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DETAILED CHARACTERIZATION OF PHYSICAL AND CHEMICAL PROPERTIES OF CELLULOSIC GASOLINE AND CELLULOSIC GASOLINE STOCKS

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Detailed Characterization of Physical and Chemical Properties of Cellulosic Gasoline and Cellulosic Gasoline Stocks

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Introduction

In 2010 CRC published its first work focused on advanced methods of analyzing diesel fuel **[1]**. In the following three years two more CRC publications on the detailed characteristics of advanced and reformulated diesel fuels were also released to the public **[2,3]**. These three works showed that both multidimensional GC and NMR techniques could provide a more nuanced and insightful description of diesel fuel than is possible with standard methods, with attendant implications for both diesel production and combustion. It seemed likely that these techniques would shed a similar light on gasoline composition relative to the higher-level view provided by the tried and true ASTM standard methods.

In order to extract additional value from the project, the Advanced Vehicle/Fuel/Lubricants Committee (AVFL) decided to try these techniques with cellulosic-sourced gasoline and gasoline blend stocks. There are several reasons for this. The literature on the composition of cellulosic gasoline or blend stocks is sparse and because cellulosic fuels are developing rapidly, the details of the likely composition of such fuels has changed concomitantly. However, as the cellulosic fuels approach market readiness the composition of the fuel and the list of possible impurities should be increasingly stable. Consequently, the risk of data taken now being outdated in a year or two is diminished. On the other hand, by taking a more detailed look at the fuels and blend stocks just prior to large scale commercialization, the data may be of greater use to both suppliers and purchasers because there is still time to tune the final product to one that optimizes resource use and meets user’s needs.

Initially AVFL intended to study ethanol samples, but in seeking such samples it was discovered that many potential suppliers were using processes that took the cellulosic feedstock and produced hydrocarbon blending stocks or even gasoline. One might imagine from this trend that the business model for producing cellulosic fuel may be evolving toward drop-in stocks, or stocks that can be tuned to some extent so that they meet purchasers’ needs. For both cellulosic ethanol and more refined stocks the detailed composition is useful, but the presence and nature of unanticipated impurities may have equal importance. We hoped to gain better insights into both aspects of cellulosic fuels and stocks by use of advanced analysis techniques.

In addition to one distillate in the jet fuel range that was studied to complete the original AVFL-19 report, in AVFL-19a several hydrocarbon samples from different raw material sources were evaluated as well as one cellulosic ethanol sample. The hydrocarbon samples were 3 naphthas (referred to as Naphtha 1 – Naphtha 3 in this report), a wood derived gasoline (referred to as Woody Biomass Gasoline in this report), and a heavier distillate-like sample from a biological source material (referred to as cellulosic jet fuel in this report). One sample was an algal lipid-derived naphtha that is a by-product of renewable diesel/jet production while the others were derived from other lipid sources. In both cases hydrotreatment and isomerization techniques were used to form the final product. The Woody Biomass Gasoline was created by gasifying wood to syngas using two steps: conversion of syngas to a mixture of methanol and dimethyl ether (DME) followed by conversion to all-hydrocarbon gasoline. Because the suppliers of these samples are naturally cautious at this early phase in their business creation, no further details of the source materials or processing routes or identification is provided.

In this report the character and impurities of these samples will be studied using standard ASTM techniques, advanced GC methods, and NMR techniques. We will seek to compare or contrast the results possible with each method, and also provide as much information as possible about the nature of the samples themselves. As you will see, these advanced techniques provide fascinating insights that are complementary to the valuable information provided in ASTM testing, insights that may allow for optimizing the value of the fuel or blend stock, and possibly in understanding and capitalizing on the combustion properties in modern engines.

Methods

All standard testing was done according to ASTM methods. Five labs participated in generating the data, though not every lab tested every sample in each standard test. ASTM tests were conducted by (alphabetically) BP, Chevron, General Motors, and Phillips 66 and additionally Southwest Research Institute (SwRI) performed standard tests under contract to CRC. The National Renewable Energy Laboratory performed simulated distillation (simdist) by ASTM Method D2887.

In addition to these standard tests, gas chromatography (GC) was conducted at Chevron, Canmet Energy, GM, and Phillips 66. The labs analyzed their samples without prior knowledge of the fuel origin, except that they came from generally cellulosic sources. GM performed GC tests using an Agilent 6890 instrument with FID and mass spectroscopy equipped with a pre-column and 100m column, and separately a 19095Z-623, HP-1, 30m column. Phillips 66 used an Agilent 6890 with an HP-TCEP packed column and a Restek RTX-1 column for oxygenate testing and an Agilent 7890 with a 40m Agilent column or an SGE 10m column for other GC tests. Also, 2D multidimensional gas chromatography was conducted by Chevron on the jet fuel sample. This analysis was conducted with a LECO Pegasus IV instrument equipped with both a time-of-flight mass spectrometer (TOFMS) and a flame ionization detector (FID). Both the TOFMS and FID systems were run under the same conditions to allow both qualitative and quantitative analysis. A 40 m x 0.18 mm x 0.2μm Restek RTX-1 column was used for the separation in the first dimension, which enables a quasi-boiling point separation. The complimentary group-type second dimension separation was achieved using a 1.8m x 0.1mm x 0.1 μm SGE BPX-50 column.

All NMR analysis was conducted exclusively at Pacific Northwest National Laboratory (PNNL). Carbon-type analysis from ^{1}H and ^{13}C{^{1}H} Nuclear Magnetic Resonance spectroscopy (NMR)[†] was performed on the three naphtha samples and the

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[†] To avoid confusion in this document, ^{13}C{^{1}H} will be the symbol used to represent "^{13}C NMR spectroscopy." ^{13}C{^{1}H} is the appropriate symbol for the proton-decoupled ^{13}C NMR experiment performed in this study. By running the experiment as ^{1}H decoupled, we improve the ^{13}C NMR signal-to-noise ratio by preventing each carbon signal from being split by attached protons, as well as reduce the signal complexity that would result from that splitting. The ^{1}H-coupled signals of a ^{13}C NMR would be largely unintelligible for a complex mixture, making interpretation of the ^{13}C spectrum either much more difficult or impossible.

gasoline sample. Spectral range assignments and interpretation of NMR results are based on ranges and methods presented by Altgelt and Boduszynski **[4]**. Further details of the methods used are available in references **1-3**.

All quantitative ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were acquired at 499.67 and 125.65 MHz, respectively, on a Varian Inova System. All spectra were recorded at 25.0°C in 5 mm outer diameter NMR tubes, spinning at 20 Hz. Spectra were processed using analysis tools from Varian VNMRJ Version 2.2 Revision D software, or MestReNova Version 8.1.0-11315 software.

Quantitative $^{13}C\{^{1}H\}$ spectra were acquired using a 45° observe pulse; acquisition and relaxation delay times of 3 and 5 seconds, respectively, with ^{1}H Waltz decoupling during the acquisition delay period for nuclear Overhauser enhancement (NOE) suppression; and 0.05 M $Cr(acac)_3$ for T_1 reduction and quenching of any residual NOE, where acac is $CH_3C(O)CHC(O)CH_3$. These conditions lead to an average integral uncertainty of about ±2 percent (in carbon aromaticity). $^{13}C\{^{1}H\}$ spectra are referenced to internal $CDCl_3$ (77.16 ppm)**[5]** or tetramethylsilane (0 ppm). Samples consisted of 0.20 mL of fuel diluted to 1.00 mL in $CDCl_3$ with 0.05 M $Cr(acac)_3$. Spectra resulted from 1,500–6,000 scans. Line broadening of 2.5 Hz was used for processing spectra to improve the signal-to-noise ratio. Quantitative results were obtained by integrating each sample spectrum on two or three separate occasions to account for variation in phasing and baseline correction approaches. Results are presented as normalized averages of the integrated area for each spectral region.

Quantitative ^{1}H spectra were acquired using a 30° observe pulse, with acquisition and relaxation delays of 3 and 8 seconds, respectively, for an 11-second recycle time. Samples consisted of about 50 mg of fuel diluted to 1.00 mL in $CDCl_3$. Addition of $Cr(acac)_3$ did not change the integration values for the proton NMR, although $Cr(acac)_3$ did affect the spectral resolution and was therefore not used in recording these spectra. Measured proton ratios are relatively insensitive to conditions as long as recycle times are kept above about 5 seconds. Chemical shifts are referenced to internal tetramethylsilane (0 ppm) or to internal residual $CHCl_3$ in solvent $CDCl_3$ (7.26 ppm).**[5]** Spectra resulted from 128 scans. Line broadening was not used. Quantitative results were obtained from single integrations of each spectrum.

Because of the rapid relaxation of the hydrogen atom from an excited state to the ground state, ^{1}H NMR is considered quantitative by nature. For many reasons described elsewhere,**[6]** this is not the case for $^{13}C\{^{1}H\}$ NMR, where differences in the carbon relaxation rates, based upon the identities of the atoms bound to the relaxing carbon, require modifications to both sample handling and data acquisition (*vide infra*). Even so, in order to balance experimental time with quantitation, reductions in quantitative accuracy, particularly for carbonyl carbons and quaternary carbons, are considered acceptable.

Quaternary carbons may not be observed directly in the ^{1}H NMR because they have no attached protons. In the $^{13}C\{^{1}H\}$ NMR they are difficult to verifiably quantitate because of long relaxation times and the lower efficacy of paramagnetic relaxation agents, and because they are considered to make up a very small portion of the overall carbon population, small quantitation differences are not likely to significantly impact the overall carbon-type analysis, so some loss in quantitation can be acceptable.

Results

Standard analysis:

A suite of standard ASTM tests was conducted by multiple labs to provide the standard high level analysis of the samples. Tables 1- 5 provide the compiled results. For each type of test the average value follows the data for each sample in cases where the data are numeric and two or more values are present. Standard deviation is included in parenthesis where three or more values are present. It should be borne in mind that the standard deviation includes test-to-test and lab-to-lab measurement errors, and furthermore this is a very small data set, so the value is best used qualitatively. In general the data are reasonably precise, with standard deviations in Table 1 less than or equal to 1.6% of the mean value. An exception is the vapor pressure value where the standard deviation is 2 to 45% of the mean, largely because the vapor pressures are quite low and the reproducibility approaches the value of the measurement. The standard deviation, where it can be obtained, is 1/3-psi or less which is good given that lab-to-lab variation and test-to-test variation.

All three naphthas are low octane (RON ≤61), but the gasoline sample is fairly normal with an octane of 87.1 (R+M)/2 and a Class E-like vapor pressure of 14.5 psi. Only the Jet fuel has an unusual density or API gravity relative to the other samples, as would be expected.

Tables 2 and 3, respectively, list the individual lab D86 analysis results and the average results (with standard deviation). Standard deviations for individual temperature points are below 7% and generally below 2%. Again with only three values these are only a qualitative affirmation that there is no particular concern about error or variability in these data. Clearly Naphthas 1 and 2 have much lighter front end volatility than Naphtha 3, but Naphtha 2 has some very heavy material in the last 5% evaporated. The three naphtha samples are each distinctly different, with Naphtha 1 having a boiling range not unlike gasoline, Naphtha 3 having a boiling range that starts at a temperature characteristic of a less volatile T50 point and ending like an average gasoline, and Naphtha 2 starting distillation like gasoline but ending at even higher temperatures than the sample intended for jet fuel. The data is also presented graphically in Figure 1. There are no unusual flat spots in the distillation curves. Two laboratories attempted to perform the ASTM D86 distillation on the Woody Biomass Gasoline sample. The data are not reported because the total sample recoveries were too low. Most likely this is a result of the very rapid flashing-off of the light compounds at the start of the test. The presence of these light compounds is consistent with the high vapor pressure and the detailed hydrocarbon analyses (discussed later) obtained for this sample. One of the labs also reported a residue in the condenser section of their equipment.

ASTM D2887 Simdist analyses of the Woody Biomass Gasoline were conducted by NREL. Those results are listed in Table 4 and the appendix. The results are also shown in figure 2 along with a reference CBOB, and the D2887 simulated distillation of the Naphthas, performed at Phillips 66.

Table 5 lists the data on other properties of the samples of frequent interest such as sulfur content or aromatics content. In general the standard deviations are 1 or 2 percent of the mean, with the exception of the elemental analysis of Naphtha 1 where the standard deviation is as much as 7% of the mean. This is due to one lab having substantially lower values, and notably the percent hydrogen plus the percent carbon add

Table 1 Summary High level Data for AVFL-19a Fuels

Specific Tests: Fuel:	**Naphtha 1**	**Naphtha 2**	**Naphtha 3**	**Woody Biomass Gasoline**	**Cellulosic Jet Fuel**
Research Octane Number (RON) (ASTM D2699):					
-Lab 1	<40	61.0	<40	91.4	<40
-Lab 4	<40	61.1	<40	91.4	<40
-Lab 5	34.3[#]	60.2	15.3[#]		
-Average (Standard deviation)	<40	60.8 (0.49)	<40	91.4	<40
Motor Octane Number (MON) (ASTM D2700):					
-Lab 1	<40	58.0	<40	82.5	<40
-Lab 4	<40	59.4	<40	83.2	<40
-Lab 5	35.2[#]	58.2	25.5[#]		
-Average (Standard deviation)	<40	58.5 (0.76)	<40	82.8	<40
IQT Derived Cetane Number (ASTM D6890): Lab 4	41.09	31.64	45.95		48.04
API Gravity (API°) (ASTM D4052):					
-Lab 1	65.9	60.2	63.8	60.1	46.4
-Lab 3	68.2	61.8	65.9		
-Lab 4	66.4	60.9	63.9	60.0	46.4
-Lab 5	66.8	60.9	63.9		
-Average	66.8 (0.99)	61.0 (0.66)	64.4 (1.02)	60.0	46.4
Density (ASTM D4052) @15.5°C:					
-Lab 1	0.7167	0.7379	0.7242	0.7381	0.7950
-Lab 3	0.7086	0.7319	0.7169		
-Lab 4	0.7148	0.7352	0.7241	0.7386	0.7950
-Lab 5	0.7141	0.7347	0.7236		
-Average	0.7136 (.0035)	0.7349 (.0025)	0.7222(.0035)	0.7383	0.7950
Vapor Pressure (psi) (D5191)					
-Lab 3	5.19	7.50	0.45		
-Lab 4	5.68	7.71	1.16	14.55	0.52
-Lab 5	5.42	7.80	0.68		
-Average	5.43 (0.25)	7.67 (0.15)	0.76 (0.36)	14.55	0.52
Net Heat of Combustion (BTU/lb):					
-Lab 4 (ASTM D4809):	18982	18836	19013	18590	18642
-Lab 5 (ASTM D240):	19083	18888	19012		

[#] **Value outside the working range of the method.**

to only 90%, which is inconsistent with every other measurement made on this sample. If that value is dropped the mean carbon content for Naphtha 1 is 84.63 (std dev= 0.540) and the hydrogen content is 15.41 (std dev= 0.50), which is much more consistent.

Table 2 Summary D86 Data for AVFL-19a Fuels

Specific Tests: **Fuel:**	**Naphtha 1**	**Naphtha 2**	**Naphtha 3**	**Woody Biomass Gasoline**	**Cellulosic Jet Fuel**
Distillation (˚F) (ASTM D86)					
-Lab 1: IBP	106.7	91.5	246.3		288.1
5%	153.5	136.0	260.3		334.2
10%	166.7	150.2	262.7		344.5
20%	183.5	170.3	266.8		359.9
30%	197.8	186.9	269.9		369.9
40%	211.1	201.7	273.3		378.5
50%	223.9	216.7	276.3		384.8
60%	236.6	232.0	280.8		391.8
70%	249.6	249.0	286.2		399.6
80%	263.7	270.1	293.6		410.0
90%	282.8	307.7	304.5		428.4
95%	295.9	399.4	313.7		450.4
FBP	316.6	483.0	359.6		462.7
-Lab 3: IBP	112.3	98.4	252.7		
5%	150.6	133.9	260.8		
10%	164.7	148.5	263.7		
20%	181.9	169.3	266.9		
30%	195.8	186.1	269.8		
40%	208.6	201.0	272.8		
50%	221.2	215.6	276.6		
60%	233.4	231.4	280.9		
70%	246.4	248.2	286.9		
80%	260.4	269.6	293.7		
90%	277.9	306.3	304.9		
95%	289.2	380.1	314.2		
FBP	309.4	510.4	362.5		
-Lab 5: IBP	101.8	94.5	249.3		
5%	145.4	125.8	259.9		
10%	161.1	142.5	261.7		
20%	179.4	164.1	264.9		
30%	193.8	181.6	268.0		
40%	206.8	196.9	271.2		
50%	219.2	211.6	275.0		
60%	232.2	227.3	279.3		
70%	245.1	244.2	284.5		
80%	259.9	264.9	291.9		
90%	277.2	297.9	302.7		
95%	288.0	348.3	311.4		
FBP	314.4	482.4	354.2		

Table 3 Average D86 Data for AVFL-19a Fuels

2 labs reported % recovered, one lab reported % evaporated; percent evaporated temperatures are typically slightly lower. This difference in techniques is expected to slightly increase standard deviation and slightly alter the mean**.**

Specific Tests: **Fuel:**	**Naphtha 1**	**Naphtha 2**	**Naphtha 3**	**Woody Biomass Gasoline**	**Cellulosic Jet Fuel**
Distillation (˚F) (ASTMD86) % recovered					
-Average IBP	106.9 (5.25)	94.8 (3.46)	249.4 (3.2)		288.1
5%	149.8 (4.10)	131.9 (5.39)	260.3 (0.45)		334.2
10%	164.2 (2.84)	147.1 (4.05)	262.7 (1.00)		344.5
20%	181.6 (2.07)	167.9 (3.33)	266.2 (1.13)		359.9
30%	195.8 (2.00)	184.9 (2.86)	269.2 (1.07)		369.9
40%	208.8 (2.16)	199.9 (2.59)	272.4 (1.10)		378.5
50%	221.4 (2.36)	214.6 (2.68)	276.0 (0.85)		384.8
60%	234.1 (2.27)	230.2 (2.56)	280.3 (0.90)		391.8
70%	247.0 (2.32)	247.1 (2.57)	285.9 (1.23)		399.6
80%	261.3 (2.06)	268.2 (2.87)	293.1 (1.01)		410.0
90%	279.3 (3.05)	304.0 (5.3)	304.0 (1.17)		428.4
95%	291.0 (4.26)	375.9 (25.8)	313.1 (1.49)		450.4
FBP	313.5 (3.69)	491.9 (16.0)	358.8 (4.21)		462.7

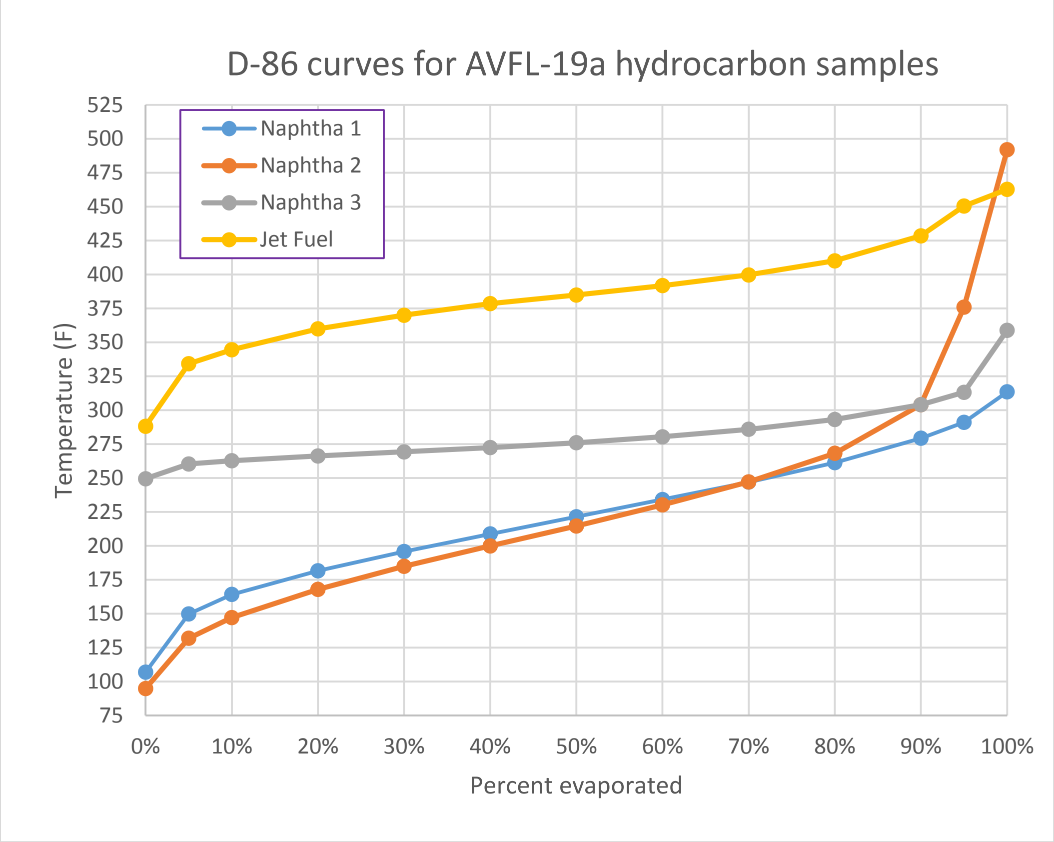

Figure 1. ASTM D-86 curves for the three naphthas and the cellulosic jet fuel. Note the distinctly different character of each sample.

Table 4 D2887 data for naphtha and gasoline samples

Percent distilled	Temperature C Woody biomass gasoline	Naphtha 1	Naphtha 2	Naphtha 3
0	-39.3	21.4	20.1	76.4
5	-1.5	36.3	35.0	113.4
10	26.5	38.9	36.8	114.8
15	28.2	67.7	55.6	115.7
20	35.4	68.8	67.8	116.8
25	59.2	69.4	69.0	117.7
30	60.5	76.1	74.5	123.8
35	64.0	94.2	81.9	126.4
40	78.1	98.1	93.9	131.7
45	91.0	98.6	98.1	133.8
50	94.0	98.9	98.8	138.2
55	107.0	102.8	103.1	140.8
60	120.1	111.0	110.9	141.6
65	137.5	122.4	116.8	142.4
70	138.6	125.9	125.7	143.4
75	157.0	126.5	129.1	150.4
80	171.6	131.4	137.8	154.9
85	172.6	139.6	146.5	158.0
90	190.5	150.2	157.2	163.7
95	198.9	151.6	200.8	166.1
100	256.6	174.1	382.3	289.9

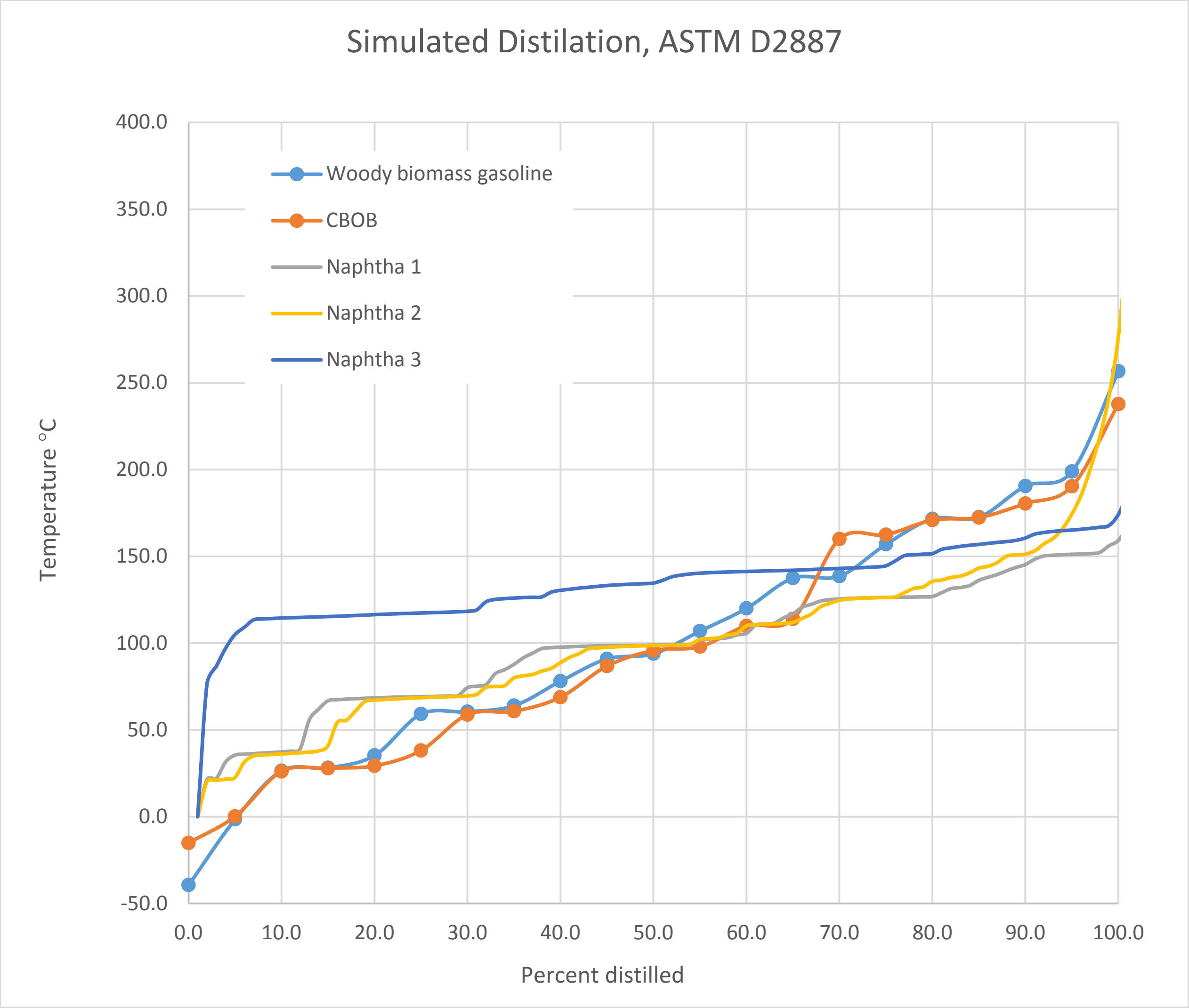

Figure 2. Simulated distillation curves for the Naphthas, and for the Woody biomass gasoline with a Conventional BOB as a reference.

Table 5 Supporting Summary Data for AVFL-19a Fuels

Specific Tests: Fuel:	**Naphtha 1**	**Naphtha 2**	**Naphtha 3**	**Woody Biomass Gasoline**	**Cellulosic Jet Fuel**
Elemental Analysis (ASTM D5291):					
-Carbon (wt.%):					
-Lab 1	84.68	86.09	84.98	87.43	85.64
-Lab 3	84.06	84.29	82.62		
-Lab 4	85.14	85.97	84.41	86.94	85.77
-Lab 5	77.16	85.92	84.26		
-Average	82.76 (3.76)	85.57 (0.85)	84.07 (1.01)	87.19	85.70
Average labs 1, 3, & 4 only	84.63 (0.54)				
-Hydrogen (wt.%):					
-Lab 1	15.97	14.36	16.10	12.57	14.36
-Lab 3	14.99	13.94	15.27		
-Lab 4	15.27	14.41	15.71	13.83	14.48
-Lab 5	13.00	13.45	15.31		
-Average	14.81 (1.27)	14.04 (0.45)	15.60 (0.39)	12.70	14.32
Average labs 1,3, & 4 only	15.41 (0.50)				
Sulfur by UV Fluorescence (ppmw) (ASTM D5453)					
-Lab 4	2.2	50.8	1.0	1.0	4.2
-Lab 5	1.5	53.0	0.5		
-Average	1.9	51.9	0.8	1.0	4.2
Oxygen by GC-AED (wt%): (Lab 5)	0.033	0.028	0.037		
CHNS by combustion (wt%): (lab 5)					
Nitrogen	0.23	<0.15	0.37		
Sulfur	<0.40	<0.40	<0.40		
Hydrocarbons by FIA (vol.%) (ASTM D1319):(Lab1)					
-Aromatics (vol.%):	8.0	24.9	0	29.9	3.6
-Alkenes (vol.%):	0.4	3.4	0	2.4	0
-Saturates (vol.%):	91.5	71.7	100.0	67.7	96.4
Aromatics by SFC (ASTM D5186): (Lab 1):					
-MonoAromatics (wt.%)					
-Lab 1	9.9	20.2	<0.5	55.5	3.7
-Lab 5	8.0	16.5	0		
-Average	9.0	18.4	<0.25	55.5	3.7
-PolyAromatics (wt.%)					
-Lab 1	0.7	1.4	<0.5	0.7	<0.5
-Lab 5	0	0.6	0		
-Average	0.4	1.0	<0.25	0.7	<0.5
-NonAromatics (wt.%)					
-Lab 1	89.4	78.4	>99.0	43.8	96.3
-Lab 5	92.0	82.9	100		
-Average	90.7	80.7	>99.5	43.8	96.3

Sulfur levels are quite low (<5ppm) except for Naphtha 2 which had a sulfur level > 50ppm. All the samples have low alkene content. Only Naphtha 2 and the Woody Biomass Gasoline have over 10% aromatics. Indeed, Naphtha 3 is 100% alkanes (*n*-alkanes, *iso*-alkanes, and naphthenes), and Naphtha 1 and the Jet fuel have >90% alkanes. Polyaromatics levels are very low (<1.5%) in all samples. A separate ICP metals analysis was run on all these samples and the only metals above the detection limit were 8ppm Si in Naphtha 3 and 15ppm Si in the cellulosic jet fuel.

Detailed hydrocarbon analysis results are compiled in Table 6 and shown graphically in Figure 3. In this GC-FID analysis it is again clear Naphtha 1 and 3 and the cellulosic Jet fuel are dominated by alkanes. A tiny aromatic composition is reported in Naphtha 3 and the Jet fuel, while 6%, 13% and 30% are reported for Naphtha 1, Naphtha 2 and the gasoline sample. Normal alkanes dominate Naphthas 1 and 2 while branched alkanes dominate Naphtha 3 and the alkane portion of the gasoline. Cycloalkanes dominate the jet sample and comprise 10 to 20% of the other samples. Alkenes content is low.

Table 6 Summary DHA Data for AVFL-19a Fuels

Specific Tests: Fuel:	**Naphtha 1**	**Naphtha 2**	**Naphtha 3**	**Woody Biomass Gasoline**	**Cellulosic Jet Fuel**
Detailed Hydrocarbon Analyses by GC-FID:					
-*n*-alkanes (vol.%):					
-Lab 1	64.3	49.1	12.5	8.1	12.8
-Lab 2	64.4	49.7	12.2		
-Lab 3	65.1	49.8	12.2		
-Lab 5	64.2	47.9	12.4		
-Average	64.5	49.1	12.3	8.1	12.8
-*iso*-alkanes (vol.%):					
-Lab 1	9.6	11.7	73.8	47.5	29.2
-Lab 2	9.4	9.5	67.6		
-Lab 3	9.7	8.7	74.1		
-Lab 5	8.6	9.3	78.5		
-Average	9.3	9.8	73.5	47.5	29.2
-cycloalkanes (vol.%):					
-Lab 1	18.0	17.5	9.9	10.2	55.7
-Lab 2	18.2	19.8	9.4		
-Lab 3	16.4	18.9	4.7		
-Lab 5	19.3	19.1	5.2		
-Average	18.0	18.8	7.3	10.2	55.7
-aromatics (vol.%):					
-Lab 1	6.3	12.8	1.3	29.8	2.3
-Lab 2	6.4	12.8	2.1		
-Lab 3	6.0	12.9	0.7		
-Lab 5	6.4	13.4	0.8		
-Average	6.3	13.0	1.2	29.8	2.3
-alkenes (vol.%):					
-Lab 1	0.2	5.9	0.2	1.9	0
-Lab 2	1.6	8.0	8.4		
-Lab 3	2.1	8.5	3.4		
-Lab 5	0.5	8.4	0		
-Average	1.1	7.7	3.0	1.9	0

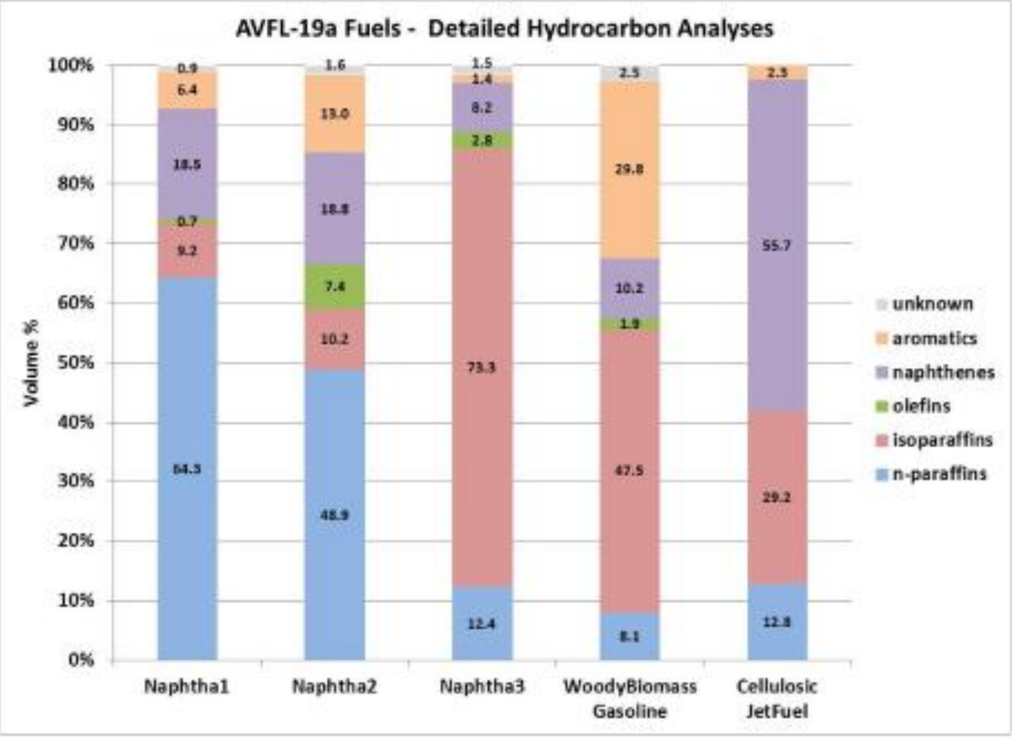

Figure 3. The average composition data for the hydrocarbon samples, from Table 6.

GC-FID analysis:

In Tables 7a-e the average DHA results are tabulated by carbon number, lab-by-lab data is presented in the appendix. At this level a much more detailed picture begins to emerge. For example, standard techniques showed a high alkane content in Naphtha 1, but in Table 7a it is clear that 2/3 of that alkane content is in the C6-C8 molecules, or

Table 7a DHA by carbon number for Naphtha 1

Naphtha 1 (vol.%) - Average							
Carbon #	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Unknown	Total
C3	0.08	0.00	0.00	0.00	0.00		0.08
C4	2.11	0.04	0.00	0.00	0.00		2.15
C5	8.50	0.55	0.00	0.80	0.00		9.85
C6	15.14	1.42	0.00	3.38	0.65		20.59
C7	17.32	1.73	0.01	6.46	2.24		27.76
C8	13.41	2.02	0.19	5.76	2.51		23.89
C9	7.32	2.58	0.46	2.03	0.91		13.30
C10	0.39	0.82	0.07	0.06	0.06		1.40
C11	0.01	0.03	0.00	0.01	0.00		0.05
C12+	0.02	0.00	0.00	0.00	0.00		0.02
Unknown						0.85	0.85
Total	64.30	9.19	0.73	18.50	6.37	0.85	99.94

roughly 45% of the naphtha is composed of C6-C8 alkanes. Similarly 2/3 of the aromatics in Naphtha 2 (Table 7b) are in C7 and C8 molecules. Also note that Naphtha 2 has about 1¼ % of its composition in molecules larger than C10 and roughly half of those are aromatics; yet by contrast Naphtha 1 has only .07% of its composition in molecules larger than C10. Another interesting and rather stark contrast is that Naphtha 3 has only 0.8% of its composition in molecules C5 or lighter and no material in the C3 or C4 range (Table 7c), while Naphtha 2 has 0.31% composition in C3 molecules and nearly 18% in C5 or lighter molecules and Naphtha 1 has 12% of its content in C5 or lighter material.

Figures 4-8 Show these trends visually in bubble plot format. The size of a specific bubble is proportional to volume percent and the color corresponds to the hydrocarbon class of the compound. The color coding makes some aspects very clear such as the much higher *iso*-alkane content of Naphtha 3 vs. Naphtha 1 and 2, while the bubble size shows up some other features for example the high volume of C10 material in Naphtha 3 and the fact that the C10 material is almost all *iso*-alkanes. Finally the rather balanced nature of the gasoline sample (Figure 7) with many moderate sized bubbles across carbon number and chemical type is in strong contrast to the fact there are only 7 bubbles in Naphtha 3 that represent 90% of the fuel. The high cycloalkane content in the jet fuel sample is also made very clear in Figure 8. Consistent with its more distillate-like nature, note that the carbon number scale is expanded relative to the other samples.

Table 7b DHA by carbon number for Naphtha 2

Naphtha 2 (vol.%) - Average							
Carbon #	***n-Paraffins***	***Isoparaffins***	***Olefins***	***Naphthenes***	***Aromatics***	***Unknown***	***Total***
C3	**0.30**	**0.00**	**0.01**	**0.00**	**0.00**		**0.31**
C4	**3.64**	**0.16**	**0.84**	**0.00**	**0.00**		**4.64**
C5	**8.83**	**0.76**	**1.56**	**1.70**	**0.00**		**12.85**
C6	**12.56**	**1.49**	**2.01**	**4.92**	**1.44**		**22.42**
C7	**11.96**	**1.68**	**1.40**	**6.40**	**4.27**		**25.71**
C8	**7.71**	**2.17**	**0.74**	**4.03**	**4.25**		**18.90**
C9	**3.50**	**2.68**	**0.67**	**1.53**	**1.58**		**9.96**
C10	**0.27**	**1.00**	**0.08**	**0.21**	**0.69**		**2.25**
C11	**0.07**	**0.17**	**0.02**	**0.04**	**0.49**		**0.79**
C12+	**0.08**	**0.06**	**0.00**	**0.01**	**0.28**		**0.43**
Unknown						**1.62**	**1.62**
Total	**48.92**	**10.17**	**7.35**	**18.84**	**12.99**	**1.62**	**99.89**

Table 7c DHA by carbon number for Naphtha 3

Naphtha 3 (vol.%) - Average							
Carbon #	*n-Paraffins*	*Isoparaffins*	*Olefins*	*Naphthenes*	*Aromatics*	*Unknown*	*Total*
C3	0.00	0.00	0.00	0.00	0.00		0.00
C4	0.00	0.00	0.00	0.00	0.00		0.00
C5	0.02	0.06	0.00	0.00	0.00		0.08
C6	0.26	0.14	0.00	0.02	0.00		0.42
C7	0.62	1.47	0.00	0.16	0.00		2.25
C8	6.65	23.32	1.71	4.38	0.14		36.20
C9	4.17	33.34	0.98	3.37	1.06		42.92
C10	0.59	14.58	0.11	0.19	0.22		15.69
C11	0.00	0.36	0.00	0.03	0.01		0.40
C12+	0.04	0.02	0.00	0.00	0.00		0.06
Unknown						1.52	1.52
Total	12.35	73.29	2.80	8.15	1.43	1.52	99.54

Table 7d DHA by carbon number for Woody Biomass gasoline

Woody Biomass Gasoline (vol.%) - Lab 1							
Carbon	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Unknown	Total
C3	0.88	0	0.02	0	0	0	0.90
C4	3.09	4.72	0.29	0	0	0	8.10
C5	2.48	13.61	0.59	0.20	0	0	16.88
C6	1.11	16.73	0.53	1.41	0.16	0	19.94
C7	0.32	8.37	0.26	3.53	1.89	0	14.37
C8	0.08	2.73	0.22	4.08	8.59	0.03	15.73
C9	0.15	1.14	0.01	0.91	10.54	0.50	13.25
C10	0	0.18	0	0.11	7.72	0.38	8.39
C11	0	0.03	0	0	0.65	0.11	0.79
C12+	0	0	0	0	0.20	1.47	1.67
Total	8.11	47.51	1.92	10.24	29.75	2.48	100.01

In Table 8 the standard ASTM, ethanol test data are presented. The ethanol contains an acceptable level of water (though more than 200 times more than the naphtha samples which ranged from 12-26ppm water as measured by Karl Fischer titration) and it has a roughly neutral pH_e (the "pH" scale in ethanol (pH_e) runs up to 16, not 14 as it does in water). Sulfate and chloride levels are low indicating few acid, base or salt impurities. The unwashed gum level is approximately 14mg/100ml with washed gum levels nearly undetectable. Metals levels are low where detected at all. Boron at 3ppm is the highest amount of a metal detected. Boron is unexpected, and it is not clear at what point it entered the ethanol. This could warrant attention in any future testing.

Table 7e DHA by carbon number for cellulosic jet fuel

Cellulosic Jet Fuel (vol.%) - Lab 1							
Carbon #	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Unknown	Total
C6	0.04	0.05	0	0.00	0.00	0	0.09
C7	0.10	0.22	0	0.00	0.30	0	0.62
C8	0.40	0.09	0	2.00	0.20	0	2.69
C9	1.26	0.82	0	4.10	0.20	0	6.38
C10	1.92	3.58	0	10.20	0.40	0	16.10
C11	3.22	7.16	0	17.20	0.40	0	27.98
C12	2.69	9.90	0	17.40	0.80	0	30.79
C13	0.42	2.37	0	2.70	0.00	0	5.49
C14	2.56	3.92	0	1.70	0.00	0	8.18
C15	0.02	0.63	0	0.40	0.00	0	1.05
C16	0.13	0.47	0	0.00	0.00	0	0.60
C17	0.00	0.03	0	0.00	0.00	0	0.03
Total	12.76	29.24	0.00	55.70	2.30	0	100.00

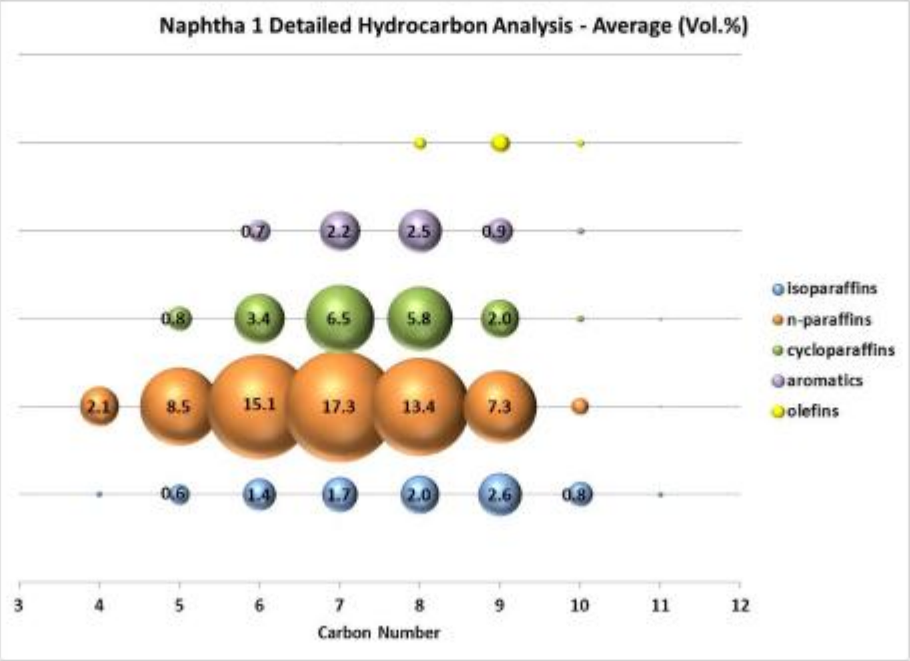

Figure 4. Bubble plot of the amount of material in each chemical type and carbon number category for Naphtha sample 1. The size of the bubble indicates the amount of material (vol.%) in that specific carbon number and chemical type.

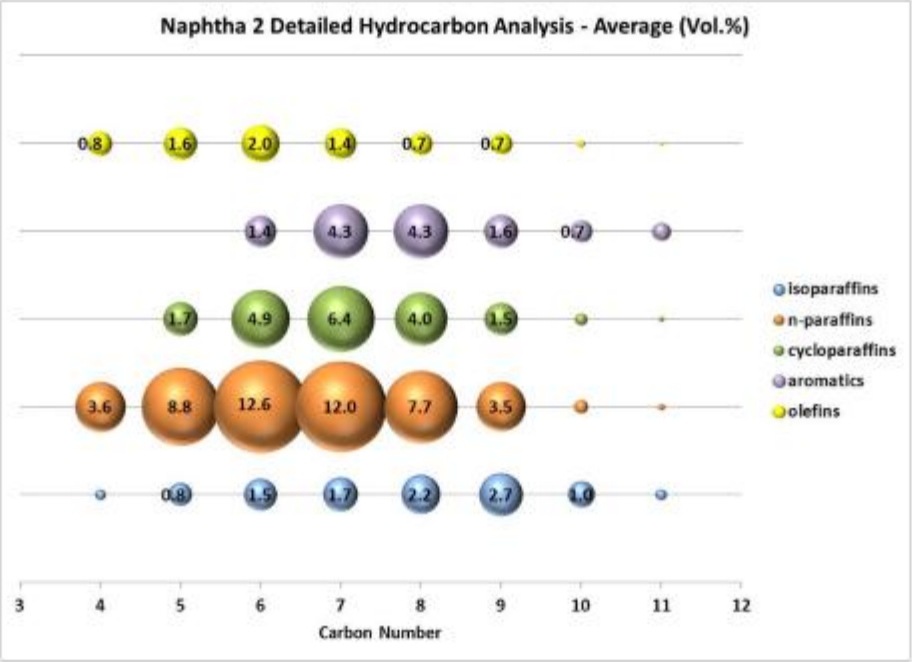

Figure 5. Bubble plot of the amount of material in each chemical type and carbon number category for Naphtha sample 2.

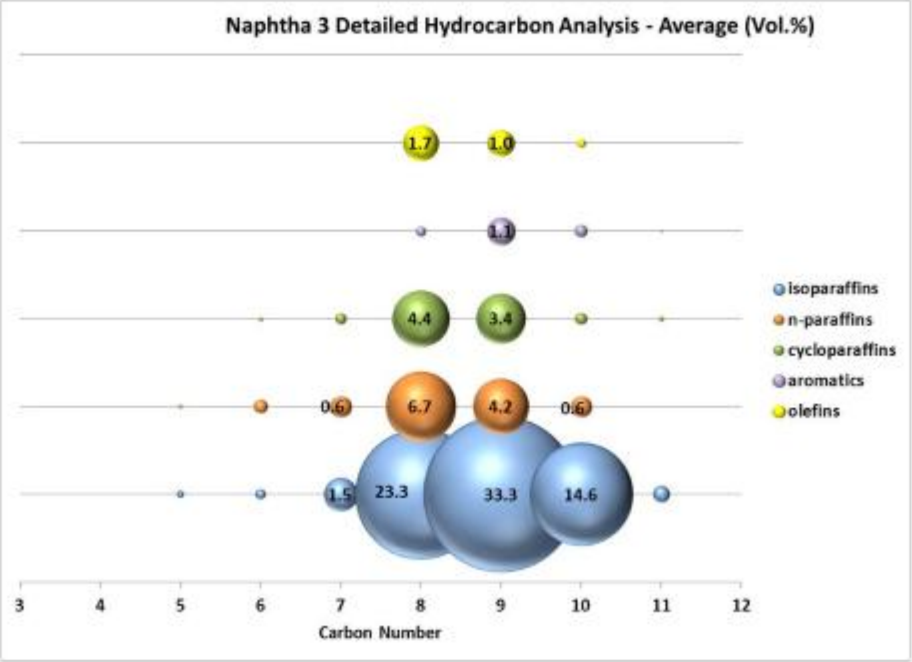

Figure 6. Bubble plot of the amount of material in each chemical type and carbon number category for Naphtha sample 3.

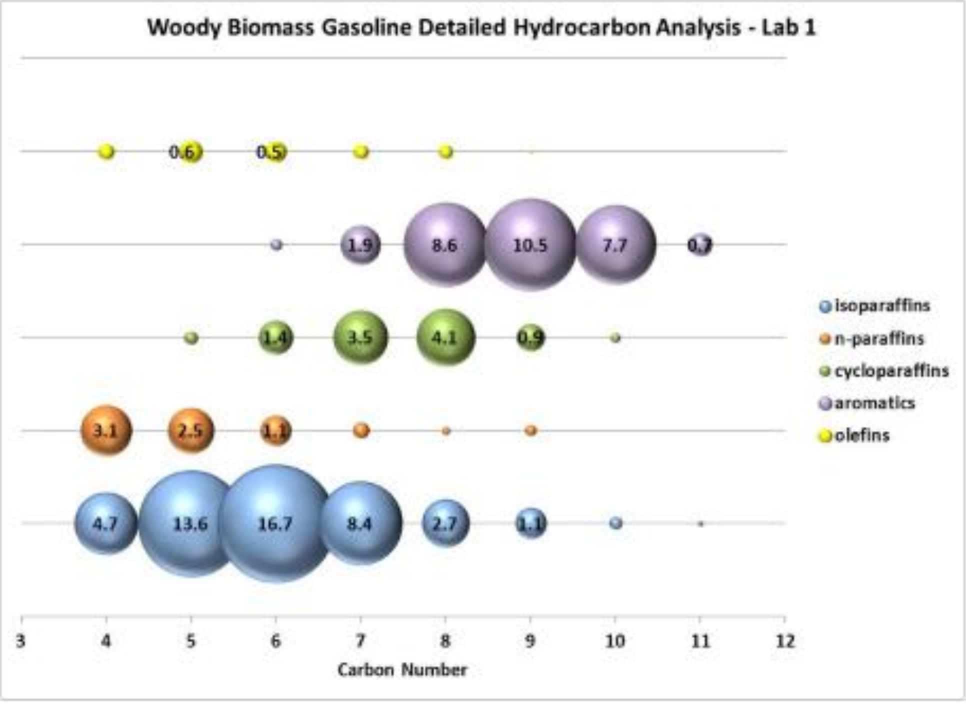

Figure 7. Bubble plot of the amount of material in each chemical type and carbon number category for the Woody Biomass Gasoline.

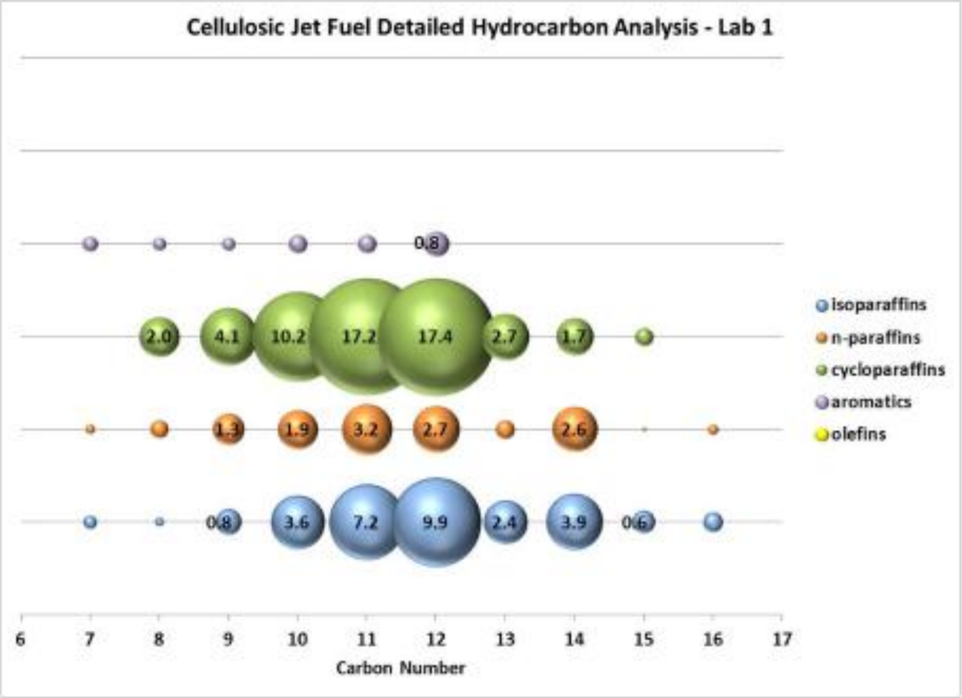

Figure 8. Bubble plot of the amount of material in each chemical type and carbon number category for the cellulosic jet fuel.

Table 8 Summary Data for AVFL-19a Cellulosic Ethanol Sample

Specific Tests: **Fuel:**	**Cellulosic Ethanol**
Ethanol Content (ASTM D4815) (vol.%): Lab 3	96.3
Ethanol Content (ASTM 5501):	
-Lab 4 (vol.%)	99.5
-Lab 4 (wt.%)	99.2
-Lab 1 (wt.%)	99.8
Water Content (ASTM D6304) (wt.%):	
-Lab 1	0.77
-Lab 3	0.79
-Lab 4	0.64
-Lab 5	0.45
Specific Gravity @60˚F (ASTM D4052):	
-Lab 1	0.7964
-Lab 4	0.7961
pHe (ASTM D6423):	
-Lab 1	8.5
-Lab 3	7.5
-Lab 4	9.5
-Lab 5	8.7
Acidity (ASTM D1613) (mg KOH) Lab 4	0.0176
Unwashed Gum (ASTM D381) (mg/100ml)	
-Lab 1	14.4
-Lab 3	13.5
-Lab 4	14.0
-Lab 5	15.5
Washed Gum (ASTM D381) (mg/100ml)	
-Lab 1	0.8
-Lab 3	1.1
-Lab 4	<0.5
-Lab 5	1.0
Chlorides (ASTM D7328) (ppm)	
-Lab 1	1.2
-Lab 3	<1
-Lab 4	1.5
Sulfates (ASTM D7328) (ppm)	
-Lab 1	3.7
-Lab 3	1.1
-Lab 4	0.29
Cu (ASTM D1688M) (ppm):	
-Lab 1	<0.1
-Lab 4	<0.05

Na (Atomic Adsorption) (ppm) Lab 1**:**	1.6
Other Metals (ICP) (ppm) Lab 1:	
-B	3.0
-K	<2.5
-Al, Ba, Ca, Cd, Cr, Fe, Mg, Mn, Mo, Ni, P, Pb, Si, Sn, Ti, V, Zn	<0.5
Sulfur (ppm):	
-Lab 1 (XRF)	<5
-Lab 3 (ASTM D7039)	0.4
-Lab 4 (ASTM D5453)	1.0
-Lab 5	0.5

NMR analysis:

The three naphtha and the gasoline samples were evaluated using NMR spectroscopy. As shown below, quantitative ^{1}H and ^{13}C{^{1}H} NMR are largely mutually supporting, with differences or inconsistencies only arising from overlapping carbon integration regions, or coincidental overlap of individual NMR resonances.

^{1}H NMR Results: The ^{1}H NMR spectra of the four samples are relatively uncomplicated and are easy to obtain; they contain a wealth of information. Carbonyl-containing species were not observed in the ^{1}H NMR spectra or the ^{13}C{^{1}H} NMR spectra of the four samples, and are therefore either not present, or present in extremely low quantities. Similarly, resonances associated with protons adjacent to heteroatoms (O, N, or S) are not observed and are therefore expected to be below the detection limit (~0.5 wt%), indicating very low concentrations of compounds containing heteroatoms, which is consistent with the standard tests, for example the elemental analysis values for S and N being below 0.5 wt% and the %C and %H summing effectively to 100% (Table 5) indicating a small concentration of hetero atoms.

To assist with comparisons of ^{1}H and ^{13}C{^{1}H} NMR data, we have related each hydrogen resonance in the ^{1}H NMR to the attached carbon type, and then normalized by carbon type, as shown in Table 9 and Figure 9.[‡] Figure 10 provides a map of carbon positions as annotated in this document with respect to either distance from an aromatic ring, or position within an aliphatic chain. Information in the appendix (Table A4) provides the normalized integration results from the ^{1}H NMR spectra broken down by unique proton environments for each of the samples.

[‡] For example, a methyl group (-CH_3) contributes 3 protons but only 1 carbon, thus the integrated value from the -CH_3 region of the ^{1}H NMR spectrum representing methyl groups was divided by 3, and so forth for the number of attached protons for each integration zone shown in Tables 1 and 2, and then normalized by the total number of carbons to reflect the corresponding carbon environments. This process does not account for carbons without protons, i.e., substituted aromatic carbons, bridgehead carbons, or quaternary carbons, so the tabulated values (Table 2) will be a little higher or lower than the actual values, depending upon the number of carbons without protons, but since these are usually small, we expect this analysis will provide results that trend correctly.

Table 9. ^1H NMR Comparison of Four Renewable Gasoline-Type Fuel Components, Normalized by Carbon Type

			Mole % C*			
Label	**Chemical shift range (ppm)**	**Chemical meaning**	**Naphtha 1**	**Naphtha 2**	**Naphtha 3**	**Woody Biomass Gasoline**
A1	9.000 - 8.200	Tri-ring aromatics	0	0	0	0
A2	8.200 - 7.551	Di-ring aromatics	0	0.2	0	0.2
A3	7.551 - 7.182	Di-ring aromatics, benzene	2.7	4.9	0	2.7
A4	7.182 - 7.130	Mono-ring aromatics	1.2	2.1	0	1.9
A5	7.130 - 6.972	Mono-ring aromatics	1.0	1.9	0	8.5
A6	6.972 - 6.785	Substituted mono-ring aromatics	0.2	0.2	0	3.7
A7	6.785 - 6.425	Highly substituted mono-ring aromatics	0	0	0	0
O1	6.425 - 4.184	Olefins	0	2.3	0	0.6
B1	4.184 - 3.306	Bridged CH_2 groups in fluorene types	0	0	0	0
SA1	3.306 - 2.883	α-CH to aromatic	0	0.2	0	0.2
SA2	2.883 - 2.641	α-CH_2 to aromatic	0.1	0.3	0	0.4
SA3	2.641 - 2.292	α-CH_2 + α-CH_3 to aromatic	1.0	2.0	0	6.2
SA4	2.292 - 2.040	α-CH_3 to aromatic	0.3	1.1	0	7.9
O2	2.040 - 1.963	Allylic CH_3 and CH_2 groups	0.2	1.7	0	0.6
P1	1.963 - 1.570	CH and CH_2 groups of naphthenes	7.9	12.1	2.1	7.5
P2	1.570 - 1.391	CH groups of *iso*-paraffins	9.8	12.1	7.7	8.1
P3	1.391 - 1.115	CH_2 groups of paraffins (*n*-and *iso*-)	48.1	34.7	48.5	20.0
P4	1.115 - 0.941	CH_2 groups of paraffins (*n*-and *iso*-)	4.1	5.5	5.8	4.9
P5	0.941 - 0.254	CH_3 groups of paraffins (*n*-and *iso*-)	23.4	18.7	35.9	26.6

*Normalized to account for protonated carbons only.

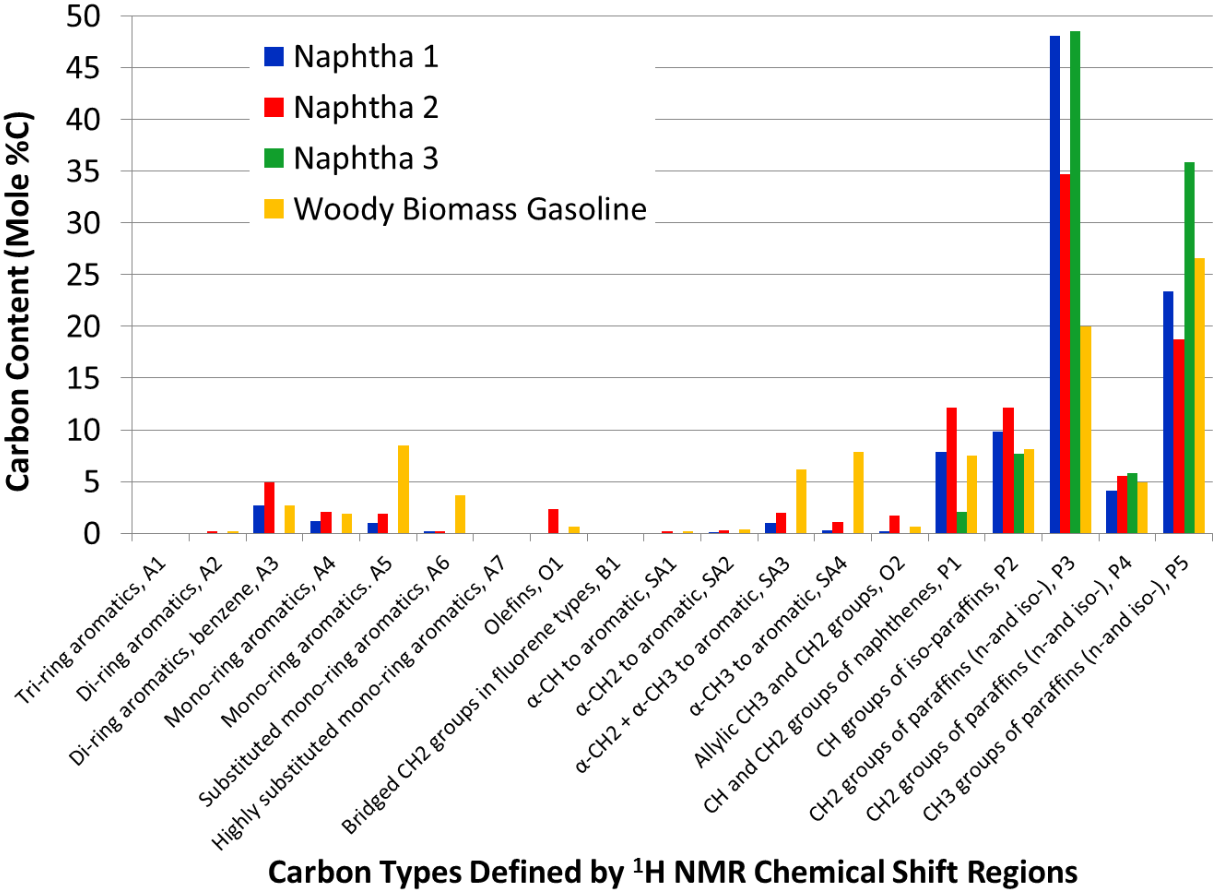

Figure 9. Normalized Carbon-Type Distribution of Four Renewable Gasoline-Type Fuel Components. Values were obtained by integrating each ^{1}H NMR chemical shift region, accounting for the number of attached hydrogen atoms and normalizing the data, shown in Table 9.

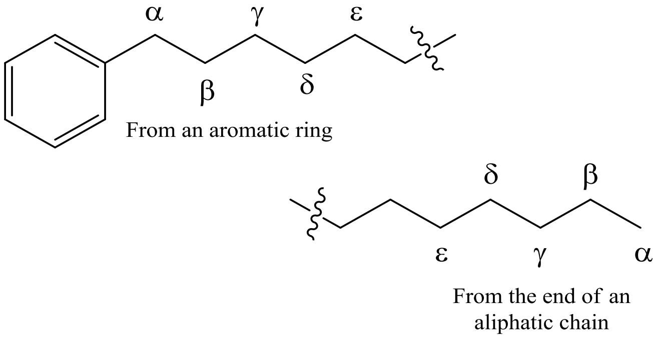

Figure 10. Nomenclature scheme describing the labeling convention carbons from an aromatic ring, or from the end of an aliphatic chain.

$^{13}C\{^1H\}$ NMR Results: The quantitative $^{13}C\{^1H\}$ NMR spectra provide a picture consistent with the ^1H NMR results described above. $^{13}C\{^1H\}$ NMR complements and expands upon the information obtained from the ^1H NMR, in particular by further defining the aromatic and aliphatic carbons, providing a better discrimination of carbon structural types. However, this additional information does not diminish the value of the ^1H NMR data, which can be more rapidly obtained and allows ready differentiation of fused ring aromatic systems and unsaturated aliphatic species, neither of which is a strength of $^{13}C\{^1H\}$ NMR.

Similar to the bar charts for the ^1H NMR spectra showing integrations by specific proton types, Figure 11 allows a visual comparison of the integrated $^{13}C\{^1H\}$ NMR data using chemical shift regions to show different carbon types. These regions are identical to those previously reported.**[2, 3]** Table 10 provides numerical values corresponding to the data in Figure 11, and Table 11 summarizes some of the key observables, particularly for the aromatic carbons.

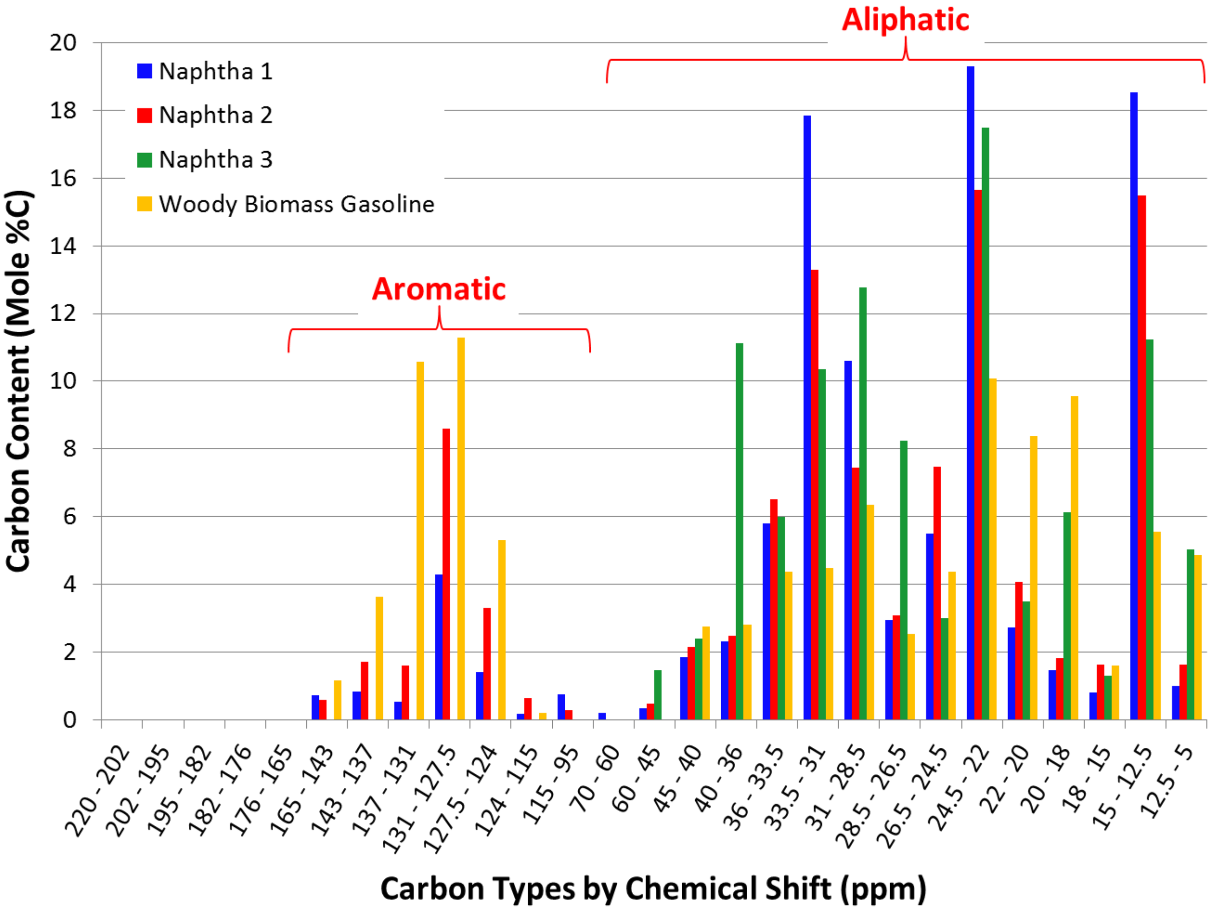

Figure 11. Normalized Carbon Type Distribution of Four Renewable Gasoline-Type Fuel Components. Values were obtained by integrating each $^{13}C\{^1H\}$ NMR chemical shift regions shown in Table 10.

Table 10. Detailed Chemical Shift Regions for Normalized $^{13}C\{^{1}H\}$ Percent Composition of Four Renewable Gasoline-Type Fuel Components, Normalized by Carbon Type

		Mole % Carbon			
Chemical Shift	**Structure Definition**	**Naphtha 1**	**Naphtha 2**	**Naphtha 3**	**Woody Biomass Gasoline**
220-202	Ketone Carbonyl	0	0	0	0
202-195	Aldehyde Carbonyl	0	0	0	0
195-182	Quinone Carboxyl	0	0	0	0
182-176	Acid Carboxyl	0	0	0	0
176-165	Ester or Amide Carboxyl	0	0	0	0
165-143	Alkyl (other than methyl), or heteroatom (N, O, S) substituted aromatic	0.7	0.6	0	1.2
143-137	Tertiary carbon in alkyl substituted aromatics	0.8	1.7	0	3.6
137-131	Tertiary carbon in naphthalene units and methyl substituted aromatics	0.5	1.6	0	10.6
131-127.5	Protonated and internal aromatic carbon, substituted carbon in alkenes ($R_2C{=}CR_2$), orth and meta CH in toluene	4.3	8.6	0	11.3
127.5-124	Protonated and internal aromatic carbon, substituted carbon in alkenes ($RHC{=}CR_2$), para CH in toluene	1.4	3.3	0	5.3
124-115	Protonated aromatic carbon, substituted carbon in alkenes ($RHC{=}CR_2$)	0.2	0.6	0	0.2
115-95	Unsubstituted carbon in alkenes ($CH_2{=}CR_2$)	0.7	0.3	0	0
70-60	CH_2 adjacent to oxygen and C in tertiary alchols	0.2	0	0	0
60-45	CH adjacent to tertiary and isopropyl groups. CH_3 in ether linkage	0.3	0.5	1.5	0
45-40	CH in allylic and benzylic groups and in joining tetralin ring	1.8	2.1	2.4	2.8
40-36	carbon	2.3	2.5	11.1	2.8
36-33.5	CH, CH_2 β from secondary carbon and in cyclopentyl and cyclohexyl rings	5.8	6.5	6.0	4.4
33.5-31	CH, CH_2 γ from CH_3. CH_2 α to allylic and beta to aromatic groups	17.8	13.3	10.4	4.5
31-28.5	C in open chains. CH_2 benzylic and CH_2 not adjacent to CH in alkyl group	10.6	7.4	12.8	6.4
28.5-26.5	CH, CH_2 in open chains. CH_2 in cyclohexyl groups and CH_3 in tert-butyl ether	2.9	3.1	8.2	2.5
26.5-24.5	Some naphthenic CH_2. CH_2 β in propyl, indan and cyclopentyl groups	5.5	7.5	3.0	4.4
24.5-22	CH_2 β from terminal CH_3. CH_2 β in unsubstituted tetralin	19.2	15.6	17.5	10.1
22-20	CH_3 α in hydroaromatics and alkyls not shielded by adjacent rings or groups	2.7	4.1	3.5	8.4
20-18	CH_3 α in hydroaromatics and alkyls shielded by adjacent rings or groups	1.5	1.8	6.1	9.5
18-15	CH_3 in cyclohexanes and β in ethyl aromatics and ethers	0.8	1.6	1.3	1.6
15-12.5	CH_3 γ to an aromatic ring or shielded by two adjacent rings or groups, chain α-CH_3	18.4	15.5	11.2	5.6
12.5-5	CH_3 γ to aromatic rings or ethyl substituted cyclohexanes	1.0	1.6	5.0	4.9

Table 11. Summary of Renewable Gasoline-Type Fuel Components Chemical Structure Characteristics from $^{13}C\{^{1}H\}$ NMR Normalized by Carbon Type

	Mole % Carbon			
	Naphtha 1	**Naphtha 2**	**Naphtha 3**	**Woody Biomass Gasoline**
General Carbon Types				
Aromatic Carbon	8.7	16.8	0	32.2
Aliphatic Carbon	91.3	83.2	100.0	67.8
CH Carbon	2.2	2.6	3.9	2.8
CH_2 Carbon	64.4	56.0	68.9	35.0
CH_3 Carbon	24.7	24.6	27.2	30.0
Aromatic Carbon Breakdown				
Phenolic Carbon	0.2	0	0	0.2
CH_2/CH Substituted Aromatic Carbon	1.2	2.6	0	4.6
Naphthene Substituted Aromatic Carbon	0.3	0.6	0	3.4
CH_3 Substituted Aromatic Carbon	0.2	0.6	0	6.3
Internal (Bridgehead) Aromatic Carbon	0.1	0.8	0	3.7
Peripheral Unsubstituted Aromatic Carbon	5.8	12.0	0	14.0
Other or Heteroaromatic Carbon	0.9	0.2	0	0.0
Total Aromatic Carbon	8.7	16.8	0	32.2

Discussion

The standard methods indicate that these cellulosic fuels do not contain large amounts of harmful impurities. For example the metals content in the ethanol (Table 8) is low, as is the washed gum. The moderate pH_e is also reassuring, as acid will stress elastomers and plastics. The washed gum meets the ASTM 4806 specification, the unwashed gum content at ~15mg/100ml is on the high end of the D5789 standard but would not violate any gasoline or ethanol specification. It is unclear if the unwashed gum material is similar to that found in ethanol today. Similarly, the detection of nitrogen (Table 5) is unexpected and while there is not a standard for N wt%, it is an area that may be worth attention in the future.

It is interesting that the number of hydrocarbon samples made available to us was greater than the number of ethanol samples. This may indicate a business trend or may be simply a chance event. Our sample size is too small to resolve this question but it may be worth watching for further developments along these lines. Regardless of the reason, it is clear these cellulosic-derived hydrocarbons span a very broad gamut from a sample that is very like winter gasoline, to a naphtha with gasoline-like distillation but low octane, to a naphtha that spans both the gasoline and diesel distillation range. It is clear there is a wide range of fuel stocks becoming available but if they fit into a particular gasoline formulator's needs is entirely a case by case question.

As noted in the results, there is a wide variation in the distribution of carbon number and chemical types across these samples. The samples were deliberately obtained from various feedstocks and processes, nonetheless the variation is significant and more than might be expected between refinery streams. This is neither bad nor good but does illustrate that naphthas from diverse biologic stocks and processing techniques are not drop in replacements for each other. Of special interest is Naphtha 3 which has a fairly tight distillation range and very low vapor pressure, no aromatics and a rather limited chemical composition dominated by *iso*-alkanes from C8 to C10, with a limited amount of C8 and C9 normal and cyclo-alkanes. To ensure good combustion in ICE or diesel engines this stock would need to be blended with care.

The standard tests, such as D86 distillation and DHA, show that the naphthas are each unique and will differ in meaningful ways from gasoline. It is only in the advanced analysis that it is possible to see why this is so. In this way the advanced techniques provide complimentary detail which would be useful in modeling the combustion of these stocks, and in determining how or even if they could be effectively blended into a finished fuel.

Both standard and advanced methods show us that the gasoline sample is really not that different from winter gasoline. Aside from very low alkene content there is a distribution of chemical types and in each type there is a distribution of carbon number. One odd feature is the large amount of butane, isobutene and isopentane. The standard methods did confirm this in that several attempts at running the D-86 procedure failed due to too much material evolving at the beginning of the test. Still, it is not at all clear that this would cause any problems in combustion or emissions. The light ends of this fuel would weather rapidly in warmer weather, much like class E winter gasoline.

The presence of Si in some hydrocarbon samples is potentially troubling as it is a known poison for the lambda (air to fuel) sensor **[8]**. It would be desirable for cellulosic fuel producers to track down the possible pathways that can introduce Si and establish QC processes to ensure this contaminant is minimized and does not reach harmful levels even in quality spills.

Sulfur is also potentially a troublesome contaminant in some samples (and production processes) but not in others. Most samples were very low in sulfur but Naphtha 2 was high enough to violate Tier 3 requirements, limiting the amount that could be blended into a finished fuel. Even the advanced analysis in this study does not indicate what chemical species is bringing the sulfur into the stock. Of course both the sulfur and the unusually heavy final 5% of Naphtha 2 could be modified with proper treatment, though such treatment would be likely to alter other aspects of the stock, at least to some extent. Similarly the benzene content was acceptable in most samples with the exception of 1.44 percent benzene in Naphtha 2, Table 7b.

All the naphthas are quite low octane, and while standard tests indicate the cause, the advanced methods pin point it. The low aromatic content and especially the high amount of mid-range *n*-alkanes in Naphthas 1 and 2 clearly will lead to low RON and

MON. Naphtha 3 has a large *iso*-alkane content but they tend to be larger molecules and the aromatic content is nearly nonexistent. The relatively balanced distribution of lighter *iso*-alkanes along with a significant C7-C10 aromatic content leads to the fairly normal octane value observed for the Woody Biomass Gasoline.

Even finer detail is available from NMR analysis. The aliphatic region of the gasoline sample has several prominent features that distinguish it from the naphtha samples. Note the very low contributions associated with *n*-alkane chains, $C_\alpha - C_{\delta/\varepsilon}$ discussed above. In contrast, the relatively high carbon content in the 12.5-5 ppm region suggests relatively high methyl carbon substitution β to an internal branching point, or methyl groups γ to an aromatic ring. The latter could be consistent with greater carbon content in the 45-40 ppm region, and may be consistent with some of the unidentified aromatic resonances greater than 140 ppm, both indicative of branched alkyl aromatic substituents. Even more prominently, two integration regions, 22-20 and 20-18 ppm, can be attributed to the large number of carbons α-to-aromatic rings. The two regions, and slightly overlapping surrounding regions, represent a variety of aromatic methyl substitution patterns.

The ^{1}H NMR integration regions in Table 9 and Figure 9 have been normalized to show the carbon-type distribution of each sample. In Figure 9 the left side of the figure contains the aromatic proton/carbon structures and the right contains aliphatic proton/carbon structures. Naphtha 3 is unique in having no hydrogen resonances associated with aromatic species. Naphthas 1 and 2, and the gasoline sample, have significant contributions from aromatic species. Also readily apparent in Naphtha 2 and the Woody Biomass Gasoline sample is the presence of non-aromatic unsaturates, region O1, that are not present above detection limits in Naphthas 1 and 3, making up about 2.3 mole percent of the carbon species identifiable from the ^{1}H NMR spectra for Naphtha 2 and about one-fourth of this for the gasoline sample. Additionally, this information is supported by the carbons in region O2, representing methyl and methylene groups adjacent to alkenes, although the value for Naphtha 2 is a little lower than might be anticipated and likely results from some overlap with adjacent integration regions. The most obvious features in the ^{1}H NMR spectra appear on the right side, represented by the integration regions in Figure 9, are the aliphatic methylene and methyl groups, regions P3-P5, accounting for better than half of the carbons in the Woody Biomass Gasoline and 90% of all carbons in Naphtha 3.

Further examination of the methylene protons and methyl protons not attached to aromatic rings, regions P3-P4 and P5, respectively, in Table 9 is needed to better understand the character of these samples. As gasoline fuel components, it is expected that paraffinic components would make up such a large portion of each sample, gasoline being in large part made up of light, highly-branched aliphatic molecules (*iso*-alkanes) with some aromatic and unsaturated content. Because the quantities of alkanes are different for each sample, Table 12 reproduces data from Table 9, but normalized by the total paraffinic carbons in each sample to allow for better relative comparisons of the quantities of each carbon type and their implications for each sample. For the three naphtha samples examined, the number of methylene carbons presented in Table 12, labeled P3 and P4, greatly exceeds the number of methyl carbons, P5, suggestive of considerable *n*-alkane character, which can be seen in the DHA results for Naphthas 1 and 2, where *n*-alkanes make up 64.3 and 48.92 percent volume, respectively. This is not the case for Naphtha 3, where *n*-alkanes make up only 12.35 percent volume, a value considerably closer to the Woody Biomass Gasoline sample, having 8.11 percent volume *n*-alkanes. Values for the methylene-to-methyl ratios are presented in Table 13. Ratios greater than one indicate a low paraffinic methyl carbon content and are suggestive of a relatively high *n*-alkane content and relatively low *iso*-alkane content, both of which are indicative of lower octane numbers. The inverse is observed for many gasoline fuels where the number of methyl carbons exceeds or roughly equals the methylene carbons, as can be seen for the Woody Biomass Gasoline sample, a finished or nearly finished gasoline fuel.[7]

Table 12. ^1H NMR Distribution of Paraffinic Carbons Types in Each Sample, Normalized to Total Alkane Content and by Carbon Type

			Relative Mole % C*			
Label	**Chemical shift range (ppm)**	**Chemical meaning**	**Naphtha 1**	**Naphtha 2**	**Naphtha 3**	**Woody Biomass Gasoline**
P1	1.963 - 1.570	CH and CH_2 groups of naphthenes	8.5	14.6	2.1	11.2
P2	1.570 - 1.391	CH groups of *iso*-paraffins	10.5	14.6	7.7	12.1
P3	1.391 - 1.115	CH_2 groups of paraffins (*n*-and *iso*-)	51.6	41.8	48.5	29.8
P4	1.115 - 0.941	CH_2 groups of paraffins (*n*-and *iso*-)	4.4	6.6	5.8	7.3
P5	0.941 - 0.254	CH_3 groups of paraffins (*n*-and *iso*-)	25.1	22.5	35.9	39.6

*Data from Table 9. Normalized by the total alkane content in each sample.

Table 13. ^1H NMR Comparison of Methylene and Methyl Carbon Ratios, Normalized to Total Alkane Content and by Carbon Type

	Naphtha 1	**Naphtha 2**	**Naphtha 3**	**Woody Biomass Gasoline**
CH_2 groups (P3+P4), %C*	55.9	48.4	54.3	37.1
CH_3 groups (P5), %C*	25.1	22.5	35.9	39.6
CH_2-to-CH_3 ratio	***2.2***	***2.1***	***1.5***	***0.9***

*Data from Table 9. Normalized by the total alkane content in each sample.

Further examination of the alkanes is necessary to draw better conclusions as to the structural origins of the low octane methylene-to-methyl ratios in Naphthas 1-3. In Tables 9 and 12 the aliphatic region from 1.963 – 0.25 ppm is broken into several sub-regions, although this deconstruction should be undertaken cautiously because of the high degree to which these sub-regions overlap. Buried within this region are protons attached to cycloalkanes (CH, methines of substituted cycloalkanes, P1), to tertiary carbons (CH, methines at alkane branch points, P2), paraffinic methylene carbons (CH_2, P3 and P4), and paraffinic methyl carbons (CH_3, P5). As can quickly be seen from the disagreement between the relative ^1H NMR magnitudes or trends among the samples (Table 12) and those shown from the DHA (Tables 7 and 5), these conservative integration estimates are insufficient to account for the quantities of cycloalkanes (P1) and *iso*-alkanes (P2) shown in the DHA, suggesting that considerable representation for these species must exist in adjacent integration regions, O2 or P3-P5. Cyclohexane and cyclopentane have unique methylene resonances that can be clearly assigned and integrated (Table 14), but instead of being located in the cycloalkane region (P1), they overlap with the methine region (P2). However, adjusting for the peak areas contributed by these species also does not account for the differences between the NMR and DHA data. As shown in Table 14, cyclohexane and cyclopentane are observed in Naphthas 1 and 2, but not the other samples, with the cyclopentane quantities roughly consistent with the 5-carbon cycloalkanes shown by DHA, while cyclohexane is consistently smaller than values for 6-carbon cycloalkanes observed by DHA. This is not surprising in that some of the 6-carbon cycloalkanes reported in the DHA analyses could result from methylcyclopentane or other structural isomers and would not be observed as either of the discrete cyclopentane or cyclohexane NMR resonances.

Calculating volumetric contributions is possible for known species by taking into account sample densities, data from the elemental analyses (Tables 1 and 4), and the species molecular weights and densities. By assuming that all remaining cycloalkane resonances result from methylcyclohexane, the volumetric contribution from region P1 for all four samples can also be estimated. The total percent volume contributions shown in Table 14 come closer to the values reported by DHA for naphthenes, and can come closer still if higher molecular weight cycloalkanes, resulting from multiple methyl substitutions or substitutions with longer alkyl chains, are assumed. But, as can quickly be seen, particularly for Naphtha 3, there is realistically a limit to how much volume could be made up using this approach, since a deficit of about six volume percent, starting from 2.1 volume percent, seems unlikely to be overcome in this manner. Higher naphthenic substitution can also be tested using GC and mass spectroscopy. It is more likely that a combination of overlap with adjacent spectral regions and contributions from heavier structural isomers accounts for the underestimation of the percent volume resulting from NMR integrations as compared to the detailed hydrocarbon analysis.

While cycloalkanes and methines are present in all of the samples, the quantities are insufficient to resolve the observed surplus of aliphatic methylene carbons. Two competing characteristics must be examined, both *n*-alkane chain length and *n*- versus *iso*-alkane content, since both characteristics impact the ratio of methylene-to-methyl groups. Table 12 normalizes the data in Table 9 to allow a better comparison of each paraffinic carbon type, and Table 13 provides a measure of the CH_2-to-CH_3 (methylene-to-methyl) ratio from Table 12. In Table 13, shorter *n*-alkane chain length and increasing *iso*-paraffinic character will contribute to lower values for this ratio, as methyl groups increase relative to methylene groups in both cases, and the effects cannot be differentiated without additional information, which is drawn from the $^{13}C\{^1H\}$ NMR analyses. In Table 13 the CH_2-to-CH_3 ratios of Naphthas 1 and 2 are basically the same.

From the $^{13}C\{^1H\}$ NMR spectrum (*vide infra, Tables 19 and 20*), Naphtha 1 is shown to have slightly longer *n*-alkane chain length than Naphtha 2, so the *iso*-alkane concentration for Naphtha 2 may be slightly greater for Naphtha 2 than Naphtha 1 to offset this small difference in order to arrive at the same value for this ratio. This is in fact the case and is reflected in the DHA *iso*-alkane values reported in Tables 7a and 7b, as well as Table 6. Naphtha 3 has a considerably lower value for the CH_2-to-CH_3 ratio than Naphthas 1 or 2, while the number of methylene carbons (P3 + P4) is nearly the same as that of Naphtha 1, and the average *n*-alkane chain length increases substantially from about seven to about eight carbons (Table 20). Taken together, these suggest that Naphtha 3 has an *iso*-alkane content substantially greater than Naphtha 1, and by extension Naphtha 2. Similarly, the Woody Biomass Gasoline has the lowest CH_2-to-CH_3 ratio, suggesting the greatest *iso*-paraffinic character or the shortest *n*-alkane chain length, or some combination of both.

From Table 20 we see the average *n*-alkane chain length drops from nearly seven for Naphthas 1 and 2, and eight for Naphtha 3, to a little less than five for the Woody Biomass Gasoline sample, while the number of methyl carbons (P5) is close to that of Naphtha 3, suggesting a lower *iso*-alkane content than Naphtha 3, but not as low as Naphthas 1 and 2. Leveraging knowledge of the average *n*-alkane chain length from the $^{13}C\{^{1}H\}$ NMR, or any other source, and the CH_2-to-CH_3 ratio from the ^{1}H NMR can allow us to conclude that Naphthas 1 and 2 are very similar with respect to *n*-alkane chain length and *iso*-alkane content, and Naphtha 3 and the Woody Biomass Gasoline are very different from Naphthas 1 and 2 and each other. Additionally, Naphtha 3 and the Woody Biomass Gasoline samples have higher *iso*-alkane content than Naphthas 1 and 2, with the former having generally longer *n*-alkanes and higher *iso*-alkane content, and the latter shorter *n*-alkanes and lower *iso*-alkane content. Higher *iso*-alkane content and shorter *n*-alkane chain lengths contribute to higher research octane numbers (RON), with the inverse also being true. The dominance of *n*-alkanes for Naphthas 1 and 2 are suggestive of low RONs, while the high *iso*-alkane content for Naphtha 3 and the Woody Biomass Gasoline are suggestive of high RONs. From the perspective of alkane content, Naphtha 1 might be expected to have a slightly lower RON than Naphtha 2 because of a slightly lower *n*-alkane chain length. Comparing the Woody Biomass Gasoline and Naphtha 3, the *n*-alkane chain lengths work in opposite directions with the shorter *n*- and *iso*-alkane chain lengths contribute to higher RON, while just the opposite is true for Naphtha 3.[7] While a structure-based RON estimate is not complete without including contributions from the aromatic species, the origins of the differences in RON can start to become clearer.

Table 14. ^{1}H NMR Assignments and Volume Percent Contributions of Cycloalkanes, Normalized by Carbon Type

Chemical	Chemical Shift (ppm)	Naphtha 1			Naphtha 2			Naphtha 3			Woody Biomass Gasoline		
		Mole % C	V%[1]	DHA[2]	Mole % C	V%[1]	DHA[2]	Mole % C	V%[1]	DHA[2]	Mole % C	V%[1]	DHA[2]
Cyclopentane	1.52	1.0	1.0	0.80	2.0	2.0	1.70	0	0	0	0	0	0.20
Cyclohexane	1.44	1.2	1.1	3.38	1.5	1.4	4.92	0	0	0.02	0	0	1.41
Cycloparaffins (P1)[2]	1.963 - 1.570	7.9	8.4	14.32	12.1	13.4	12.22	2.1	2.3	8.13	7.5	8.5	8.63
Naphthenic Carbon Contribution		*10.1*	-		*15.6*	-		*2.1*	-		*7.5*	-	
Total Carbon Contribution		*11.4*	-		*17.6*	-		*2.5*	-		*8.8*	-	
% Volume Contribution		-	10.5	*18.50*	-	16.8	*18.84*	-	2.3	*8.15*	-	8.5	*10.24*

[1] Volume percent uses density of each species.

[2] DHA values from Tables M. C5 values were used to represent "cyclopentane," C6 for "cyclohexane," and C7-C12 for "cycloparaffins."

[3] Assumes that "cycloparaffins" are only made up of methylcyclohexane.

At the other end of the ^{1}H NMR spectrum, near 7 ppm, a close examination of the aromatic region yields information regarding two specific compounds that have unique ^{1}H NMR resonances, specifically benzene and naphthalene. Benzene has a unique resonance at 7.36 ppm, while naphthalene has two uniquely distinguishable resonances near 7.8 and 7.5 ppm. Hydrogen atoms from benzene make up 0.3 and 0.6 mole percent of the hydrogen atoms in Naphthas 1 and 2, respectively, but were not observed in the gasoline sample. The ability to readily assess fused-ring aromatic content is an advantage of ^{1}H NMR that is more difficult to obtain from ^{13}C{^{1}H} NMR spectra. Presented in Table 15 are generally accepted ^{1}H NMR regions associated with fused ring di- and triaromatics, i.e. substituted naphthalenes, and anthracenes or phenylanes/phenanthrenes, respectively.**[4]** These are largely absent in the gasoline and gasoline-component samples, but minor contributions in the diaromatic region can be observed primarily from the presence of naphthalene, having uniquely distinguishable ^{1}H NMR resonances, at 0.009 mole percent hydrogen for Naphtha 1 and 0.025 mole percent for Naphtha 2, with other diaromatic species making up the balance. Naphthalene is not observed in the gasoline sample, but there is a small contribution from diaromatic species. Species having greater than two fused aromatic rings were not observed. Monoaromatic species other than benzene have splitting patterns consistent with either one or two alkyl substituents, with the majority of the alkyl substituents being methyl groups. From the ^{13}C{^{1}H} NMR data (*vide infra*), we can observe that these are largely made up of toluene and xylenes, as well as ethylbenzene.

Table 15 ^{1}H NMR Aromatic Region, Breakdown of Fused, Protonated Aromatic Rings, Results Normalized by Carbon Type

		Mole % C*			
Structure	Chemical Shift	Naphtha 1	Naphtha 2	Naphtha 3	Woody Biomass Gasoline
polyaromatic	8.3-10.7	0	0	0	0
triaromatic	7.8-8.3	0	0	0	0
diaromatic	7.2-7.8	0	0.3	0	0.2
monoaromatic	6.2-7.2	5.3	10.2	0	18.6

*Normalized to account for protonated carbons only.

Considering carbons from the aromatic region, A1-A7, and those representing substituted aromatic carbons, regions SA1-SA4, several additional observations can be made. There are effectively no aromatic species having greater than two, fused-aromatic rings. Close observation of the ^{1}H NMR resonances associated with regions A2 and A3, fused di-ring aromatic compounds, for Naphtha 2 reveals that very nearly all of the di-ring aromatic compounds can be attributed to unsubstituted naphthalene, represented by two characteristic doublets of equal intensity, contributing approximately 0.2%. There are effectively no di-aromatic resonances that can be observed in Naphtha 1, while the di-aromatic resonances observable in the Woody Biomass Gasoline sample represent a mixture of substituted naphthalenes with no naphthalene present, making up about 0.2% of the overall carbon contributions in A2 and 0.2% in A3. The remaining area in region A3 for each sample can be assigned either to benzene, clearly distinguishable by a characteristic singlet at 7.36 ppm,[5] or other mono-ring aromatic species. If the remaining areas associated with aromatic rings are assumed to be six-membered, then by summing regions SA1-SA4, as a means of accounting for the substituted aromatic carbons, and regions A3(minus di-aromatic species)-A7 to represent unsubstituted mono-aromatic carbons, the overall aromatic content of the samples can be compared. This results in an aromatic content for Naphtha 2 that is approximately twice that of Naphtha 1, and the Woody Biomass Gasoline having nearly five-times the number of aromatic ring carbons as Naphtha 1. Additionally, the average number of alkyl substituents per aromatic molecule can be calculated as 1.3, 1.7, and 2.8 for Naphthas 1 and 2, and Woody Biomass Gasoline, respectively.

Increasing aromatic substitution contributes to increasing octane values, thus, based on number of aromatic substitutions alone,[7] octane contributions from aromatic components would increase from Naphtha 1 to Woody Biomass Gasoline. Looking at the types of aromatic substituents represented in each sample, SA1-SA4, summarized in Table 17, Naphthas 1 and 2 have the greatest representation in region SA3, a region with overlapping methyl and methylene groups directly bound to an aromatic ring (see Figure 10), while the Woody Biomass Gasoline sample has a substituent distribution with the greatest population found in SA4, methyl groups directly bound to an aromatic ring, and a slightly lower population in SA3. If region SA3 is split evenly between methyl and methylene groups, all three samples have roughly equal relative populations of methylene groups adjacent to an aromatic ring, but the populations of methyl groups adjacent to an aromatic ring increases significantly, from Naphtha 1 to Woody Biomass Gasoline, with the Woody Biomass Gasoline having roughly 3-to-1 and 2-to-1 more methyl groups than Naphtha 1 and Naphtha 2, respectively. These results are in keeping with the DHA results (Tables 7 and 6) for aromatic compounds having carbon numbers greater than six, where carbon numbers 8, 9, and 10 are more likely indicative of multiple aromatic substitutions, as opposed to increased alkyl chain length. A highly substituted-aromatic content and a high methyl-to-alkyl aromatic substitution ratio are expected to contribute positively to octane values for the gasoline sample, relative to the two naphtha samples, as can be seen from the research octane numbers reported in Table 1. Contributions to octane are based upon the relative positions of the alkyl groups on the aromatic ring, but generally, methyl substitution has a higher research octane number than an equivalent ethyl substitution, and greater alkyl substitution increases octane, although greater than three can reduce the research octane number.[7] The impact of these characteristics, the number of aromatic substituents per molecule and the type of aromatic substituent, methyl or alkyl, is amplified by the relative quantities of aromatic carbons in each sample, as discussed above. With the Woody Biomass Gasoline having nearly five-times the aromatic content of Naphtha 1, and roughly 2.5-times that of Naphtha 2, the impact on octane from the aromatic portions of each sample should be considerable.

As with the ^{1}H NMR data, there are several readily observable pieces of information available from the ^{13}C{^{1}H} NMR results. Foremost, there are no significant resonances associated with carbonyl-containing compounds observable in any of the samples, or other clearly definable oxygenate species, such as alcohols or ethers, indicating that concentrations are below the NMR detection limits (~0.5 wt%), consistent with the GC-AED analysis (<0.04 wt%). Naphtha 3 is strictly aliphatic with no observable aromatic resonances, while Naphthas 1 and 2, and the Woody Biomass Gasoline sample, have significant contributions from aromatic species.

Table 16. ^{1}H NMR Comparison of Four Renewable Gasoline-Type Fuel Components, Normalized by Carbon Type and Aromatic Content

			Relative Mole % C*			
Label	**Chemical shift range (ppm)**	**Chemical meaning**	**Naphtha 1**	**Naphtha 2**	**Naphtha 3**	**Woody Biomass Gasoline**
SA1	3.306 - 2.883	α-CH to aromatic	0	1.6	-	0.6
SA2	2.883 - 2.641	α-CH_2 to aromatic	1.5	2.4	-	1.3
SA3	2.641 - 2.292	α-CH_2 + α-CH_3 to aromatic	15.4	16.0	-	19.8
SA4	2.292 - 2.040	α-CH_3 to aromatic	4.6	8.8	-	25.2
		Relative Totals	21.5	28.8	-	47.0
SA2 + ½SA3		Assumed CH_2	9.2	10.4	-	11.2
SA4 + ½SA3		Assumed CH_3	12.3	16.8	-	35.1

Table 17. Comparison of the characteristics of aromatic molecules, normalized by carbon type.

		Relative Mole % C*			
Operation	**Description**	**Naphtha 1**	**Naphtha 2**	**Naphtha 3**	**Woody Biomass Gasoline**
Total Aromatic Carbons Normalized to Naphtha 1	Normalized Aromatic Carbon Content (sub and unsub)	1.0	1.9	-	4.8
Sum of A3-A7[1]	Unsubstituted aromatic carbons	5.1	8.9	-	16.6
Sum of SA1-SA4	Substituted aromatic carbons	1.4	3.6	-	14.7
Total	Total aromatic carbons (sub and unsub)	6.5	12.5	-	31.3
((Sum SA1-SA4)/Total)*6	Substituted aromatic carbons per molecule[2]	1.3	1.7	-	2.8
6 - Sub per molecule	Unsubstituted aromatic carbons per molecule[2]	4.7	4.3	-	3.2
Normalized to All Aromatic Carbons in Sample	Normalized Substituent Carbon Content %	21.5	28.8	-	47.0

[1] Accounts for di-aromatic species in A3.

[2] Assumes only mono-aromatic species and 6-membered aromatic rings.

From Figure 11, the resonances of the naphtha and gasoline samples have features that differentiate them. A more detailed examination of the aliphatic region can provide some insight into the types of molecules making up the naphtha samples, and is show in Figure 12 as a bar chart, normalized by aliphatic carbon type, so as to best compare the relative differences in carbon type for the aliphatic species. This is necessary, in order to provide the best aliphatic carbon-type comparison among samples having widely different volumetric contributions, particularly volumetric contributions that may arise from blending decisions.

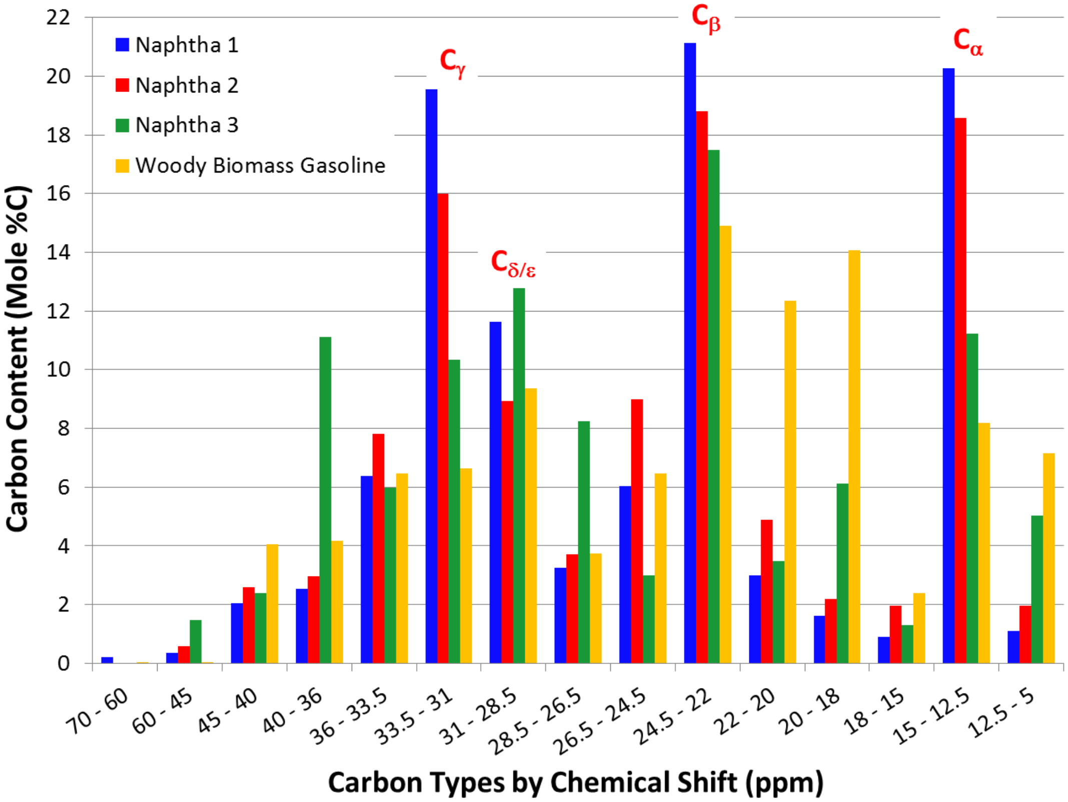

Figure 12. Carbon Type Distribution Normalized to the Aliphatic Carbons of Four Renewable Gasoline-Type Fuel Components. Values were obtained by integrating each aliphatic $^{13}C\{^1H\}$ NMR chemical shift regions shown in Table 10, and normalizing to 100 percent.

Let us return to the differences between Naphthas 1 and 2 which can be observed in the aliphatic region. These appear to be most distinct in spectral regions associated with *n*-alkane segments. The low boiling points of gasoline-type fuel components are consistent with small, branched molecules containing between four and twelve carbons, having relatively short *n*-alkane segments. Figure 10 shows the systematic designation of carbons in an *n*-paraffinic segment. There is a characteristic pattern of 4-6 resonances, depending upon the NMR instrument field strength and resolution, that develops for long-chain, *n*-alkanes resulting from the overlap of each of these carbon types, with only the relative intensities varying with average *n*-alkane chain length and not the chemical shifts. For *n*-alkane chains of greater than 10 carbons, the chemical shifts are reliable, with C_α being the methyl group at the end of the segment (~14.1 ppm), followed by C_β (~22.8 ppm), C_γ (~32.1 ppm), C_ε (~29.9 ppm), and C_δ (~29.5 ppm). Sample concentration will cause the precise position to vary slightly, and C_ε has a nearly coincident, but recognizable, resonance on the upfield side in higher-field instruments.

For gasoline-like samples, the majority of the *n*-alkane species are shorter than 10 carbons, reducing the utility of these standard resonances, however two benefits may be drawn from this realization. The first is that the equivalently positioned carbons in the shorter *n*-alkanes are for the most part contained within the same chemical shift regions, Table 10, and secondly, many of the shorter *n*-alkanes have at least one carbon with a unique chemical shift, allowing for reasonable quantitation of each *n*-alkane species, as shown in Table 19. Armed with this information, the integration regions, shown in Figure 12 and Table 10, containing these carbon types show that Naphtha 1 has about 2 percent more C_α, C_β, and $C_{\delta/\varepsilon}$ carbons than Naphtha 2, and 3.5 percent more C_γ carbons than Naphtha 2, suggesting that Naphtha 1 has more molecules containing *n*-paraffinic segments, and that those segments are generally longer. Integration of the resonances from each *n*-alkane and then converting to percent volume contributions, Table 19, shows close agreement between results derived from $^{13}C\{^1H\}$ NMR and DHA measurements.

To perform the volumetric contributions for propane and butane, it was necessary to make assumptions for the densities of each because both are gaseous at room temperature and atmospheric pressure; using the density of the gas under these conditions or the density of liquid propane or butane at room temperature, did not return reasonable results. Densities of 0.3 and 0.5 g/ml were assumed because these values provided reasonable results, as well as seemed commensurate with the observed integration areas observed in the NMR, when compared to other *n*-alkanes. Also interesting to note is that in the cases of the Naphtha 2 and Woody Biomass Gasoline samples, the values for propane and butane are lower than reported by DHA, which could reflect either handling or storage losses for the NMR samples, since no particular precautions were taken to avoid the loss of either highly volatile component. In the case of Naphtha 1, arguably, the value for propane is on the lower edge of accurate quantification by $^{13}C\{^1H\}$ NMR and the value is not distinguishable from that provided by DHA.

Table 19 also reports discrete values for components up to *n*-heptane, and includes *n*-nonane, but groups together *n*-octane and *n*-alkanes with ten or more carbons. *N*-alkanes with seven or fewer carbons have at least one unique resonance that can be extrapolated to prove compositions of each species, as does *n*-nonane, where the center-most carbon also has a unique resonance. *N*-octane and *n*-alkanes with ten or more carbons have resonances that are coincident, as described above, and are not able to be distinguished by NMR. Table 20 shows a comparison of the average *n*-alkane chain length calculated from the weighted average of each *n*-alkane component from Table 19. The values in Tables 19 and 20 compare favorably with values obtained by DHA, particularly for Naphthas 1 and 2, and show that Naphtha 1 has a slightly greater average *n*-alkane chain length than Naphtha 2. From the DHA, Naphthas 1 and 2 have effectively the same cycloalkane content, and the highest cycloalkane contents of the four samples. Looking strictly at the $^{13}C\{^1H\}$ NMR, regions associated with cycloalkanes, 28.5-26.5 ppm, 26.5-24.5 ppm and 22-20 ppm, do not follow this trend and must have other species present that degrade the value of these regions, in the absence of other data, as a reliable indicator of cycloalkanes. As discussed, while Naphthas 1 and 2 are very similar, some differences among the *n*-alkanes can be observed from the $^{13}C\{^1H\}$ NMR spectra.

As mentioned above, Naphtha 3 stands out from Naphthas 1 and 2 in several prominent characteristics. The region from 40-36 ppm shows more than four times the number of methylene carbons adjacent to tertiary, or branching carbons in Naphtha 3, as compared to Naphthas 1 and 2 (Table 10), corroborating the lower CH_2-to-CH_3 ratio found in the ^1H NMR. This suggests considerably more branching in Naphtha 3, which is borne out by greater carbon populations in the following regions: 60-45 ppm, where a methylene carbon α to two branching points would be expected, and 12.5-5 ppm where a methyl carbon β to a branching point might be expected. Naphtha 3 also has a higher carbon content in the region between 20-18 ppm, a region that is usually associated with cycloalkanes and substituted aromatics, but another explanation must be examined as there appear to be insufficient cycloalkanes, as determined by ^1H NMR (Table 14) and DHA (Tables 7), to account for this difference, and no aromatic carbons in Naphtha 3. An alternative explanation is that these carbons are associated with methyl branches at least three carbons from a terminal or branched position in both directions, such as 3-methylhexane, which would also contribute to the increases noted previously for 40-36 ppm for Naphtha 3 compared to Naphthas 1 and 2. Regarding *n*-alkanes, Naphtha 3 ranks third, behind Naphthas 1 and 2 for total normalized areas in chemical shift regions containing *n*-alkane resonances (33.5-31, 31-28.5, 24.5-22, and 15-12.5 ppm), and is indeed third in total *n*-alkane content by DHA. This suggests that a rough estimate of relative *n*-alkane content may be obtained in this manner, although the areas do not correspond directly to volume percent and should be used cautiously in large part because of overlap of resonances from other paraffinic species with these regions. Additionally, Naphtha 3 has the highest value in the region assigned to $C_{\delta/\varepsilon}$ carbons, the carbons furthest from terminal methyl groups, yet the lowest value among the Naphthas in the other regions. This suggests a lower *n*-alkane content, as mentioned previously, but also *n*-alkanes with longer chain lengths than Naphthas 1 and 2. This can be seen in Tables 19 and 20 and is substantiated in figures 4 - 6. In summary, Naphtha 3 has characteristics consistent with significantly higher instances of methyl branches, as well as contributions from characteristic alkyl branches, than Naphthas 1 and 2.

The Woody Biomass Gasoline sample has very low contributions associated with *n*-alkane chains in the $C_\alpha – C_{\delta/\varepsilon}$ regions discussed above, as compared to the naphtha samples. The normalized $C_{\delta/\varepsilon}$ carbon region for this sample has a relatively high value in comparison to the C_γ region, which could suggest the presence of longer-chain *n*-alkanes. But such an interpretation would be misleading because there is a discontinuity in the compound-specific integration results presented in Table 19 at *n*-heptane. Discontinuities are not observed for the other samples, and are not evident in the DHA analysis for this sample. Rather, a smooth decline in *n*-alkane values following *n*-butane is observed. This suggests that values presented for *n*-alkanes greater than octane are incorrectly assigned and representative of species with coincident or nearly coincident resonances, but not *n*-alkanes. By ignoring the integration results in the greater than *n*-octane category, the average *n*-alkane chain length becomes nearly the same as the result from the DHA analysis, and is presented as a footnote in Table 20. Considering resonances associated with *iso*-alkanes, the relatively high carbon content in the 12.5-5 ppm region suggests relatively high methyl carbon substitution β to an internal branching point, as with Naphtha 3, or methyl groups γ to an aromatic ring. For this sample, the latter could be associated with some of the unidentified aromatic resonances greater than 140 ppm; a region indicative of alkyl-substituted aromatic ring carbons. Even more prominently, two integration regions, 22-20 and 20-18 ppm, can be attributed to the large number of carbons α-to-aromatic rings, previously discussed in the ^{1}H NMR section. The two regions, and slightly overlapping surrounding regions, represent a variety of aromatic methyl substitution patterns. Differences in the aliphatic region between the Woody Biomass Gasoline sample and Naphtha 3 are clear for *n*-alkanes, but less so for *iso*-alkanes, and between Naphthas 1 and 2 for *n*-alkanes and alkyl groups alpha to an aromatic ring.

In examining the aromatic regions of Naphthas 1 and 2, and the Woody Biomass Gasoline sample, resonances for several identifiable aromatic species were observed above, in particular benzene, toluene, and xylenes. The mole percent composition for carbon atoms in each of these chemicals are shown in Table 18. Also distinguishable are resonances from both ethyl and propylbenzene. Resonances for benzene and propylbenzene do not appear in the gasoline sample. Taken together, the specific chemicals listed in Table 18 make up two-thirds to three-quarters of the aromatic carbons, and contribute 7.2, 11.8, and 12.4 percent of the total carbons in Naphthas 1 and 2, and the gasoline samples, respectively. These data when combined with elemental analyses (Table 5) and the sample densities (Table 1) allow the volume percent of each of the identifiable components to be calculated, also shown in Table 18, which compare favorably with the DHA results listed in Table 7. Different quantities of these chemicals in Naphthas 1 and 2 are visually apparent in the aromatic carbon integration regions shown in Figure 11, and Tables 10 and 11.

The aromatic region of the gasoline sample has several notable resonances that are not as readily interpretable, specifically, those found in the 143-131 and 131-127.5 ppm regions, as well as the two adjacent regions. Likely explanations include aromatic species containing branched alkyl substituents, with the possibility of multiple aromatic substitutions highly likely, which increases the complexity of the spectrum. Also possible are resonances that may be attributable to conjugated double bond from unsaturated alkanes.

The advanced methods offer further insight into the fuels. For example Naphtha 3 has roughly half its volume in *iso*-alkanes with only three different carbon numbers, 8-10 (see Figure 6), and 90% of its content in only 7 carbon number – chemical type combinations. This is not all that far from a surrogate fuel made with only a few pure compounds. Yet the D-86 curve seems perfectly reasonable for a mid to tail end blend stock. A complimentary view is provided by NMR, where in Table 18 we see that not only does Naphtha 2 include about 12% aromatics, but for example about 5% is toluene. Furthermore NMR directly measures the amount of aromatic carbon and non-aromatic carbon (in the fully hydrogenated substituent groups) that is contributed by aromatic molecules, for example in the gasoline sample about 20% of the carbon atoms in the aromatics portion of the fuel are not aromatic carbons.

Table 18. Normalized Integration of Aromatic Carbons Associated with Specific Chemical Structures from $^{13}C\{^1H\}$ NMR

	Naphtha 1		Naphtha 2		Naphtha 3		Woody Biomass Gasoline	
Chemical	**Mole % C**	**V%[1]**	**Mole % C**	**V%[1]**	**Mole % C**	**V%[1]**	**Mole % C**	**V%[1]**
Benzene	0.8	0.6	1.9	1.5	0	0	0	0
Toluene	2.9	2.2	4.7	3.7	0	0	2.3	1.9
o-xylene	0.9	0.7	1.3	1.0	0	0	2.4	1.9
m-xylene	0.7	0.6	1.2	0.9	0	0	4.8	3.9
p-xylene	0.4	0.3	0.6	0.5	0	0	2.3	1.9
Ethylbenzene	1.2	0.9	1.8	1.4	0	0	0.6	0.5
Propylbenzene	0.3	0.2	0.3	0.2	0	0	0	0
Total Carbons[2]	7.2		11.8		0		12.4	
Aromatic Ring Carbons[3]	*5.9*		*9.5*		*0*		*9.9*	
***Partial** Volume*[4]		5.5		9.2		0		10.1

[1] Volume percent uses the density of each species.

[2] Total Carbons accounts for aromatic and nonaromatic carbons associated with these species.

[3] Aromatic Ring Carbons accounts for only the carbons in the aromatic rings of these species.

[4] Partial volume is the volume contributed only by these specific aromatic compounds, not total aromatic volume.

Table 19. Comparison of $^{13}C\{^1H\}$NMR and DHA values for *n*-alkanes.

		Naphtha 1			Naphtha 2			Naphtha 3			Woody Biomass Gasoline		
		NMR		DHA[1]	NMR		DHA[1]	NMR		DHA[1]	NMR		DHA[1]
Name	Carbon #	**Mole % C**	**V%[2]**	**V%**	**Mole % C**	**V%[2]**	**V%**	**Mole % C**	**V%[2]**	**V%**	**Mole % C**	**V%[2]**	**V%**
Propane	3	0.06	0.11	0.08	0.07	0.14	0.3	0	0	0	0.24	0.46	0.88
n-Butane	4	1.3	1.9	2.11	2.0	3.0	3.64	0	0	0	1.6	2.6	3.09
n-Pentane	5	6.6	7.6	8.5	5.8	7.0	8.83	0.0	0.0	0.02	1.8	2.3	2.48
n-Hexane	6	12.3	13.6	15.14	9.8	11.3	12.56	0.4	0.5	0.26	0.5	0.6	1.11
n-Heptane	7	17.7	18.7	17.32	10.1	11.1	11.96	2.0	2.1	0.62	0	0	0.32
≥ *n*-Octane[3]	>8	12.8	13	13.83	7.4	7.9	8.14	11.5	11.8	7.28	3.8	4.1	0.08
n-Nonane	9	7.3	7.3	7.32	3.1	3.2	3.5	0[4]	0[4]	4.17	0	0	0.15
	Total	58.1	***62.2***	***64.30***	38.3	***43.6***	***48.93***	13.9	***14.4***	***12.35***	7.9	***10.1***	***8.11***

[1] DHA data from Tables M.

[2] Volume percent derived from the NMR measurements uses the density of each species, except propane and *n*-butane where the blending densities are assigned values of 0.3 and 0.5 g/ml, respectively.

[3] Rolls up the values of *n*-paraffins larger than eight carbons, except for nonane which has a unique resonance.

[4] No clearly distinguishable resonance for n-nonane could be assigned because of coincidental overlap with another resonance. Values were included in the ≥ n-Octane figures.

Table 20. Comparison of NMR and DHA values for the weighted average *n*-alkane chain length.

	Naphtha 1	Naphtha 2	Naphtha 3	Woody Biomass Gasoline
NMR	6.9	6.6	7.8	5.9*
DHA	6.9	6.5	8.3	4.7

*Becomes 4.5 if *n*-paraffins >octane are removed.

Overall the various methods are complimentary to each other. ASTM tests for impurities were in no way duplicated or superseded by the advanced methods work. On the other hand multidimensional GC gave a much more detailed picture of the distribution of compounds which could for example be useful in optimizing combustion and providinge customer satisfaction. The even more chemically nuanced information from the NMR results indicated the amount of various CH_x groups in various types of molecules, which may be important in developing fuels and engines with lower emissions. While the information available in ASTM methods can point to general trends in combustion and emissions this more detailed information would be required to understand or model performance and emissions.

Conclusions

- Biologically derived gasoline and alcohol samples, from various sources and processed by differing methods result in fuel stocks with very different chemical profiles.
- Many bulk properties were within the normal range for gasoline or gasoline blend stocks for one or more of the samples.
- Research octane levels varied from 91.4 to 15.3 depending on the sample.
- Impurity levels tended to be low, but individual samples showed high levels of Si, S, or gum, and the unexpected detection of nitrogen, indicating that byproducts and impurities are possible, and accordingly a need for vigilance in quality control once the final processes are developed.
- Standard tests are highly effective for determining bulk physical and combustion properties such as gravity, octane, and distillation.
- Substantial compositional differences among the samples are clearly identifiable in the NMR, multidimensional GC, and by ASTM methods. Such chemical detail provides better insight into the probable behavior of the fuels and stocks and permits more effective levels of modeling.
- Multidimensional gas chromatography and nuclear magnetic resonance techniques can be used to determine levels of chemical detail the standard fuel test methods do not.
- Differences among the naphtha and gasoline samples are observable in the multidimensional GC data in both chemical type and the distribution across carbon number within a chemical type.
- Differences among the naphtha and gasoline samples are observable in the NMR spectra in chemical type and chain length, and additionally the number and distribution of molecular structures within a chemical type.

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Appendix

Table A.1 Summary Data for AVFL-19a Fuels – Detailed Hydrocarbon Analyses – Naphtha 1

Naphtha 1 (vol.%) - Lab 1

Carbon #	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Unknown	Total
C3	0.10	0.00	0.00	0.00	0.00	0.00	0.10
C4	2.11	0.04	0.00	0.00	0.00	0.00	2.15
C5	8.64	0.56	0.00	0.81	0.00	0.00	10.02
C6	15.27	1.44	0.01	3.39	0.65	0.00	20.76
C7	17.30	1.75	0.01	6.40	2.22	0.00	27.67
C8	13.24	1.96	0.15	5.47	2.42	0.00	23.24
C9	7.19	2.68	0.00	1.91	0.92	0.40	13.10
C10	0.38	1.18	0.00	0.07	0.10	1.11	2.84
C11	0.01	0.02	0.00	0.00	0.00	0.04	0.06
C12+	0.05	0.00	0.00	0.00	0.00	0.00	0.06
Total	64.30	9.62	0.18	18.04	6.32	1.55	100.00

Naphtha 1 (vol.%) - Lab 2

Carbon #	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Unknown	Total
C3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C4	2.01	0.03	0.00	0.00	0.00	0.00	2.04
C5	8.41	0.53	0.00	0.80	0.00	0.00	9.74
C6	15.21	1.40	0.00	3.40	0.66	0.00	20.67
C7	17.49	1.73	0.00	6.50	2.27	0.00	27.99
C8	13.46	2.05	0.40	5.68	2.56	0.00	24.15
C9	7.46	2.73	1.23	1.72	0.93	0.00	14.07
C10	0.39	0.86	0.00	0.06	0.00	0.00	1.32
C11	0.00	0.02	0.00	0.00	0.00	0.00	0.02
C12+	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	64.43	9.37	1.63	18.16	6.42	0.00	100.00

Naphtha 1 (vol.%) - Lab 5

Carbon #	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Unknown	Total
C3	0.13	0.00	0.00	0.00	0.00		0.13
C4	2.22	0.04	0.00	0.00	0.00		2.26
C5	8.45	0.57	0.00	0.80	0.00		9.82
C6	14.94	1.43	0.00	3.36	0.64		20.37
C7	17.16	1.71	0.01	6.49	2.22		27.59
C8	13.52	2.06	0.03	6.12	2.54		24.27
C9	7.32	2.33	0.25	2.46	0.89		13.25
C10	0.39	0.42	0.21	0.05	0.07		1.14
C11	0.01	0.04	0.00	0.01	0.00		0.06
C12+	0.01	0.00	0.00	0.00	0.00		0.01
Total	64.16	8.60	0.52	19.29	6.38	1.01	99.96

Table A.2 Summary Data for AVFL-19a Fuels – Detailed Hydrocarbon Analyses – Naphtha 2

Naphtha 2 (vol.%) - Lab 1							
Carbon #	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Unknown	Total
C3	0.49	0.00	0.02	0.00	0.00	0.00	0.52
C4	3.86	0.17	0.89	0.00	0.00	0.00	4.91
C5	9.00	0.78	1.59	1.70	0.00	0.00	13.07
C6	12.52	1.51	1.89	4.93	1.42	0.00	22.26
C7	11.84	1.81	0.93	6.26	4.13	0.00	24.97
C8	7.53	2.10	0.54	3.01	4.09	0.01	17.27
C9	3.44	3.72	0.00	1.41	1.57	0.48	10.62
C10	0.26	1.45	0.00	0.20	0.81	0.83	3.55
C11	0.07	0.14	0.00	0.00	0.53	0.43	1.17
C12+	0.13	0.06	0.00	0.00	0.29	1.17	1.65
Total	49.14	11.74	5.86	17.51	12.83	2.93	100.00

Naphtha 2 (vol.%) - Lab 2							
Carbon #	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Unknown	Total
C3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C4	3.52	0.15	0.79	0.00	0.00	0.00	4.45
C5	9.01	0.76	1.53	1.75	0.00	0.00	13.05
C6	13.02	1.52	2.21	5.09	1.49	0.00	23.33
C7	12.31	1.65	1.32	6.59	4.55	0.00	26.41
C8	7.83	2.31	0.68	4.69	4.37	0.00	19.88
C9	3.61	2.17	1.40	1.43	1.67	0.00	10.27
C10	0.30	0.86	0.05	0.27	0.27	0.10	1.74
C11	0.06	0.07	0.00	0.00	0.35	0.04	0.48
C12+	0.05	0.00	0.00	0.03	0.06	0.10	0.12
Total	49.71	9.47	7.98	19.84	12.77	0.24	100.00

Naphtha 2 (vol.%) - Lab 5							
Carbon #	*n-Paraffins*	*Isoparaffins*	*Olefins*	*Naphthenes*	*Aromatics*	*Unknown*	*Total*
C3	0.42	0.00	0.02	0.00	0.00		0.44
C4	3.54	0.16	0.85	0.00	0.00		4.55
C5	8.47	0.75	1.56	1.65	0.00		12.43
C6	12.13	1.45	1.93	4.75	1.42		21.68
C7	11.73	1.59	1.95	6.35	4.12		25.74
C8	7.76	2.09	1.00	4.39	4.28		19.52
C9	3.46	2.14	0.61	1.75	1.49		9.45
C10	0.25	0.68	0.18	0.15	0.96		2.22
C11	0.07	0.29	0.07	0.12	0.60		1.15
C12+	0.05	0.10	0.00	0.00	0.50		0.65
Total	47.88	9.25	8.17	19.16	13.37	1.70	99.53

Table A.3 Summary Data for AVFL-19a Fuels – Detailed Hydrocarbon Analyses – Naphtha 3

Naphtha 3 (vol.%) - Lab 1

Carbon #	*n-Paraffins*	*Isoparaffins*	*Olefins*	*Naphthenes*	*Aromatics*	*Unknown*	*Total*
C3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C5	0.02	0.07	0.00	0.00	0.00	0.00	0.09
C6	0.28	0.15	0.00	0.02	0.00	0.00	0.45
C7	0.64	1.59	0.00	0.16	0.00	0.00	2.39
C8	6.90	24.17	0.04	6.89	0.27	0.00	38.27
C9	4.05	33.06	0.20	2.59	0.89	0.09	40.88
C10	0.52	14.57	0.00	0.19	0.17	1.43	16.88
C11	0.00	0.18	0.00	0.08	0.00	0.16	0.34
C12+	0.06	0.00	0.00	0.00	0.00	0.54	0.60
Total	12.48	73.79	0.24	9.93	1.33	2.22	99.99

Naphtha 3 (vol.%) - Lab 2

Carbon #	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Unknown	Total
C3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C4	0.00	0.00	0.00	0.00	0.00	0.00	0.01
C5	0.02	0.06	0.01	0.00	0.00	0.00	0.09
C6	0.25	0.13	0.00	0.03	0.00	0.00	0.41
C7	0.61	1.42	0.00	0.16	0.01	0.00	2.20
C8	6.37	20.41	5.14	4.26	0.14	0.10	36.32
C9	4.33	32.41	2.93	4.65	1.70	0.21	46.02
C10	0.64	12.69	0.33	0.27	0.26	0.00	14.19
C11	0.01	0.44	0.00	0.00	0.02	0.00	0.46
C12	0.01	0.00	0.00	0.00	0.00	0.00	0.01
Total	12.24	67.55	8.40	9.37	2.13	0.31	100.00

Naphtha 3 (vol.%) - Lab 5

Carbon #	*n-Paraffins*	*Isoparaffins*	*Olefins*	*Naphthenes*	*Aromatics*	*Unknown*	*Total*
C3	0.00	0.00	0.00	0.00	0.00		0.00
C4	0.00	0.00	0.00	0.00	0.00		0.00
C5	0.02	0.06	0.00	0.00	0.00		0.08
C6	0.25	0.13	0.00	0.02	0.00		0.40
C7	0.61	1.41	0.00	0.17	0.00		2.19
C8	6.68	25.34	0.00	1.99	0.00		34.01
C9	4.13	34.54	0.00	2.88	0.58		42.13
C10	0.62	16.49	0.00	0.12	0.23		17.46
C11	0.00	0.45	0.00	0.00	0.00		0.45
C12+	0.04	0.06	0.00	0.00	0.00		0.10
Unknown						2.57	2.57
Total	12.35	78.48	0.00	5.18	0.82	2.57	99.40

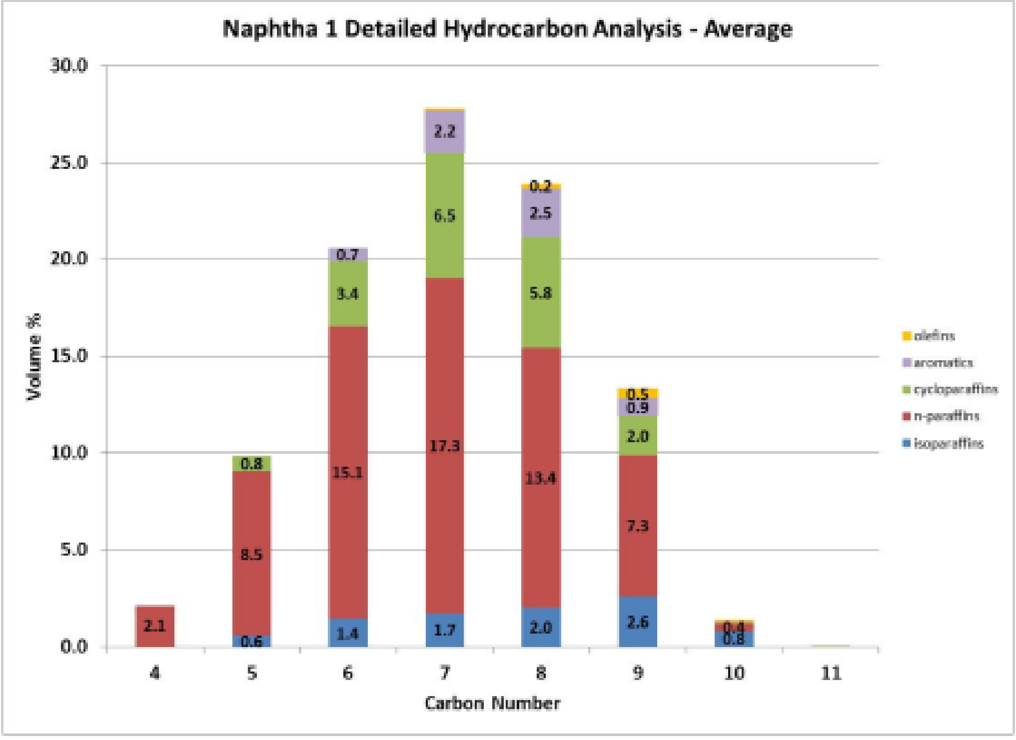

Figure A1: DHA for Naphtha 1

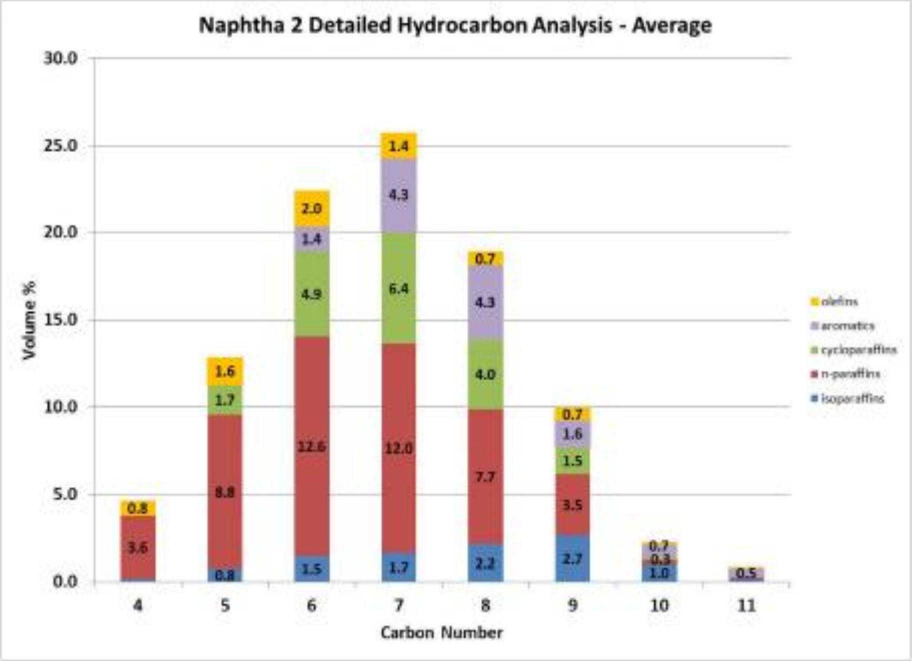

Figure A2: DHA for Naphtha 2

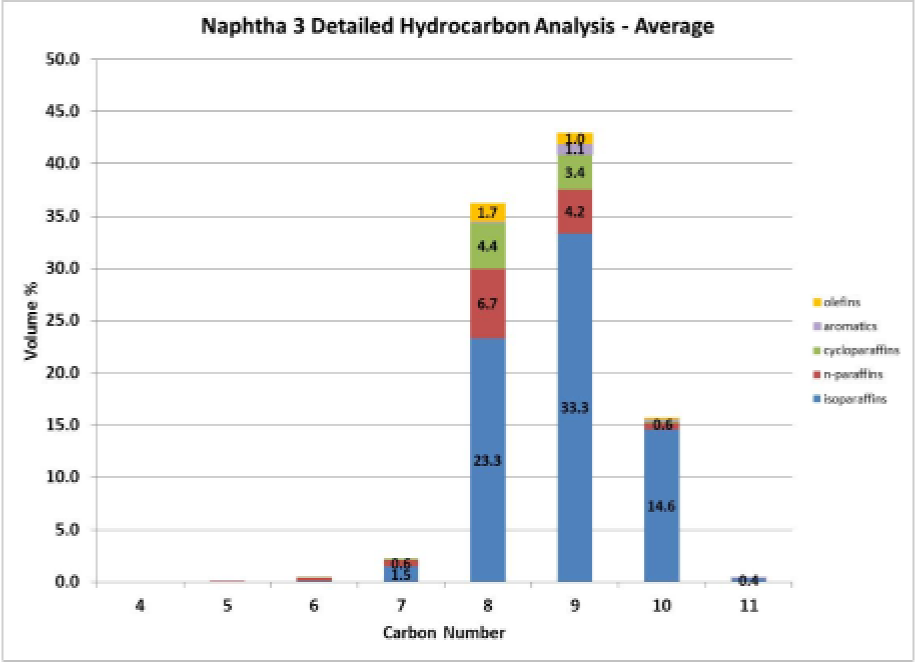

Figure A3: DHA for Naphtha 3

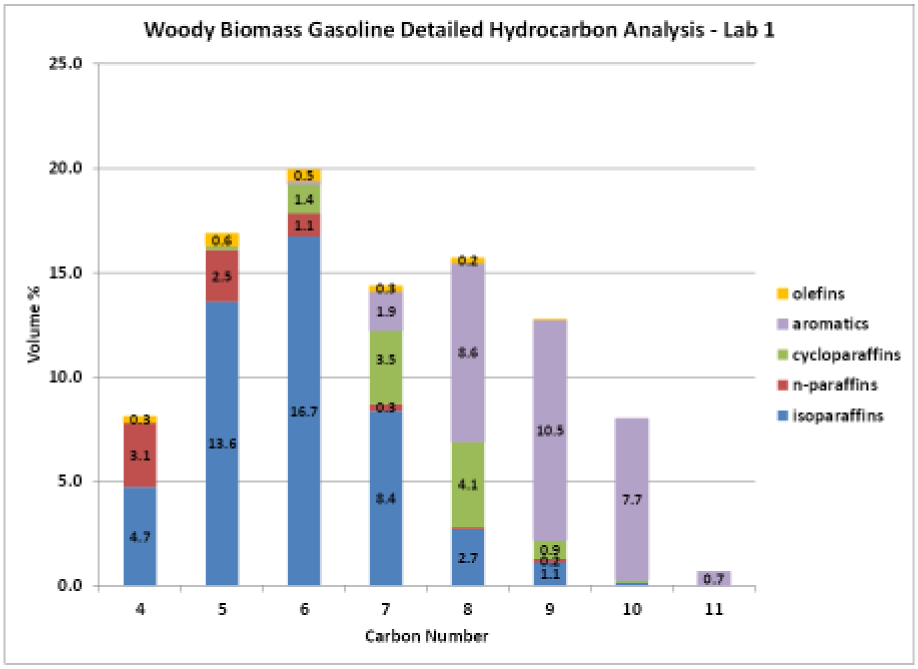

Figure A4: DHA for Woody Biomass Gasoline

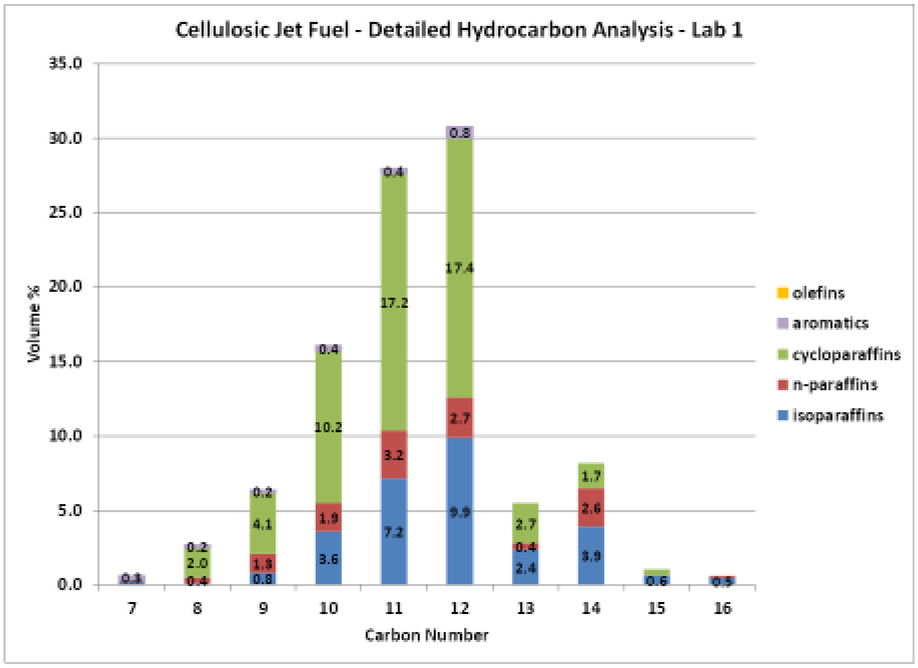

Figure A5: DHA for Cellulosic jet fuel

Table A4. ^{1}H NMR Comparison of Four Renewable Gasoline-Type Fuel Components, Normalized by Hydrogen Type

Label	Structure	Definition	Chemical Shift (ppm)	Mole % H Naphtha 1	Naphtha 2	Naphtha 3	Woody Biomass Gasoline
HA1	polyaromatic	H	7.4-10.7	0	0.1	0	0.1
HA2	monoaromatic	H	7.4-6.2	2.4	4.7	0	8.2
HO1	olefinic	CH	5.1-6.2	0	1.0	0	0.2
HO2	olefinic	CH2	4.8-5.1	0	0.1	0	0
HO3	olefinic	CH2	4.3-4.8	0	0.1	0	0.1
HP1	α-to-aromatic	CH2	2.4-4.3	0.3	0.9	0	1.3
HP2	α-to-aromatic	CH3	2.0-2.4	1.7	4.5	0.1	18.4
HP3	aliphatic	CH2	1.09-2.0	57.8	53.5	49.2	29.1
HP4	aliphatic	CH3	0.5-1.09	37.8	35.0	50.7	42.6

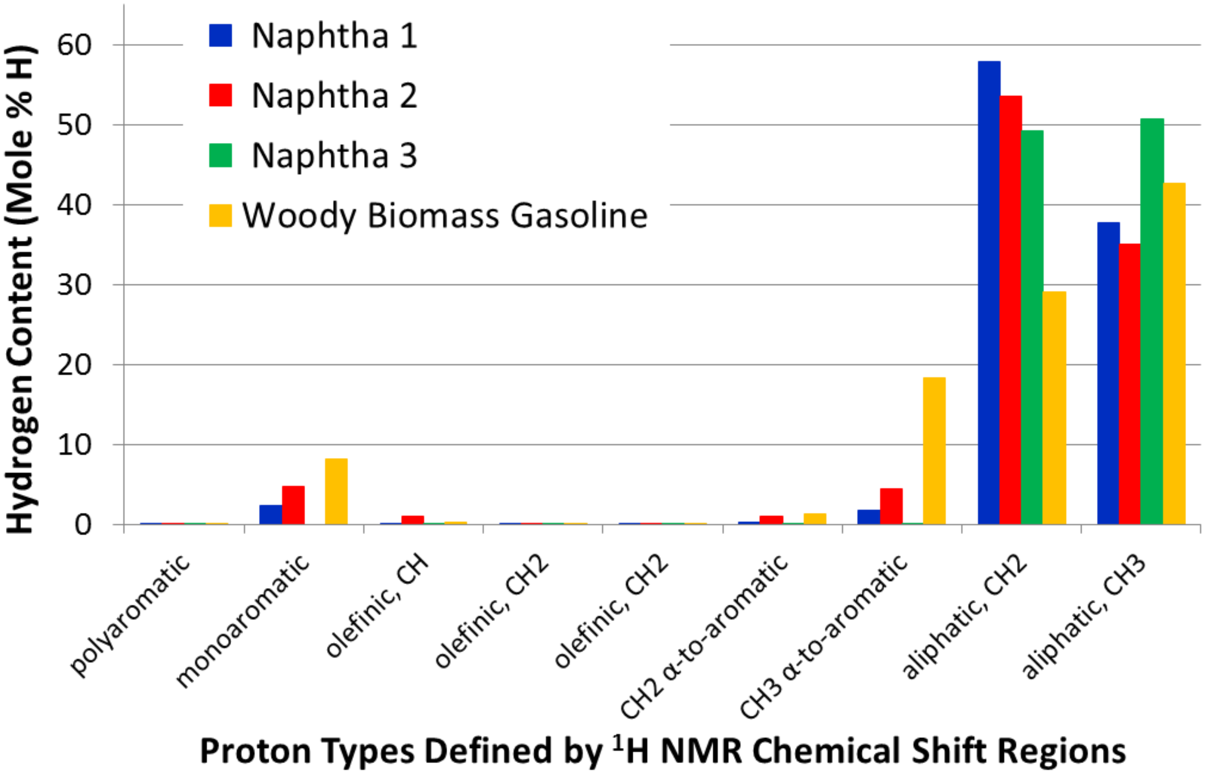

Figure A6. Normalized Proton-Type Distribution of Four Renewable Gasoline-Type Fuel Components. Values were obtained by integrating each of the ^{1}H NMR chemical shift regions shown in Table A4.