petroleum resources.[9] Through distillation, the crude is fractionated to give desired cuts of fuels of certain boiling point ranges.[9] For aviation fuel, this is a cut similar to that of kerosene. The crude-derived cuts of fuel can vary significantly from source-to-source and from batch-to-batch, so a consistent product is hard to attain.[9,10]

Given the increasing scarcity and cost of petroleum, however, new research has delved into generating similar fuels from different bio-mass sources. One of the great benefits to this is the production of bio-synthetic paraffinic kerosene (BIO-SPK) from these feed stocks. The BIO-SPK fuel is mainly comprised of normal or isoparaffins with a significant lack of other hydrocarbon types.[9,10] This lack of diversity can be problematic since a certain aromatic content is required in aviation fuel to swell o-rings and other seals to increase their effectiveness and longevity, but additions or blending can be used post-production to resolve this. The reactions involved in generating BIO-SPKs also allow for a great deal of tailoring so that certain ideal properties can be achieved, which is especially helpful considering the strict requirements set on aviation fuel.[9,10]

The process of producing BIO-SPKs is typically two-fold. The first step involves breaking down biological triglyceride oils into free fatty acids. This can be done using transesterification which involves using an alcohol to replace the fatty acid on the glycerine chain. This produces fatty acid esters (FAEs) or, if methanol was the alcohol used, fatty acid methyl esters (FAMEs). In most cases, biological oils have aliphatic chain lengths between 16 and 20 and typically are 18 carbon units long.[9] This is a very narrow range of hydrocarbon chain lengths and the carbonyl group involved makes these compounds less volatile and easier to freeze and, as a result, more suited to diesel purposes than for aviation fuel. Hence the need for a second processing step.

The second step of creating BIO-SPKs is a deoxygenation hydrotreating reaction, which removes the oxygenated group, and a hydrocracking treatment, which breaks up the long chains and provides a variety of hydrocarbons that can be fractionated similar to crude petroleum.[9] The hydrotreating is a catalytically-driven process which saturates compounds containing double bonds, as a portion of bio-oils do, and removes the oxygenated carbonyl to leave behind a long-chained normal paraffin.[9,10] After that, hydrocracking breaks up the long carbon chains so that a full range of fuels can be derived, one of these being the kerosene-like aviation fuel.[9,10]

Due to the requirements and specifications for aviation fuel, additives will likely be necessary to make these BIO-SPKs viable, but it would be worth it to help drive us away from the dependence on crude petroleum.

2.3 Fuel Characterization

2.3.1 ASTM D2789. This was the first method I found which involved a chemical characterization of fuels. Specifically for low-olefinic gasoline, this method did not correlate directly to aviation fuel, but sparked an idea for the methodology by which to perform the characterization.

This method involved matrix calculations to solve for multiple parameters simultaneously. The method allows you to solve for the fractional compositions of paraffins, mono-cycloparaffins, di-cycloparaffins, alkylbenzenes, indanes and tetralins, and napthalenes.[11] It used a large table of calibration data that were, I found, the coefficients for contributions from each of the hydrocarbon types to each m/z ratio summation. By identifying specific sets of m/z ratios which were indicative of the different hydrocarbon types, the method was able to use those to quantitatively identify them and determine their composition.[11]

Since this method did not correlate very well to aviation fuel, searching continued for something more applicable.

2.3.2 ASTM D2425. As described above, a few ASTM methods were found that gave quantitative information on hydrocarbon types present in a given fuel. One of these, ASTM D2425 dealt with characterization of middle distillates, which was the closest to aviation fuel. This method used a similar matrix calculation approach as ASTM D2789, which was employed in my own method, in order to calculate the amount of paraffins, cycloparaffins, alkylbenzenes, indanes, tetralins, etcetera present in the fuel.[12] Upon investigation, the parameters chosen in this method did not seem to be the optimal ones for the specific cut which is aviation fuel. For accurate determination regardless of branching, a wider set of m/z ratios was necessary for the three main hydrocarbon types I focused on: paraffins, cycloparaffins, and alkylbenzenes.

It is important to note that these methods also stop after determining hydrocarbon type fractions. That is where this method begins to embark on new territory and add to the academic community. Noticing that there were not only trends for hydrocarbon types, but also for branching, I began looking for correlations that would allow for characterization of branching.

CHAPTER 3

New Chemical Characterization Method

3.1 Overview

The following characterization method is designed to calculate the mole fractions of three different hydrocarbon types in an aviation fuel mixture. Additionally, it will calculate the fractions of each based on carbon number as well. The three hydrocarbon types are paraffins, cycloparaffins, and alkylbenzenes. Paraffins are alkane hydrocarbons with a chemical formula of C_nH_{2n+2} that lack double or triple bonds and may be branched or unbranched. In the boiling point range being investigated (approximately 180°C to 320°C), the value of n in the chemical formula will range from 10 to 18. Cycloparaffins, like paraffins, are hydrocarbons that lack double or triple bonds and may be branched or unbranched. Unlike paraffins, however, these compounds will also include a cyclic group—typically a cyclopentyl (C_5) ring or cyclohexyl (C_6) ring. These hydrocarbons follow the chemical formula C_nH_{2n}. As in paraffins, n will range from 10 to 18. Alkylbenzenes will contain a benzyl group—a conjugated (contains shifting double bonds) six-membered ring. Aside from the benzyl group, these compounds will not contain double or triple bonds and they may be branched or unbranched. Alkylbenzenes follow the chemical formula C_nH_{2n-6} where n will range from 10 to 18. The carbon number determinations will be based off of elution times of compounds from the gas chromatograph. Different time slices taken of the total ion chromatogram (TIC) will correspond to different carbon numbers.

This method will also attempt to determine the degree of branching in paraffins by carbon number. Degree of branching will be broken into straight-chain, lightly-branched, medium-branched, and heavily-branched compounds. Straight-chain compounds do not have any branching and contain only primary carbons (a carbon bonded to only one other carbon) and secondary carbons (a carbon bonded to two other carbons). Lightly-branched compounds will have alkane branches coming off of the compound's main chain. This will result in tertiary and quaternary carbons (a carbon bonded to three or four other carbons respectively). Lightly-branched compounds will typically only include up to three methyl groups, one ethyl groups, or one propyl group. Medium-branched compounds will be contain up to four methyl branches, two ethyl groups, two propyl groups, or a butyl group off of the main chain. Heavily-branched compounds will also have tertiary and quaternary carbons, but will have larger numbers of branching groups coming off of the main chain.

For all runs performed in this work the GCMS parameters were consistently set as defined in Table 3.1 below.

Table 3.1

GCMS Parameters for Experimental and Test Runs

	Parameter	Setting
GC	Ti	50°C
	Hold	3min
	T Ramp	5°C/min
	Tf	140°C
	Hold	For Baseline
	Inlet T	300°C
	Injection	1µL
	Flow Rate	1.6mL/min
	Split	40:1
MS	Source T	180°C
	Quadrupole T	230°C
	m/z Scan	10-300

This allowed for identification of the straight chain elution times of each carbon number. This provided the basis used for splitting the chromatogram up into individual carbon number slices for analysis since elution times were consistent for each compound. For all runs performed, an HP-INNOWAX polar column was used which was 30m long with a .25mm inner diameter and a .25µm pore size in the packing.

3.2 Determining Hydrocarbon Mole Fractions

Using the NIST 2008 mass spectral library, specific compounds and their m/z ratios were obtained for the three hydrocarbon types being analyzed: paraffins, cycloparaffins, and alkylbenzenes. Their distribution by carbon number can be found in Table 3.2 below.

Table 3.2

Compound Totals and Carbon Number Distribution for the Compounds Obtained from the NIST 2008 Mass Spectral Library

Carbon #	10	11	12	13	14	15	16	17	18	Total
Paraffins	40	21	30	71	15	11	23	7	10	228
Cycloparaffins	29	17	21	8	8	4	8	6	11	112
Alkylbenzenes	22	23	33	16	24	15	8	7	20	168

Further, a complete listing of all compounds whose mass spectra were obtained from the NIST 2008 database can be found in Appendices A.1, A.2, and A.3 for paraffins, cycloparaffins, and alkylbenzenes respectively.

From inspection of mass spectral data found in the NIST 2008 compound library, a set of m/z ratios were found that were uniquely high in abundance for one of the hydrocarbon types, but not the other two. Since part of the scope of this work is to characterize branching, sets of the m/z ratios were found that resulted in minimal variation with branching. While certain m/z ratios may drop off with increased branching, other ones may begin to dominate.

By taking the sum of the set of these characteristic m/z ratios, a hydrocarbon type can be identified regardless of carbon number or branching. A good example of this can be seen with dodecane, 3,8-dimethyldecane, and 2,2,4,6,6-pentamethylheptane. All three compounds have a carbon number of 12, but they have different branching. From the mass spectrum of dodecane, as shown in Figure 3.1, it can be seen that m/z ratios 43, 57, 71, and 85 are all relatively high. In 3,8-dimethyldecane, seen in Figure 3.2, all the m/z ratios decrease slightly, but m/z ratio 57 still dominates. For 2,2,4,6,6-pentamethylheptane, shown in Figure 3.3, everything but m/z ratio 57 has dropped off significantly. The sum of the abundances as a fraction of the total signal abundance for m/z ratios 43, 57, 71, and 85 are 0.56, 0.58, 0.48 for dodecane, 3,8-dimethyldecane, and 2,2,4,6,6-pentamethylheptane respectively. This puts the fractional value fairly close together and shows relatively little dependence based on branching. ASTM D2425 only uses m/z ratios 71 and 85 in the paraffinic summation, but as can be seen in Figures 3.1 through 3.3, those two m/z ratios have significant dependence on branching.

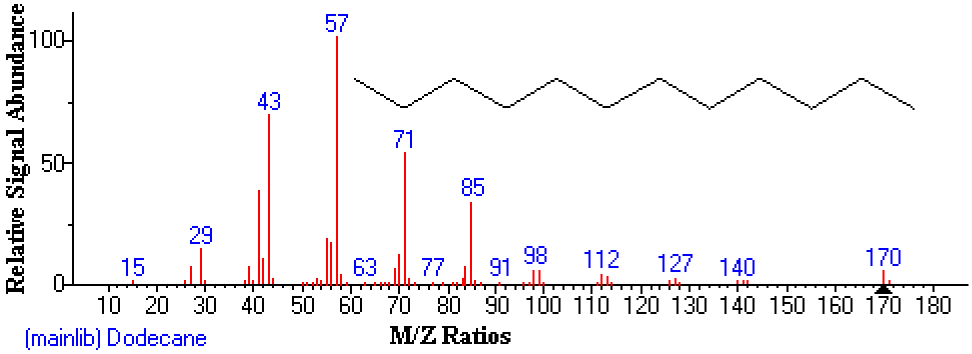


Figure 3.1. Mass spectrum of dodecane from NIST 2008 mass spectral library.

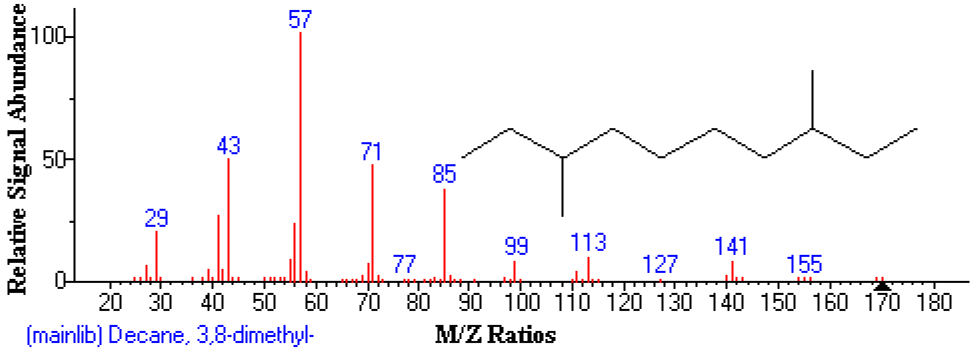


Figure 3.2. Mass spectrum of 3,8-dimethyldecane from NIST 2008 mass spectral library.

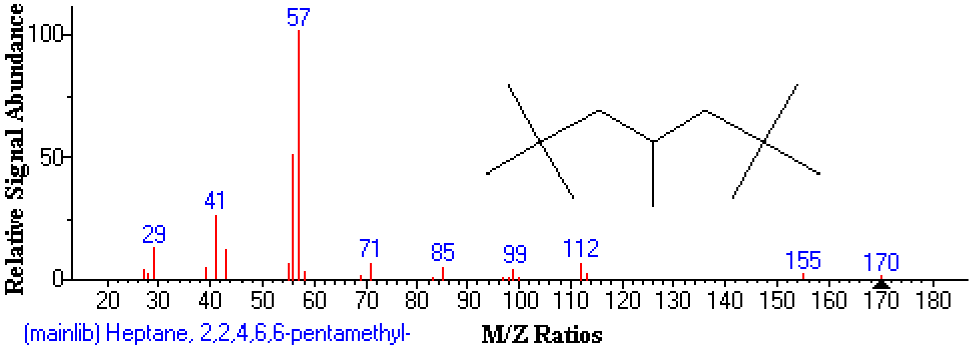


Figure 3.3. Mass spectrum of 2,2,4,6,6-pentamethylheptane from NIST 2008 mass spectral library.

For cycloparaffins, a more complicated summation was necessary. Figures 3.4 through 3.6 show a set C_{12} cyclohexyl cycloparaffins: hexylcyclohexane, 3-methylpentylcyclohexane, and 1-isopropyl-1,4,5-trimethylcyclohexane. While similar m/z ratios appear in all three, their fractional abundance is heavily dependent on branching. As a result, it is not possible to get good agreement with branching using just m/z ratios 41, 55, 69, and 83. Therefore, all the m/z ratios corresponding to different carbon numbers of cycloparaffins were included—essentially summing the apparent m/z ratios as well as the m/z ratios of fragments from the highest cycloparaffinic m/z ratio, m/z ratio 251, all the way down to the smaller m/z ratios described above in CH_2 increments, or in m/z increments of 14. Using this method for C_{12} cycloparaffins gave an average fractional abundance of 0.67 with a standard deviation of 0.05. Using just the lower m/z ratios for the same set of C_{12} compounds gave an average fractional abundance of 0.50 with a standard deviation of 0.12. The smaller standard deviation for the larger summation means that the calculations performed using that average will be more accurate.

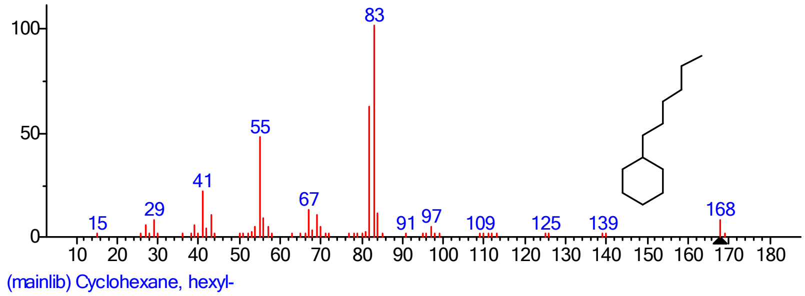


Figure 3.4. Mass spectrum of hexylcyclohexane from NIST 2008 mass spectral library.

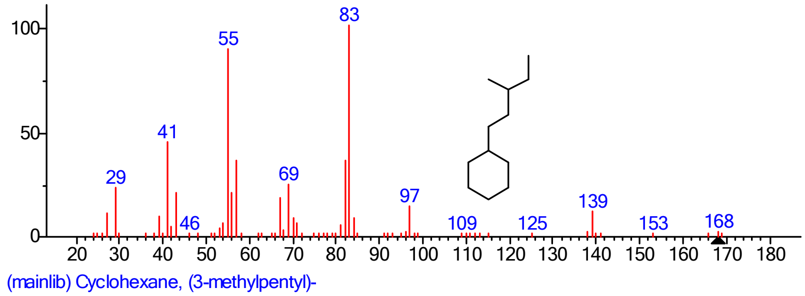


Figure 3.5. Mass spectrum of 3-methylpentylcyclohexane from NIST 2008 mass spectral library.

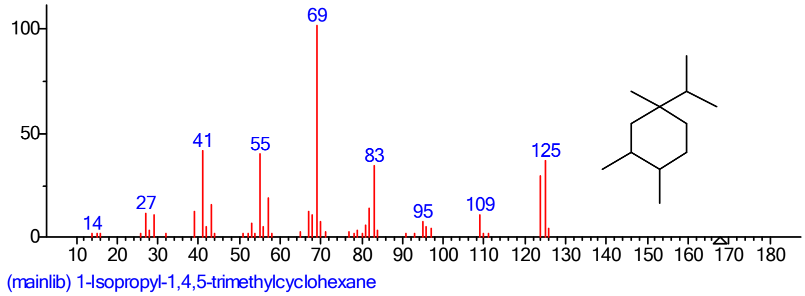


Figure 3.6. Mass spectrum of 1-isopropyl-1,4,5-trimethylcyclohexane from NIST 2008 mass spectral library.

For alkylbenzenes, a similar problem arose as that observed for cycloparaffins. Using a summation of the abundance of the lower, more apparent m/z ratios led to a large standard deviation as well as a dependence on branching. As can be seen, m/z ratio 91 is very abundant for the straight-branched hexylcyclohexane, shown below in Figure 3.7, but it drops off significantly in the relatively lightly-branched 1-(1-ethylpropyl)-4-methylbenzene, shown in

Figure 3.8, and to almost nothing in 1,3,5-trimethyl-2-propylbenzene shown in Figure 3.9. By including fractional parts with a m/z ratio difference of 14, it was possible to bring the standard deviation down to 0.12 for C_{12} alkylbenzenes with an average fractional abundance of 0.62.

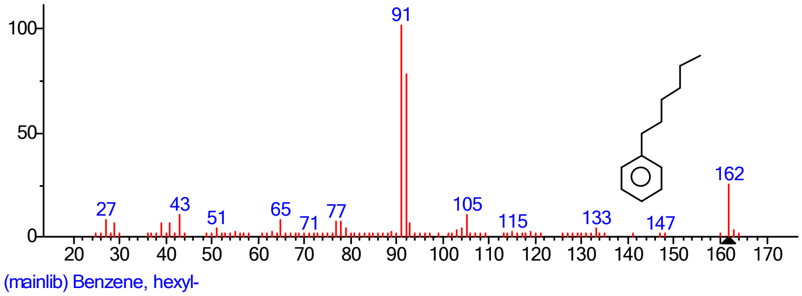


Figure 3.7. Mass spectrum of hexylbenzene from NIST 2008 mass spectral library.

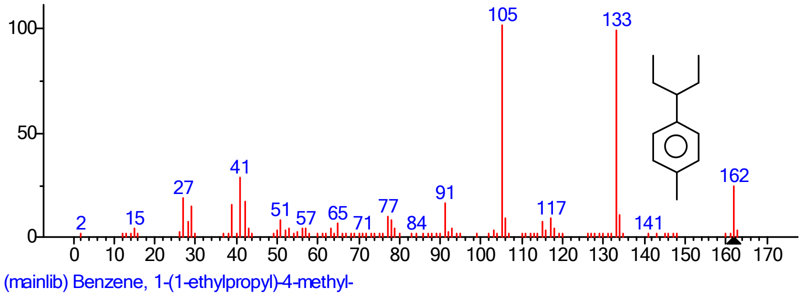


Figure 3.8. Mass spectrum of 1-(1-ethylpropyl)-4-methylbenzene from NIST 2008 mass spectral library.

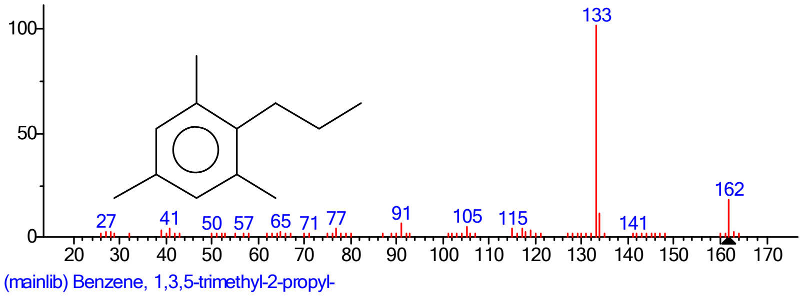


Figure 3.9. Mass spectrum of 1,3,5-trimethyl-2-propylbenzene from NIST 2008 mass spectral library.

To determine the mole fraction of the different hydrocarbon groups, the abundance of m/z ratios characteristic of each group will be determined and added together. Each of the three hydrocarbon groups has its own summation which will be referred to as Σ43 for paraffins, Σ41 for cycloparaffins, and Σ75 for alkylbenzenes. The actual m/z ratio abundances to add for each summation are outlined in Equations 1 through 3. Each value shown in Equations 1 through 3 is the given m/z ratio. The actual summation is of the signal abundance for the corresponding m/z ratios given. These summations will be calculated for each carbon number group based on elution time from the gas chromatograph.

$$\sum 43 = 43,57,71,85 \qquad 1$$

$$\sum 41 = 41,55,56,67,68,69,81,82,83,\sum_{n=0}^{11} 96+14n,97+14n \qquad 2$$

$$\sum 75 = 75,76,77,78,\sum_{n=0}^{11} 91+14n,92+14n \qquad 3$$

In order to determine the actual mole fractions of each hydrocarbon type present, a few steps have to be taken. The m/z ratios listed in Equations 1 through 3 are characteristic for their given hydrocarbon type, but they are not perfectly unique. For instance, while Σ43 is comprises approximately 50% of the total signal abundance for paraffins, cycloparaffins and alkylbenzenes show abundances of that summation around 5% and 3% respectively.

For a C_{12} paraffin, the average fraction for Σ43 is 0.54 ± 0.07. The average Σ43 fraction for C_{12} cycloparaffins and alkylbenzenes are 0.10 ± 0.04 and 0.05 ± 0.08 for cycloparaffins and alkylbenzenes. These amounts are smaller than the fraction observed for paraffins, so they still allow for individual determination, but they are significant enough not to be ignored. As a result, it has to be assumed that for any given time slice of the TIC, Σ43, Σ41, and Σ75 are going to be a combination of some amount observed for paraffins, cycloparaffins, and alkylbenzenes.

For example, using a subscript p for paraffins, c for cycloparaffins, and a for alkylbenzenes, Σ43 should be a result of some amount from paraffins ($\Sigma 43_p$), cycloparaffins ($\Sigma 43_c$), and alkylbenzenes ($\Sigma 43_a$) as shown in Equation 4. These summations are actually a result of the average fraction of the total abundance (P_p, P_c, and P_a for paraffins, cycloparaffins, and alkylbenzenes respectively) multiplied by the total signal abundance from each hydrocarbon type with T_p, T_c, and T_a representing the total signal abundance for paraffins, cycloparaffins, and alkylbenzenes respectively. This is shown in Equation 5. Following this same methodology for $\Sigma 41$ and $\Sigma 75$, Equations 6 and 7 are derived.

In Equations 5 through 7, the summations ($\Sigma 43$, $\Sigma 41$, and $\Sigma 75$) are known values that will be calculated from the run of a fuel sample. The coefficient values (P_n, C_n, and A_n; where n is the hydrocarbon type and P is used for the paraffin $\sum 43$ coefficient, C for $\sum 41$, and A for $\sum 75$) are known values determined from the database of compounds. It was observed that there was very little dependence of these values on both carbon number and branching. As a result, averaged values for each were calculated and used in this method. These values are presented in Table 3.3.

Therefore, the unknown values to calculate are the total signal values T_p, T_c, and T_a, the total m/z ratio abundances attributed to each hydrocarbon type. Setting the equations up in a matrix calculation format, shown in Equation 8, these three values can be found by inverting the coefficient matrix and multiplying it by the solution matrix. Once the total signal abundances for each hydrocarbon type are found for each slice of the TIC, the mole fractions of each can be found using the mole sensitivity data.

The mole sensitivities are the amount of signal that correlates to one mole of a particular compound or hydrocarbon type. This data was obtained from actual experimental runs on the GC-MS. A small number of compounds were purchased with which to do this determination; see Appendix A.4 for the list of compounds. These compounds were run and then the total ion chromatograms were analyzed to give the mole sensitivity data. After identifying each peak, the area of the peak from the x-axis was found using a manual integration setting in the GC-MS analysis software. The area of a clear section of the chromatogram was also taken as the baseline and subtracted from each one. Then, since each compound was mixed at the same volume for better reproducibility, the number of moles for each was calculated from its density at 25°C. These moles, while not the actual number of moles for each compound that made it onto the column, are the same relative number of moles, so they were used directly. By dividing the above integrations by the corresponding number of moles gives the mole sensitivity value: the integration signal per mole of compound. All of these values for all compounds were then divided by the value obtained for decane in order to yield an easier number to use. Then, gaps in the values were obtained through interpolation and extrapolation of already calculated values. Values for compounds of carbon number 17 and 18 are not shown because these were not purchased at this time. Similarly, carbon number 10 compounds are not included because nonane had not been purchased to determine where the carbon number 10 slice should start. Therefore, analysis of these compounds was not possible.

Using the mole sensitivity values for each carbon number of each hydrocarbon type, the relative number of moles can be determined from Equation 9. The mole sensitivity value ($S_{t,n}$) is the unit signal observed for a given hydrocarbon type, where t is p for paraffins, c for cycloparaffins, and a for alkylbenzenes, per relative mole of sample for a given carbon number n. The mole sensitivity values for the different hydrocarbon types by carbon number can be found in Table 3.4. By dividing the total signal abundance T of a certain hydrocarbon type t and carbon number n by the appropriate mole sensitivity value, the relative number of moles of that hydrocarbon type at the given carbon number n ($m_{t,n}$) will be found. Then, by dividing each number of relative moles of a given hydrocarbon type t by the sum of all the relative moles of that type, the carbon number fractions within the compound type ($x_{t,n}$) can be found, as shown in Equation 10. The overall mole fractions of the hydrocarbon types can be obtained by dividing the sum of all the relative moles of different carbon numbers n of a given hydrocarbon type t by the sum of all the carbon numbers of all the types as shown in Equation 11.

$$\sum 43 = \sum 43_p + \sum 43_c + \sum 43_a \tag{4}$$

$$\sum 43 = P_p T_p + P_c T_c + P_a T_a \tag{5}$$

$$\sum 41 = C_p T_p + C_c T_c + C_a T_a \tag{6}$$

$$\sum 75 = A_p T_p + A_c T_c + A_a T_a \tag{7}$$

$$\begin{bmatrix} P_p & P_c & P_a \\ C_p & C_c & C_a \\ A_p & A_c & A_a \end{bmatrix} \begin{bmatrix} T_p \\ T_c \\ T_a \end{bmatrix} = \begin{bmatrix} \sum 43 \\ \sum 41 \\ \sum 75 \end{bmatrix} \tag{8}$$

$$m_{t,n} = \frac{T_{t,n}}{S_{t,n}} \tag{9}$$

$$x_{t,n} = \frac{m_{t,n}}{\Sigma_{n=10}^{18} m_{t,n}} \tag{10}$$

$$x_t = \frac{\Sigma_{n=10}^{18} m_{t,n}}{\Sigma_{n=10}^{18} m_{p,n} + \Sigma_{n=10}^{18} m_{c,n} + \Sigma_{n=10}^{18} m_{a,n}} \tag{11}$$

Table 3.3

Coefficient Matrix Values Averaged from Database Compounds

Coefficient	Paraffins (p)		Cycloparaffins (c)		Alkylbenzenes (a)	
	Average	Stdev	Average	Stdev	Average	Stdev
43	0.497	0.037	0.042	0.023	0.037	0.023
41	0.211	0.004	0.706	0.012	0.032	0.001
75	0.001	0.001	0.008	0.002	0.678	0.002

Table 3.4

Mole Sensitivity Values for Paraffins, Cycloparaffins, and Alkylbenzenes of Different Carbon Numbers

Carbon #	S_p	S_c	S_a
11	1.108	1.113	0.829
12	1.317	1.36	1.032
13	1.515	1.469	1.249
14	1.693	1.52	1.478
15	1.853	1.591	1.693
16	1.979	1.647	1.885

3.3 Determining Degree of Branching in Paraffins

Inspection of mass spectral data showed many trends with branching for paraffins. Some of these included higher abundances for the m/z ratios correlating to loss of actual branches from a particular compound. For example, if 3-methyl decane were analyzed in the MS, there would be a higher abundance for the m/z corresponding to the loss of this methyl group (142-15=127). The same thing is observed for ethyl, propyl, and butyl chains as well. As the number of these branches increases, or the size of them goes beyond 4 carbon units, the correlation begins to disappear. This is likely due to the fact that with that many branch points, or that large of a branch, there are several good options for fragmentation instead of just the single small branch in other compounds. This correlates with the higher paraffin trend discussed above: as branching becomes heavy, the higher paraffinic m/z ratios disappear. While this and many other trends seemed promising, there was no clear way how to get a full analysis from them, so other observed trends were explored. The best trends to yield

One of the apparent trends was the fact that as branching increased, the abundance of m/z ratios 43, 71, and 85 decreased while m/z ratio 57 stayed high. This trend can be seen in Figures 3.10 through 3.12 below. Figure 3.10 shows the straight-chain C_{16} compound hexadecane. In Figure 3.10, the paraffinic m/z ratios 43, 57, 71 and 85 can all be seen in fairly good abundance. Figure 3.11 shows a lightly-branched C_{16} compound, 6-methylpentadecane. For 6-methylpentadecane, the drop in abundance of m/z ratios 43, 71, and 85 relative to m/z ratio is significant. This trend continues with the heavily-branched 2,2,4,4,5,5,7,7-octamethyloctane shown in Figure 3.12 where m/z ratios 43, 71, and 85 are almost gone. From the NIST mass spectral data, the fractional abundance of m/z ratio 57 to the total observed abundance of all m/z ratios was found to be fairly constant for straight-chain, lightly-branched, and medium-branched compounds, but jumps up significantly for heavily-branched compounds.

Another observed trend was the parent ion abundance. It was observed in nearly all cases that straight-chain compounds had the highest parent ion fractional abundance (typically around 0.01 to 0.02) when compared with lightly-branched compounds which have fractional parent ion abundances around 0.002 to 0.008. Further, heavily-branched compounds very often show no parent ion abundance, and when they do, it is a very small fractional abundance around 0.0001 to 0.0003 making the parent ion abundance a good parameter.

Finally, it was observed that m/z ratios near the parent ion were higher for lightly-branched compounds than for straight-chain compounds and these same m/z ratios were typically non-existent for heavily-branched compounds. These m/z ratios correspond to the parent ion losing a methyl group (CH_3), an ethyl group (C_2H_5), a propyl group (C_3H_7), or a butyl group (C_4H_9). These groups, except for the loss of a methyl group, all show up in fairly small abundances for straight-chain compounds. In lightly-branched compounds, however, one or more of these groups are typically in fairly high abundance like in the case of 4,11-dimethyltetradecane shown in Figure 3.13. The compound 4,11-dimethyltetradecane has two tertiary carbons, one at the "4" position and one at the "11" position. These tertiary carbons are good fragmenting points for the compound because they can better distribute the charge it gains after it loses an electron. As a result, the mass spectrum shows peaks around m/z ratio 210, representing the loss of a methyl group since there are methyl groups attached to those tertiary carbons.

Additionally, when compared with hexadecane in Figure 3.10, 4,11-dimethyltetradecane shows a large peak around m/z ratio 183 which corresponds to the loss of a propyl group. This is due to the fact that the same tertiary carbons holding the methyl groups also have propyl groups hanging off of them. While the compound name considers these pieces to be part of the main chain, they are able to break off just like the methyl groups, and are more likely to do so since the multiple carbons can better stabilize the radical. For a heavily-branched compound, like 2,2,4,4,5,5,7,7-octamethyloctane in Figure 3.12, none of these peaks are observed. The highest m/z ratios are around 155, which corresponds to the loss of a pentyl group (C_5H_{11}). Using this parameter, in conjunction with the parent ion abundance, makes determination of branching in paraffins possible.

For the paraffin branching determination, the term parent ion refers to the m/z ratio for the intact, unfractured compound. For instance, for hexadecane (chemical formula $C_{16}H_{34}$), the parent ion would be 226. Just as its molecular weight or atomic mass would be assuming all the carbons were ^{12}C and all the hydrogens were ^{1}H.

The other term that will be used here is higher paraffins. This term is defined as the set of m/z ratios for a given paraffinic compound corresponding to the loss of a methyl group, the loss of an ethyl group, and the loss of a propyl group. The abundances for the m/z ratios for each of these are added together. Additionally, as a result of possible compound fracturing, one m/z ratio above and below are also included for each.

Continuing with the hexadecane example, the higher paraffinic m/z ratios for loss of a methyl group are 210, 211, and 212. For loss of an ethyl group they are 196, 197, and 198. For loss of a propyl group, the m/z ratios are 182, 183, and 184.

The purpose for selection of these m/z ratios can be seen in the mass spectra of hexadecane, 6-methylpentadecane, 4,11-dimethyltetradecane, and 2,2,4,4,5,5,7,7-octamethyloctane shown below in Figures 3.10, 3.11, 3.12, and 3.13 respectively.

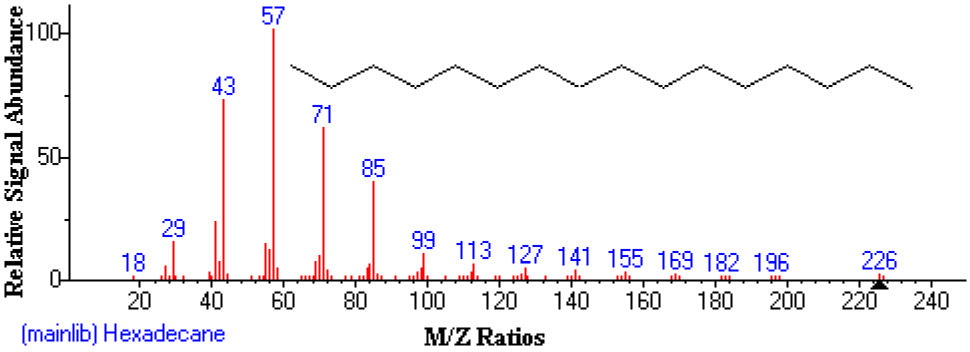


Figure 3.10. Mass spectrum of hexadecane from NIST 2008 mass spectral library.

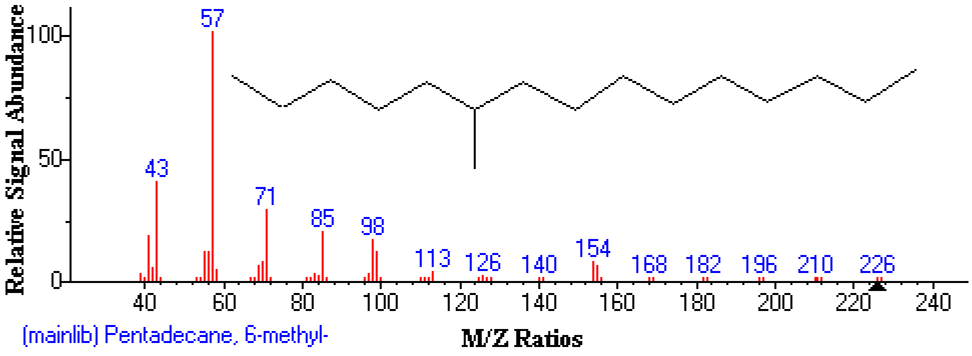


Figure 3.11. Mass spectrum of 6-methylpentadecane from NIST 2008 mass spectral library.

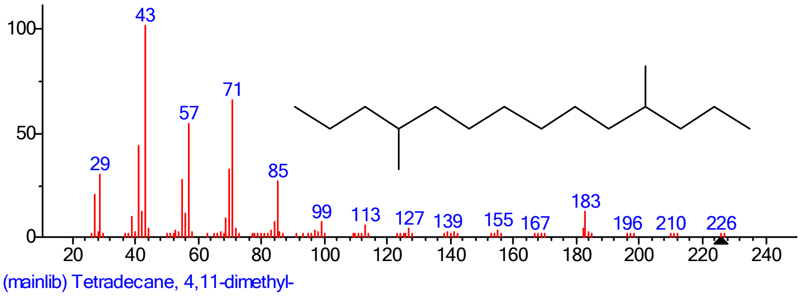


Figure 3.12. Mass Spectrum of 4,11-dimethyltetradecane from NIST 2008 mass spectral library.

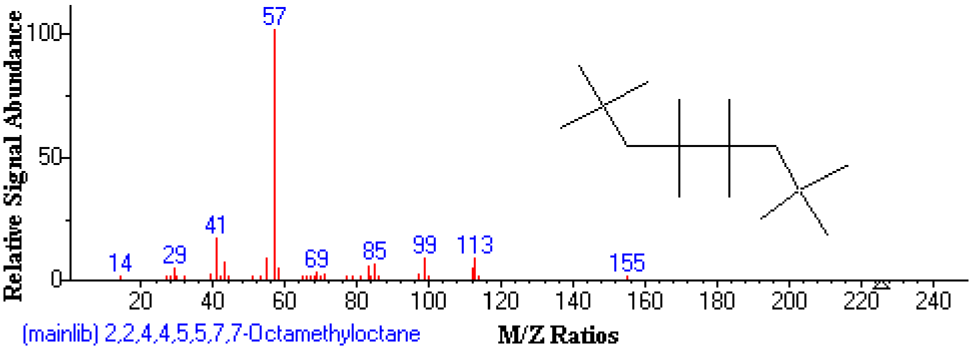


Figure 3.13. Mass spectrum of 2,2,4,4,5,5,7,7-octamethyloctane from NIST 2008 mass spectral library.

In the mass spectrum of hexadecane, the m/z ratio for the parent ion, 226, has a small abundance. As branching increases in 6-methylpentadecane, the abundance decreases slightly and even more so for 4,11-dimethyltetradecane, but as branching becomes much heavier, as in 2,2,4,4,5,5,7,7-octamethyloctane, there is no signal observed for the parent ion as is denoted by the empty triangle below m/z ratio 226. The trend with higher paraffins is also apparent. For hexadecane, the cluster of peaks around m/z ratio 169, 182, and 196 represent the higher paraffinic m/z ratios. Similarly, in 6-methylpentadecane, the clusters around m/z ratios 168, 182, 196, and 210 represent the higher paraffins. Due to the decrease in the more abundant m/z ratios of 43, 71, and 85, the higher paraffinic peaks in 6-methylpentadecane encompass a larger fraction of the total abundance. For a heavily-branched compound like 2,2,4,4,5,5,7,7-octamethyloctane, however, none of these peaks are observed as only larger fragments will come off of the compound.

Of interesting note is that dues to branching, the volatility of compounds change. The branching types were determined because four regimes of elution for compounds of the same carbon number and hydrocarbon type were observed and depended on the branching. Straight chain compounds have the lowest volatility and elute last of a carbon number and hydrocarbon type set. This is due to increased ability of hydrogen bonding among molecules of the hydrocarbon.

Lightly-branched molecules have a slightly higher volatility, eluting before the straight-chain molecule of that carbon number, but after the straight-chain molecule of one carbon number before. In other words, lightly-branched C_{16} molecules will elute after pentadecane, but before hexadecane.

The defined medium-branched compounds elute in the carbon number slice before their carbon number would suggest. Their volatility is higher than that of lightly-branched compounds and they move through the column faster, eluting earlier. This means, medium-branched C_{16} molecules will elute between tetradecane and pentadecane.

Finally, for heavily-branched compounds, elution is observed two slices before their carbon number would suggest. These molecules have great disruption to their hydrogen bonding between molecules and, as a result, have a much higher volatility than their straight-chain parent compounds. Continuing the C_{16} example, its heavily-branched molecules will elute between tridecane and tetradecane.

Using the abundance for each of the higher paraffinic m/z ratios along with the parent ion abundance, it is possible to characterize the branching in paraffins. Obviously, the sum of the mole fractions of straight-chain (T_s), lightly-branched (T_l), medium-branched (T_m), and heavily-branched (T_h) paraffins should equal the total observed paraffin signal, as shown in Equation 12. Additionally, the fraction of the parent ion signal (π) relative to the total paraffin signal (T_p) of the given elution slice (calculated from Equation 8 above) should be a sum of the parent ion fraction expected from straight-chain and lightly-branched compounds only, since medium and heavily-branched compounds do not show the parent ion m/z ratio, as is shown in Equation 13. These expected fractions (σ_s and σ_l for straight-chain and lightly-branched paraffins respectively) are tabulated in Table 3.5A by carbon number.

Similarly, the fraction of the higher paraffinic sum (P_{sum}) relative to the total paraffin signal (T_p) of the given elution slice should be the sum of the fraction expected for straight-chain, lightly-branched, and medium-branched compounds. The expected fractions (φ_s, φ_l, and φ_m for straight-chain, lightly-branched, and heavily-branched compounds respectively) for the higher paraffinic sums are collected in Table 3.5B below. These values were averaged for all carbon numbers because of the close fit of the values.

The last piece of the calculation is the abundance of m/z 57 as a fraction of the $\sum 43$ value. The total signal observed for each type of branching, multiplied by the fraction of its signal that will be from m/z ratio 57 out of the ∑43 total, should add to give the total fraction observed for m/z ratio 57 in ∑43 of the slice. Additionally, the values derived from cycloparaffins and alkylbenzenes are subtracted as they do contribute to m/z 57 and ∑43, as can be seen in Table 3.3.

The expected fractions for straight, light, medium, and heavily-branched compounds (θ_s, θ_l, θ_m, and θ_h) can be found in Table 3.6 below. Using these four equations, Equations 12, 13, 14 and 15, will be used to solve for the four unknown values: T_s, T_l, T_m, and T_h. Solving the four equations simultaneously using a matrix inversion will yield the unknown T values which will be used to solve for the fractional abundance of each type of branching. These values were all calculated from values obtained from the NIST MS database.

$$T_s + T_l + T_m + T_h = T_p \tag{12}$$

$$\sigma_s T_s + \sigma_l T_l = \frac{\pi}{T_p} \tag{13}$$

$$\varphi_s T_s + \varphi_l T_l + \varphi_m T_m = \frac{P_{sum}}{T_p} \tag{14}$$

$$\theta_s T_s + \theta_l T_l + \theta_m T_m + \theta_h T_h = \frac{57}{\sum 43} \tag{15}$$

Table 3.5

Coefficient Values for Parent Ion Fraction (3.5A) and Higher Paraffinic Sum Fraction (3.5B) in Paraffins for Straight-Chain, Lightly-Branched, Medium-Branched, and Heavily-Branched Mole Fraction Determinations in Equations 13 and 14

3.5A

Carbon #	Br. Type	σ	Stdev
10	Straight	0.0134	--
	Light	0.0022	0.0025
11	Straight	0.0088	--
	Light	0.0012	0.0014
12	Straight	0.0116	--
	Light	0.002	0.0022
13	Straight	0.0034	--
	Light	0.0003	0.0007
14	Straight	0.0106	--
	Light	0.0008	0.0009
15	Straight	0.0052	--
	Light	0.0013	0.001
16	Straight	0.0044	--
	Light	0.001	0.0011
17	Straight	0.0083	--
	Light	0.0013	0.0012
18	Straight	0.0161	--
	Light	0.0031	0.0039

3.5B

Br. Type	φ
s	0.0082
l	0.0329
m	0.0108
h	0.0000

Table 3.6

Expected Fractions for m/z 57 to the ∑43 Total in Paraffins by Carbon Number

Slice	Branching	Average
C11	Straight	0.365
	Light	0.293
	Medium	0.376
	Heavy	0.853
C12	Straight	0.349
	Light	0.281
	Medium	0.360
	Heavy	0.817
C13	Straight	0.345
	Light	0.278
	Medium	0.356
	Heavy	0.807
C14	Straight	0.338
	Light	0.272
	Medium	0.349
	Heavy	0.791
C15	Straight	0.333
	Light	0.268
	Medium	0.343
	Heavy	0.779
C16	Straight	0.320
	Light	0.257
	Medium	0.330
	Heavy	0.748

3.4 Other Branching Determinations for Paraffins

While trying to determine a way to quantify branching in paraffins, it was observed that compounds with certain groups hanging off of tertiary or quaternary carbons would generate larger abundances for the m/z ratios corresponding to the loss of that specific group. As a result, there is another way to characterize branching. Since heavily-branched compounds do not show the higher paraffins discussed above, this characterization will only determine types of branching in lightly-branched compounds.

Essentially, if a large abundance is observed for the m/z ratios corresponding to the loss of a propyl group, then the compound being analyzed will have a propyl group hanging off of a tertiary or quaternary carbon. This trend will be used to determine the fraction of lightly-branched compounds with and without methyl groups, ethyl groups, propyl groups, and butyl groups.

From the higher paraffinic sum, m/z ratios for loss of a methyl, ethyl, propyl, and butyl group were used. By separating these m/z ratios based on leaving group, the prevalence of compounds with a given branch type can be determined. The ability to do this is a result of the fact that if an ethyl, propyl, or butyl group (in any formation) hanging off of a tertiary or quaternary carbon in the chain, then these groups will fragment off of the compound with greater frequency than with a straight-chain compound or a compound lacking those leaving groups. The observed signal abundances for the m/z ratios associated with the loss of a methyl group are always zero unless there is a methyl group.

The leaving groups discussed are not just limited to the groups hanging off in the IUPAC name for the compound. For instance, 4-methylundecane, shown in Figure 3.14 would show peaks for the loss of a methyl group m/z ratios since it has a methyl group, but it would also show a larger-than-normal peak when compared to dodecane, shown in Figure 3.15, for the loss of a propyl group m/z ratios because the methyl group is on the “4” position, leaving three carbons hanging off. For dodecane, the fraction of the loss of a propyl abundance is 0.01 while the fraction for the loss of a propyl in 4-methylundecane is 0.04.

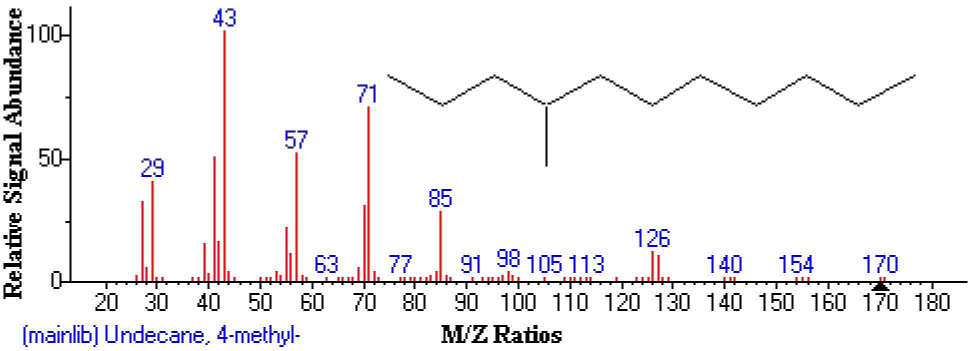


Figure 3.14. Mass spectrum of 4-methylundecane from the NIST 2008 mass spectral library.

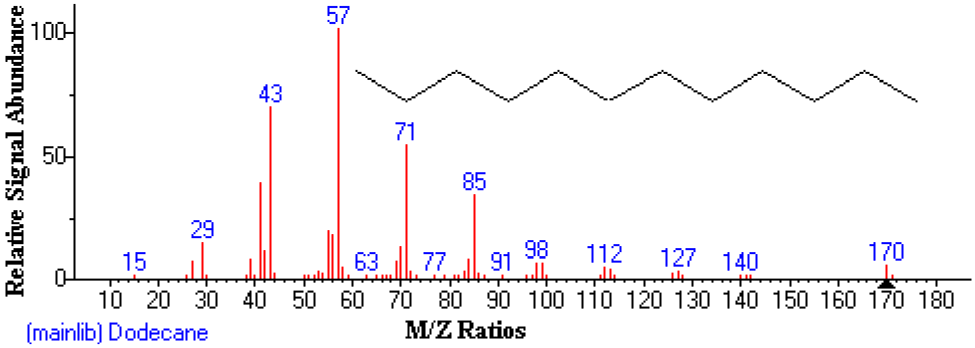


Figure 3.15. Mass spectrum of dodecane from the NIST 2008 mass spectral library.

Using this trend, the fraction of lightly-branched compounds with methyl, ethyl, propyl, and butyl groups can be found. Since heavily-branched compounds do not show these higher paraffins, they do not factor in with Equations 16 through 19 and since straight chain compounds do not have a methyl group in order to give the methyl group signal, straight chain compounds are not included in Equation 16. Equations 16 through 19 use α to represent fractions for straight chain compounds, β to represent fractions for lightly-branched compounds, θ to represent the fraction of lightly-branched compounds with the given branch group, and P to represent the higher paraffin abundance observed for the given branch group. The branch groups are denoted by the subscripts m, e, p, and b to represent methyl, ethyl, propyl, and butyl groups respectively. Additionally, the β terms also have a subscript *0* or *1* to signify whether it is the coefficient for lightly-branched groups without the given branch group (subscript *0*) or with the given branch group (subscript *1*). The x_s and x_l values are the ones obtained from solving Equations 12 through 14 and the T_p values are the ones obtained from Equation 8. Each equation is solved separately to give the θ_n values—the fractions of lightly branched compounds with the given branch group *n*. The coefficient α and β values are displayed in Tables 3.7 and 3.8 respectively.

$$\beta_{m1}[\theta_m x_l] = \frac{P_m}{T_p} \qquad 16$$

$$\alpha_e x_s + [\beta_{e0}(1-\theta_e) + \beta_{e1}\theta_e]x_l = \frac{P_e}{T_p} \qquad 17$$

$$\alpha_p x_s + [\beta_{p0}(1-\theta_p) + \beta_{p1}\theta_p]x_l = \frac{P_p}{T_p} \qquad 18$$

$$\alpha_b x_s + [\beta_{b0}(1-\theta_b) + \beta_{b1}\theta_b]x_l = \frac{P_b}{T_p} \qquad 19$$

Table 3.7

Fractional Abundance Coefficient Values for Higher Paraffinic Branches in Straight-Chain Paraffins

Carbon #	α_e	α_p	α_b
10	0.0137	0.0291	0.0790
11	0.0083	0.0146	0.0238
12	0.0055	0.0116	0.0186
13	0.0010	0.0032	0.0066
14	0.0042	0.0074	0.0114
15	0.0026	0.0046	0.0076
16	0.0022	0.0038	0.0062
17	0.0026	0.0047	0.0081
18	0.0023	0.0041	0.0063

Table 3.8

Fractional Abundance Coefficient Values for Higher Paraffinic Branching Values in Lightly-Branched Paraffins

Carbon #	θ_{m1}	θ_{e0}	θ_{e1}	θ_{p0}	θ_{p1}	θ_{b0}	θ_{b1}
10	0.0032	0.0027	0.0363	0.0081	0.0542	--	--
Stdev	0.0043	0.0036	0.0253	0.0152	0.0399	--	--
11	0.0013	0.0037	0.0189	0.0059	0.0369	0.0061	0.0338
Stdev	0.0017	0.0069	0.0168	0.0137	0.0152	0.0060	0.0150
12	0.0033	0.0018	0.0256	0.0062	0.0303	0.0098	0.0337
Stdev	0.0041	0.0019	0.0182	0.0113	0.0223	0.0129	0.0270
13	0.0013	0.0004	0.0190	0.0024	0.0268	0.0042	0.0272
Stdev	0.0017	0.0009	0.0147	0.0059	0.0207	0.0060	0.0213
14	0.0021	0.0013	0.0235	0.0062	0.0294	0.0027	0.0307
Stdev	0.0016	0.0014	0.0120	0.0088	0.0242	0.0028	0.0037
15	0.0033	0.0024	0.0280	0.0085	0.0288	0.0028	0.0469
Stdev	0.0033	0.0016	0.0278	0.0157	0.0229	0.0028	--
16	0.0034	0.0015	0.0326	0.0049	0.0269	0.0032	0.0188
Stdev	0.0025	0.0016	0.0150	0.0106	0.0189	0.0034	0.0081
17	0.0043	0.0019	0.0226	0.0097	0.0336	0.0026	0.0427
Stdev	0.0044	0.0015	--	0.0189	--	0.0014	0.0385
18	0.0044	0.0028	0.0423	0.0092	0.0734	0.0026	--
Stdev	0.0024	0.0029	--	0.0175	0.0039	0.0023	--

While this methodology seems to be helpful in characterization of types of branching and probably also in degree of branching determinations, it is actually very limited to methyl, ethyl, propyl, and, to a small degree, butyl groups. Essentially, these values became the higher paraffinic branching parameter described above. The reason for this is that as branching increases to a heavily-branched compound, these m/z ratios are no longer seen, even if all the aforementioned branches are methyl groups. This fact did, however, give way to one of the necessary parameters in the branching determination.

CHAPTER 4

Experimental Results

4.1 JP-8 Fuel

During the course of this research, we were fortunate to receive a sample of JP-8 aviation fuel from Angela Surgenor at NASA-GRC. An actual fuel, like JP-8, is far more complex and contains many more compounds than we could reproduce in the lab. As such, samples of JP-8 for the GC-MS were made at 1000ppm instead of the 100ppm used for individual compounds. The same run parameters on the GC-MS were used in order to obtain comparable results. The total ion chromatogram obtained for this run is displayed in Figure 4.1 below. This figure also has the carbon number slices shown, which are a part of the analysis of the fuel. From observation of the TIC, it appears that the fuel favors the straight-chain compounds like undecane, dodecane, etcetera. This is due to the large peaks observed at the right-hand sides of the proposed slices which count as the cutoff before moving into a new carbon number slice.

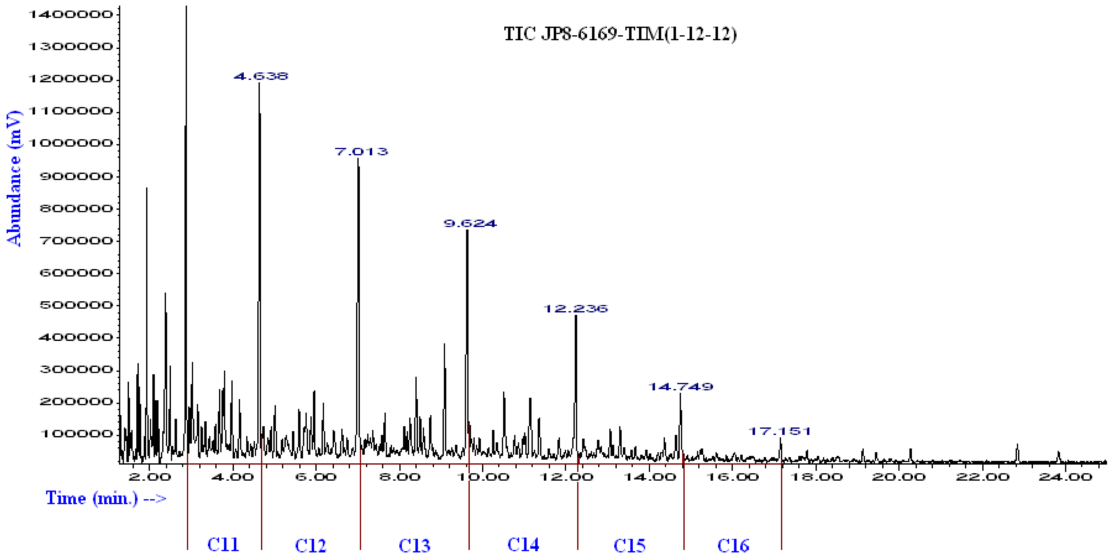


Figure 4.1. Total Ion Chromatogram for JP-8 fuel JP8-6169-TIM(1-12-12) with carbon number slices displayed.

For the analysis, integrations of the carbon number slices were taken from the elution time of decane to undecane to make the C11 slice, undecane to dodecane to make the C12 slice, and so forth. Additionally, a flat section of the chromatogram analyzed at around 30 minutes was taken in order to subtract the baseline from the spectra. Then, the averaged mass spectrum for each slice was obtained and the averaged mass spectrum for the baseline region was subtracted from that.

Using Excel, the hydrocarbon type determination calculation was performed through matrix inversion of the coefficients matrix and multiplication to the summation values obtained from the above mass spectrum. An example calculation is shown below for the C11 slice of the chromatogram. This process was performed for each slice separately.

$$\begin{bmatrix} .497 & .042 & .037 \\ .211 & .706 & .032 \\ .001 & .008 & .678 \end{bmatrix} \begin{bmatrix} Tp \\ Tc \\ Ta \end{bmatrix} = \begin{bmatrix} 1614413371 \\ 1782616146 \\ 35901783 \end{bmatrix} \tag{20}$$

Using the total signals calculated (T_p=3,110,828,430, T_c=1,594,574,230, and T_a=29,109,785 for the C11 slice), a relative number of moles (m) was calculated for each hydrocarbon type in each slice by dividing the total signals T by the mole sensitivity value for that hydrocarbon type in that slice from Table 3.4. For ease of simple numbers to work with, each resulting number of moles was then multiplied by 10^{-3} to give a more manageable, but still relative, number of moles. Continuing with the C11 slice example, this gave relative mole values of $mole_p$=7.484, $mole_c$=3.240, and $mole_a$=0.050.

Then, by adding all the relative moles and dividing each one by the total, the actual mole fraction (m) for each was found. This data is shown in Table 4.1 below.

Table 4.1

Hydrocarbon Type Mole Fraction Data from JP-8 Fuel Analysis

Slice	mole (p)	mole (c)	mole (a)	m (p)	m (c)	m (a)
11	7.484	3.240	0.050	0.695	0.301	0.005
12	4.164	1.775	0.418	0.655	0.279	0.066
13	2.301	1.186	1.441	0.467	0.241	0.292
14	1.272	0.608	1.100	0.427	0.204	0.369
15	0.410	0.218	0.761	0.295	0.157	0.548
16	0.087	0.032	0.157	0.316	0.116	0.568
			Total Fuel Fractions	0.589	0.264	0.147

Next, the degree of branching calculation, described in Section 3.3, was performed using the mass spectral data already obtained. The branching calculation was performed separately for each slice and the data was compiled to give overall fractions. This calculation, however, resulted in large negative values for many of the branching types, so refinement of parameters is necessary.

CHAPTER 5

Conclusions and Future Research

This characterization method is based off of well-established ASTM methods that are able to accurately calculate the hydrocarbon compositions present in a fuel sample. As a result, I have good confidence in composition values obtained for the JP-8 fuel sample above. The more explicit parameters I developed for aviation fuel offered a lack of dependence on both carbon number and branching, which will allow for simpler and more accurate calculation.

Given that the branching determination was new territory, a lot of trial and error went into developing the proposed method and, while it did not work, it will hopefully have laid ground work to refining the parameters for branching so that this may be done with a great degree of accuracy.

Despite the fact that the branching calculation did not work, I believe the parent ion parameter is still a strong parameter for distinguishing the lighter-branched compounds from heavier ones. Perhaps modification of the other two parameters will yield better results for this determination.

Future work for this project will include purchasing additional chemicals so that calculations may be performed over the full range of a possible aviation fuel. Additionally, as discussed above, work must be done on the branching parameters for paraffins to enhance the already established parameters or find new ones that will offer better analysis of the fuel. Additionally, branching parameters should be found for cycloparaffins and alkylbenzenes so that they too can be characterized by this method.

REFERENCES

1. Blakey, Simon; Rye, Lucas; Wilson, Christopher William. *Aviation gas turbine alternative fuels: A review.* Proceedings of the Combustion Institute. 2011. Vol 33. pp 2863-2885.
2. ASTM D1655-13a. *Standard Specification for Aviation Turbine Fuels*. 2013. ASTM International. West Conshohocken, Pennsylvania.
3. *NIST Chemistry WebBook.* NIST Standard Reference Database. www.webbook.nist.gov/chemistry/.
4. Skoog, Douglas A.; Holler, F. James; Crouch, Stanley R. *Principles of Instrumental Analysis*. 6th Edition. 2007. Thomson Brooks/Cole. pp. 281-290.
5. Bansal, V.; Vatsala, S.; Kapur, G. S.; Basu, B.; and Sarpal, A. S. *Hydrocarbon-Type Analysis of Middle Distillates by Mass Spectrometry and NMR Spectroscopy Techniques—A Comparison*. 2004. Energy and Fuels. Vol. 18. pp. 1505-1511.
6. Gill, SS, et al. *Combustion characteristics and emissions of Fisher-Tropsch diesel fuels in IC engines.* Progress in Energy and Combustion Science. 2010. doi:10.1016/j.pecs2010.09.001.
7. Kumabe, Kazuhiro, et al. *Production of hydrocarbons in Fischer-Tropsch synthesis with Fe-based catalyst: Investigations of primary kerosene yield and carbon mass balance.* Fuel. 2010. Vol. 89. pp. 2088-2095.
8. Huffman, Gerald P. *Incorporation of catalytic dehydrogenation into Fischer-Tropsch synthesis of liquid fuels from coal to minimize carbon dioxide emissions.* Fuel. 2011. doi:10.1016/j.fuel.2011.03.001.
9. UOP. *Opportunities for Biorenewables in Oil Refinieries. Appendix: Background and Experiment Summary.* Prepared for DOE.

10. ASTM International. *Evaluation of Bio-Derived Synthetic Paraffinic Kerosenes (Bio-SPKs)*. Research Resport D02-1739. 2011. Committee D02 on Petroleum Products and Lubricants. Subcommittee D02.J0.06 on Emerging Turbine Fuels.

11. ASTM D2789-95. *Standard Test Method for Hydrocarbon Types in Low Olefinic Gasoline by Mass Spectrometry*. 2011. ASTM International. West Conshohocken, Pennsylvania.

12. ASTM D2425-04. *Standard Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry.* 2009. ASTM International. West Conshohocken, Pennsylvania.

APPENDIX

A.1 Paraffins in the Database

decane
3-ethyloctane
5-methylnonane
4-propylheptane
4-ethyloctane
3-methylnonane
4-methylnonane
2-methylnonane
3,5-dimethyloctane
3-ethyl-3-methylheptane
3,6-dimethyloctane
4,4-dimethyloctane
3,4-dimethyloctane
2,3-dimethyloctane
2,2-dimethyloctane
4,5-dimethyloctane
5-ethyl-2-methylheptane
3,4-diethylhexane
3-ethyl-4-methylheptane
3-ethyl-2-methylheptane
3-ethyl-5-methylheptane
2,7-dimethyloctane
4-isopropylheptane
3,3-dimethyloctane
2,5-dimethyloctane
2,6-dimethyloctane
2,5,5-trimethylheptane
3,4,5-trimethylheptane
3,3,4-trimethylheptane
4-ethyl-2,2-dimethylhexane
2,4,6-trimethylheptane
3-ethyl-2,5-dimethylhexane
2,2,4-trimethylheptane
2,3,5-trimethylheptane
3,3,5-trimethylheptane
2,3,6-trimethylheptane
2,3,4-trimethylheptane
2,3-dimethylundecane
2,8-dimethylundecane
3,4-dimethylundecane
4,4-dipropylheptane
2,10-dimethylundecane
3,7-dimethylundecane
3,6-dimethylundecane
3,5-dimethylundecane
5,7-dimethylundecane
4,6-dimethylundecane
4,7-dimethylundecane
3,8-dimethylundecane
6-ethyl-2-methyldecane
4,4-dimethylundecane
4-methyl-5-propylnonane
2,2-dimethylundecane
2,7-dimethylundecane
5-methyl-5-propylnonane
3,3-dimethylundecane
5,5-dimethylundecane
3,9-dimethylundecane
5-isobutylnonane
5-(1-methylpropyl)nonane
2,5-dimethylundecane
3,3,4-trimethyldecane
2,3,4-trimethyldecane
2,5,6-trimethyldecane
2,2,4-trimethyldecane
2,2,3-trimethyldecane
2,2,8-trimethyldecane
2,4,6-trimethyldecane
2,5,9-trimethyldecane
2,2,5-trimethyldecane
2,3,6-trimethyldecane
2,2,6-trimethyldecane
2,3,7-triemthyldecane
2,2,7-trimethyldecane

2,2,5,5-tetramethylhexane
3,3,4,4-tetramethylhexane
2,2,3,3-tetramethylhexane
undecane
2-methyldecane
3-methyldecane
4-methyldecane
5-methyldecane
6-ethyl-2-methyloctane
2,5-dimethylnonane
2,6-dimethylnonane
5-ethyl-2-methyloctance
4,5-dimethylnonane
3,7-dimethylnonane
2,3-dimethylnonane
2,5,6-trimethyloctance
2,3,3-trimethyloctane
2,2,6-trimethyloctane
2,3,7-trimethyloctane
2,4,6-trimethyloctane
2,6,6-trimethyloctane
2,3,6-trimethyloctane
2,2,3,5-tetramethylheptane
2,2,6,6-tetramethylheptane
Dodecane
4-methylundecane
6-methylundecane
3-methylundecane
2-methylundecane
5-methylundecane
5-ethyldecane
4-ethyldecane
5-propylnonane
2,3-dimethyldecane
3,7-dimethyldecane
3,8-dimethyldecane
2,2-dimethyldecane
2,6-dimethyldecane
2,4-dimethyldecane
3,4-dimethyldecane
2,5-dimethyldecane
2,6,6-trimethyldecane
2,2,9-trimethyldecane
2,6,7-trimethyldecane
2,6,8-trimethyldecane
2,8,8-trimethyldecane
2,3,5-trimethyldecane
3,3,5-trimethyldecane
3,3,6-trimethyldecane
3,3,8-trimethyldecane
2,3,8-trimethyldecane
4-ethyl-2,2,6,6-tetramethylheptane
tetradecane
3-methyltridecane
7-methyltridecane
6-methyltridecane
4-methyltridecane
2-methyltridecane
5-methyltridecane
4,5-dipropyloctane
2,4-dimethyldodecane
2,5-dimethyldodecane
2,3-dimethyldodecane
3,5-dimethyldodecane
4,6-dimethyldodecane
2,3,5,8-tetramethyldecane
2,2,3,3,5,6,6-heptamethylheptane
pentadecane
4-methyltetradecane
3-ethyltridecane
2-methyltetradecane
3-methyltetradecane
5-methyltetradecane
2,5-dimethyltridecane
4,8-dimethyltridecane
2,7,10-trimethyldodecane
2,6,10-trimethyldodecane
2,6,11-trimethyldodecane
hexadecane
5-propyltridecane
6-methylpentadecane
4-ethyltetradecane

5,6-dimethyldecane
3,6-dimethyldecane
2,9-dimethyldecane
4-ethyl-5-methylnonane
4,5-diethyloctane
2,2,3-trimethylnonane
3-ethyl-2,7-dimethyloctane
2,3,6,7-tetramethyloctane
3,4,5,6-tetramethyloctane
5-ethyl-2,2,3-trimethyl
2,2,7,7-tetramethyloctane
2,2,4,4-tetramethyloctane
2,2,4,6,6-pentamethylheptane
tridecane
6-ethylundecane
5-propyldecane
4-methyldodecane
6-methyldodecane
3-methyldodecane
3-ethylundecane
2-methyldodecane
5-ethylundecane
4-ethylundecane
5-methyldodecane
5-butylnonane
4,8-dimethylundecane
2-methyl-5-propylnonane
5,6-dimethylundecane
3-methyl-5-propylnonane
5-ethyl-5-methyldecane
2,6-dimethylundecane
6,6-dimethylundecane
3-ethyl-3-methyldecane
2,4-dimethylundecane
2,9-dimethylundecane
4,5-dimethylundecane
7-propyltridecane
6-propyltridecane
3-methylpentadecane
7-methylpentadecane
2-methylpentadecane
4-methylpentadecane
5-methylpentadecane
4,11-dimethyltetradecane
5,6-dipropyldecane
5-ethyl-5-propylundecane
2,2-dimethyltetradecane
6,9-dimethyltetradecane
2,5-dimethyltetradecane
5,8-diethyldodecane
2-methyl-8-propyldodecane
2-methyl-6-propyldodecane
2,2,11,11-tetramethyldodecane
2,2,4,4,6,8,8-heptamethylnonane
2,2,4,4,5,5,7,7-octamethyloctane
heptadecane
4-methylhexadecane
7-methylhexadecane
3-methylhexadecane
2-methylhexadecane
5,5-dibutylnonane
2,6,10-trimethyltetradecane
octadecane
7-methtylheptadecane
4-methylheptadecane
2-methylheptadecane
8-methylheptadecane
3-methylheptadecane
7,9-dimethylhexadecane
4,9-dipropyldodecane
2,6,10-trimethylpentadecane
3,4-di-t-butyl-2,2,5,5-tetramethylhexane

A.2 Cycloparaffins in the Database

butylcyclohexane
(2-methylpropyl)cyclohexane
1,4-diethylcyclohexane
1,2-diethylcyclohexane
1-methyl-2-propylcyclohexane
1-methyl-3-propylcyclohexane
(1-methylpropyl)cyclohexane
1-tbutylcyclohexane
1-ethyl-1,3-dimethylcyclohexane
1-ethyl-1,4-dimethylcyclohexane
1-ethyl-1,4-dimethylcyclohexane
1-ethyl-2,3-dimethylcyclohexane
1-ethyl-2,4-dimethylcyclohexane
1-methyl-3-isopropylcyclohexane
1-isopropyl-methylcyclohexane
1-isopropyl-4-methylcyclohexane
2-ethyl-1,3-dimethylcyclohexane
1-ethyl-1,3-dimethylcyclohexane
1,1,3,5-tetramethylcyclohexane
1,1,4,4-tetramethylcyclohexane
1,1,2,3-tetramethylcyclohexane
1,1,3,5-tetramethylcyclohexane
pentylcyclopentane
(1-methylbutyl)cyclopentane
1,2,3,4,5-pentamethylcyclopentane
(2-methylbutyl)cyclopentane
2-isopropyl-1,3-dimethylcycopentane
1-methyl-3-(2-methylpropyl)cyclopentane
(3-methylbutyl)cyclopentane
1,1-dimethyl-2-propylcyclohexane
pentylcyclohexane
1-t-butyl-4-methylcyclohexane
2-methylbutylcyclohexane
1,1,3,3,5-pentamethylcyclohexane
1,2-dimethylpropylcyclohexane
1-ethyl-2,2,6-trimethylcyclohexane
1-ethylpropylcyclohexane
1,1-dimethylpropylcyclohexane
2,4-diethyl-1-methylcyclohexane
1-isobutyl-2,5-dimethylcyclohexane
2-propyl-1,1,3-trimethylcyclohexane
1,5-diethyl-2,3-dimethylcyclohexane
1,3-diisopropylcyclohexane
1,4-diisopropylcyclohexane
1,4-dimethyl-2-isobutylcyclohexane
1-isopropyl-1,4,5-trimethylcyclohexane
1-methyl-2-(4-methylpentyl)cyclopentane
1-methyl-2-(4-methylpentyl)cyclohexane
1-hexyl-3-methylcyclopentane
1-butyl-2-propylcyclopentane
heptylcyclohexane
2-butyl-1,1,3-trimethyl
3,3-dimethylpentylcyclohexane
1,2,2-trimethylbutylcyclohexane
1-ethyl-2-(4-methylpentyl)cyclohexane
3-hexyl-1,1-dimethylcyclopentane
1-pentyl-2-propylcyclopentane
1,2-dibutylcyclopentane
octylcyclohexane
(1-methylheptyl)cyclohexane
1,2,4,5-tetraethylcyclohexane
2,4-diisopropyl-1,4-dimethylcyclohexane
1,4-ditbutylcyclohexane
1,5-diisopropyl-2,3-dimethylcyclohexane
1-butyl-2-pentylcyclopentane
nonylcyclopentane
nonylcyclohexane
1,1,3-trimethyl-2-(3-methylpentyl)cyclohexane
1-(1,5-dimethylhexyl)-4-methylcyclohexane
decylcyclopentane
decylcyclohexane
(1-methylnonyl)cyclohexane
(1-propylheptyl)cyclohexane
(1-butylhexyl)cyclohexane
(1-ethyloctyl)cyclohexane
1-methyl-3-nonylcyclohexane
1,2-dimethyl-3pentyl-4-propylcyclohexane
undecylcyclopentane

1-ethyl-2-propylcyclohexane
1-methylbutylcyclohexane
1,2-diethyl-1-methylcyclohexane
1,2-diethyl-3-methylcyclohexane
1,2-dipropylcyclopentane
1-butyl-2-ethylcyclopentane
hexylcyclopentane
hexylcyclohexane
(3-methylpentyl)cyclohexane
1-methyl-2-pentylcyclohexane
1-methyl-3-pentylcyclohexane
(4-methylpentyl)cyclohexane
1-methyl-4-(1-methylbutyl)cyclohexane
3-ethyl-5-methyl-1-propylcyclohexane
(1,2-dimethylbutyl)cyclohexane
(1,3-dimethylbutyl)cyclohexane
1,3-dimethyl-5-isobutylcyclohexane
undecylcyclohexane
1-ethylnonylcyclohexane
1-butylheptylcyclohexane
1-pentylhexylcyclohexane
1-methyldecylcyclohexane
1-propyloctylcyclohexane
dodecylcyclohexane
(1-butyloctyl)cyclohexane
(1-pentylheptyl)cyclohexane
(1-methylundecyl)cyclohexane
(1-ethyldecyl)cyclohexane
(1-propylnonyl)cyclohexane
1,3-dihexylcyclohexane
1,3-dimethyl-5-decylcylohexane
1,3-dimethyl-1(3,7-dimethyloctyl)cyclohexane
1,2,3,4,5,6-hexaethylcyclohexane
1,2,3,5-tetraisopropylcyclohexane

A.3 Alkylbenzenes in the Database

butylbenzene
1,4-diethylbenzene
1,3-diethylbenzene
(2-methylpropyl)benzene
(1-methylpropyl)benzene
1-methyl-3-propylbenzene
1-methyl-4-propylbenzene
1-methyl-2-propylbenzene
1,2-diethylbenzene
1-ethyl-3,5-dimethylbenzene
tert-butylbenzene
1-methyl-2-isopropylbenzene
2-ethyl-1,3-dimethylbenzene
1-methyl-4-isopropylbenzene
1-ethyl-2,3-dimethylbenzene
4-ethyl-1,2-dimethylbenzene
2-ethyl-1,4-dimethylbenzene
1-ethyl-2,4-dimethylbenzene
1-methyl-3-isopropylbenzene
1,2,3,4-tetramethylbenzene
1-methyl-4-hexylbenzene
1-methyl-2-hexylbenzene
1-methylhexylbenzene
1-methyl-3-hexylbenzene
1,1-diethylpropylbenzene
2,4-dimethylpentylbenzene
1-isoproyl-3-t-butylbenzene
1-t-butyl-3-ethyl-5-methylbenzene
1-ethyl-2,3,4,5,6-pentamethylbenzene
1,2,3,4-tetramethyl-5-isopropylbenzene
octylbenzene
(1-propylpentyl)benzene
(1-methylheptyl)benzene
(1-ethylhexyl)benzne
5-methylheptylbenzene
1-(1-ethylpropyl)-4-propylbenzene
1-(1-ethylpropyl)-2-propylbenzene
1,2,4,5-tetraethylbenzene
1,3-bis(1-methylpropyl)benzene
1-ethyl-3,5-diisopropylbenzene

1,2,3,5-tetramethylbenzene
1,2,4,5-tetramethylbenzene
pentylbenzene
(3-methylbutyl)benzene
(1-methylbutyl)benzene
(1-ethylpropyl)benzene
(2-methylbutyl)benzene
1-ethyl-4-isopropylbenzene
(1,2-dimethylpropyl)benzene
1-ethyl-3-isopropylbenzene
(2,2-dimethylpropyl)benzene
1-methyl-4-isobutylbenzene
1-methyl-4-(1-methylpropyl)benzene
2,4-diethyl-1-methylbenzene
1,4-diethyl-2-methylbenzene
(1,1-dimethylpropyl)benzene
1,3-diethyl-5-methylbenzene
1,3-dimethyl-5-isopropylbenzene
1-(1,1-dimethylethyl)-3-methylbenzene
1-methyl-4-tertbutylbenzene
1-methyl-2-tertbutylbenzene
2,4-dimethyl-1-isopropylbenzene
1-ethyl-2,4,5-trimethylbenzene
1,4-dimethyl-2-isopropylbenzene
1,2,3,4,5-pentamethylbenzene
hexylbenzene
(2-ethylbutyl)benzene
(1-methylpentyl)benzene
1,4-dipropylbenzene
(1-ethylbutyl)benzene
2-methylpentylbenzene
(3-methylpentyl)benzene
1,3,5-triethylbenzene
1,2,4-triethylbenzene
(1-ethyl-1-methylpropyl)benzene
(1,3-dimethylbutyl)benzene
(2,2-dimethylbutyl)benzene
1-(1-ethylpropyl)-4-methylbenzene
1-methyl-2-(1-ethylpropyl)benzene
1-ethyl-4-(2-methylpropyl)benzene
(1,1-dimethylbutyl)benzene
1-(3-Methylbutyl)-2,3,6-trimethylbenzene
1-(3-Methylbutyl)-2,3,4-trimethylbenzene
1-isopentyl-2,4,5-trimethylbenzene
1-(3-Methylbutyl)-2,4,6-trimethylbenzene
1-(3-Methylbutyl)-2,3,5-trimethylbenzene
1-(2,2-dimethylpropyl)-2,4,5-trimethylbenzene
1,3-ditertbutylbenzene
1,4-ditertbutylbenzene
1,2-diethyl-3,4,5,6-tetramethylbenzene
1,4-diethyl-2,3,5,6-tetramethylbenzene
1,3-diethyl-2,4,5,6-tetramethylbenzene
1-methyl-3-isopropyl-5-tertbutylbenzene
1,4-dimethyl-2,5-diisopropylbenzene
1,5-dimethyl-2,4-diisopropylbenzene
nonylbenzene
1-(1,5-dimethylhexyl)-4-methylbenzene
1-butylpentylbenzene
(1-methyl-2-propylpentyl)benzene
1,3-di-t-butyl-5-methylbenzene
1,3,5-triisopropylbenzene
1,2,4-tripropylbenzene
(1-methyl-1-propylpentyl)benzene
1-(3-methylbutyl)-2,3,4,5-tetramethylbenzene
1-(3-methylbutyl)-2,3,5,6-tetramethylbenzene
1,2,4,5-tetramethyl-3-(2,2-dimethylpropyl)benzene
1-(3-methylbutyl)-2,3,4,6-tetramethylbenzene
(1-ethylheptyl)benzene
(5-methyloctyl)benzene
2-methyloctylbenzene
decylbenzene
(1-propylheptyl)benzene
(1-butylhexyl)benzene
(1-methylnonyl)benzene
(1-ethyloctyl)benzene
1,4-bis(1-ethylpropyl)benzene
para-ditertpentylbenzene
(1,2-ditertbutylethyl)benzene
(1-propyloctyl)benzene
(1-methyldecyl)benzene
(1,1-dimethylnonyl)benzene
(1-pentylhexyl)benzene

(3,3-dimethylbutyl)benzene
1-tertbutyl-4-ethylbenzene
1,4-dimethyl-2-(2-methylpropyl)benzene
1,3,5-trimethyl-2-propylbenzene
2,4-dimethyl-1-(1-methylpropyl)benzene
1,2-diisopropylbenzene
1,4-diisopropylbenzene
1,2-diethyl-3,4-dimethylbenzene
(1,2,2-trimethylpropyl)benzene
(1,1,2-trimethylpropyl)benzene
1,3-diisopropylbenzene
1-tertbutyl-3-ethylbenzene
1-tertbutyl-3,5-dimethylbenzene
3-ethyl-1,2,4,5-tetramethylbenzene
1,2,4-trimethyl-5-isopropylbenzene
1,2-dimethyl-4-tertbutylbenzene
1,2,3,4,5,6-hexamethylbenzene
heptylbenzene
(2-methyl-1-(1-methylethyl)propyl)benzene
1-propylbutylbenzene
1-methyl-3,5-diisoproylbenzene
2-methyl-1,4-diisopropylbenzene
5-t-butyl-1,2,3-trimethylbenzene
(1-ethylnonyl)benzene
(1-butylheptyl)benzene
undecylbenzene
dodecylbenzene
(1-propylnonyl)benzene
(1-butyloctyl)benzene
(1-methylundecyl)benzene
(1-pentylheptyl)benzene
(1-ethyldecyl)benzene
1,2,4-tributylbenzene
(3,3-dimethyldecyl)benzene
(2,3-dimethyldecyl)benzene
(1,1-dimethyldecyl)benzene
(9,9-dimethyldecyl)benzene
1,3,5-tributylbenzene
(1,3,3-trimethylnonyl)benzene
1,4-dimethyl-2-(3,7-dimethyloctyl)benzene
1-(1,2,2-trimethylpropyl)hexylbenzene
(1,1,4,6,6-pentamethylheptyl)benzene
1,3,5-tris(1-methylpropyl)benzene
1,2,3,4,5,6-hexaethylbenzene
1,2,4,5-tetraisopropylbenzene
1,3,5-tritertbutylbenzene

A.4 Chemicals Purchased for Analysis

Paraffins
Decane
Dodecane
2,2,4,4,6,8,8-heptamethylnonane
2,6,10-trimethyldodecane
Tetradecane
Pentadecane
3-ethyltetradecane
Hexadecane

Cycloparaffins
Isobutylcyclohexane
Butylcyclohexane
Pentylcyclohexane
1,3-diisopropylcyclohexane
Heptylcyclohexane

Alkylbenzenes
Butylbenzene
1,4-di-tert-butylbenzene
Octylbenzene
Decylbenzene