

^1H and ^{13}C NMR Analysis of Gas Turbine Fuels As Applied to the Advanced Distillation Curve Method

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Supporting Information

ABSTRACT: The analysis of gas turbine fuels by ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy as applied to the composition-explicit advanced distillation curve method is reported. To demonstrate the general applicability for such fuels, eight independent fuel samples were characterized: one sample of JP-5, one sample of JP-8, and six samples of Jet-A. Distillate fractions were obtained for each fuel by use of the advanced distillation curve (ADC) method. These fractions were analyzed by ^1H and ^{13}C NMR, along with the undistilled residue (i.e., the undistilled liquid remaining in the kettle after 90 vol % had been distilled) and the neat fuel. NMR spectroscopy is useful for the analysis of complex hydrocarbon mixtures because it provides the mole fractions of various classes of hydrocarbons, such as aromatics and linear alkanes, without the need to calibrate. NMR spectroscopy also gives ready access to other average properties for the components of each fuel sample, such as the extent and type of alkane branching. For example, the abundance of branch points at the β position of aliphatic chains changes little for the various distillate fractions; however, branching on the interior of the aliphatic chains approximately doubles over the course of the distillation. For the heavier fractions of the fuel, interior branching becomes as important as branching at the β and γ positions. Such information is useful for the development of realistic fuel surrogates required for reliable thermophysical models. Finally, we compare the results obtained by NMR spectroscopy to previously reported GC-MS and GC-FID analyses of the same fuel samples.

■ INTRODUCTION

The distillation curve of a complex mixture provides a great deal of information about the mixture's properties; indeed it is one of the few volatility measurements that can be used for complex fluids.^{1–4} Moreover, when measured properly, it is useful for thermodynamic modeling and for the development of surrogate mixtures.^{5–7} A recent approach to distillation, known as the composition-explicit advanced distillation curve (ADC) method, has proven to be especially useful for the characterization of complex mixtures such as fuels.^{8–17} The ADC method offers several improvements over earlier distillation methods (such as ASTM D-86);^{8–14} one of the most valuable improvements is that it provides detailed information about the composition of each distillate fraction. This method uses a specially designed adapter that allows discrete distillate fractions to be sampled with a syringe. The samples can then be submitted to any desired quantitative or qualitative analysis methods.

The distillate fractions from the ADC method typically have been analyzed by gas chromatography with flame ionization detection (GC-FID) or mass spectral detection (GC-MS). GC-FID is useful for the quantitative analysis of fuels because, for hydrocarbons, the detector response is (to a good approximation) proportional to the number of moles of carbon.¹⁸ However, by itself, GC-FID provides very little detail about the identity or structure of the compounds in the mixture beyond their relative volatility. On the other hand, GC-MS provides detailed information about the structures and identities of compounds in a complex mixture, but quantification can be difficult. For example, approaches such as ASTM D-2789 (for mass spectral analysis of low olefinic

gasolines) require complex, mixture-specific calibrations in order to achieve quantitative results.¹⁹

For the analysis of distillate fractions from the ADC method, GC-FID and GC-MS have often been used in combination to yield the relative concentrations for major components in fuel samples.^{13,14,20,21} Chromatograms are collected on both types of instruments with the same temperature program and the same type of column. The identities of the major peaks are determined from the GC-MS chromatogram and their relative concentrations are determined from the GC-FID chromatogram. For complex mixtures, this approach, which is referred to herein as GC-MS/FID, is laborious and peak overlap can be a significant problem. Nevertheless, GC-MS/FID does allow detailed compositional information to be obtained with limited calibration.

Nuclear magnetic resonance (NMR) spectroscopy is a valuable complement to chromatographic analysis of hydrocarbon mixtures.^{22–29} One significant benefit of NMR spectroscopy is that, for the determination of relative concentrations in a mixture, no calibration is required. One simply uses experimental parameters that ensure quantitative peak integrals.^{30–34} NMR spectroscopy can also provide a great deal of “average” chemical structure information about a complex mixture in a straightforward manner. For example, it is possible to perform certain types of functional group analysis, such as determination of the relative concentration of aromatics or alkenes.^{35–37} With this type of NMR analysis, the

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complications of peak overlap are limited by the fact that similar types of carbon (or hydrogen) are grouped together in a particular spectral region. NMR spectroscopy also provides easy access to other “average” fuel properties such as the extent and types of hydrocarbon branching.^{38–40}

In this paper, we report the application of quantitative ^1H and ^{13}C NMR spectroscopy to the analysis of distillate fractions from the ADC method. Eight gas turbine fuel samples were chosen for this study: six samples of Jet-A, one sample of JP-8, and one sample of JP-5. Quantitative ^1H and ^{13}C NMR spectra were collected for each neat fuel and for distillate fractions of each fuel that were obtained by the ADC method. The results of these NMR analyses are discussed and compared to previously reported analyses by GC–MS and GC-FID. We demonstrate that NMR spectroscopy is a useful addition to the chromatographic analyses that are commonly applied to the ADC method.

EXPERIMENTAL SECTION

Gas Turbine Fuel Samples. Two samples of Jet-A were obtained from airports located in Colorado. Four samples of Jet-A, one sample of JP-8, and one sample of JP-5, representing different processing lots, were obtained from the Fuels Branch of the Air Force Research Laboratory (AFRL, Wright Patterson Air Force Base). The Jet-A samples from Colorado are designated with the three letter airport codes, the other Jet-A samples are designated numerically, and the JP-8 and JP-5 samples are designated with JP-8 and JP-5 followed by a numerical identifier. The samples were maintained in sealed metal containers and no solidification or phase separation was noted during storage.

Fuel Distillation and Sampling with the ADC Method. The ADC apparatus and distillation procedure, especially as applied to turbine fuels, have been described previously.^{8,9,13,14,20,41,42} Thus, only a brief description as it applies to this study will be given here. For each measurement, 200 mL of fuel was placed in a boiling flask. Thermocouples were then inserted into appropriate locations to monitor the kettle temperature (T_k), which is the temperature in the liquid, and the head temperature (T_h), which is the temperature of the vapor at the bottom of the takeoff position in the distillation head. T_k provides a thermodynamically defined temperature point, whereas T_h approximates what might be obtained from the classical distillation measurement procedure. Enclosure heating was achieved with a model-predictive temperature controller.¹² The heating profile was designed to be of similar shape to that of the distillation curve, but it leads the distillation curve by approximately 20 °C. As heating progressed, the volume of the distilled liquid was measured in a level-stabilized receiver. Measurements of the temperature data grid were reported previously,¹⁵ but have been reproduced in the [Supporting Information](#) as Tables S1 and S2, and Figure S1 for the convenience of the reader. For this study, the distillation of each fuel was repeated so that samples for NMR analysis could be obtained. The distillation curves were unchanged, within experimental uncertainty, to those reported earlier.¹⁵ During the course of each distillation, sample aliquots were collected at the receiver adapter hammock with a 100–1000 μL pipettor. At each sampling point, a 500 μL aliquot was withdrawn; 7 μL of this aliquot was used to prepare a ^1H NMR sample, and the rest was used to prepare a ^{13}C NMR sample.

Analysis of the Neat Gas Turbine Fuels and Distillate Fractions by NMR Spectroscopy. A commercial 600 MHz NMR spectrometer with a cryoprobe, operated at 150.9 MHz for ^{13}C , was used to obtain quantitative ^1H and ^{13}C spectra.⁴³ Samples for ^1H NMR spectroscopy were prepared by dissolving 7 μL of the fuel sample (either the whole composite sample or distillate fraction samples) in 1 mL of acetone- d_6 ; this NMR solvent contained 0.05% of the chemical shift reference tetramethylsilane (TMS). Samples for ^{13}C NMR spectroscopy were prepared by mixing 0.5 mL of the fuel with 0.5 mL of chloroform- d ; this NMR solvent contained 1.5% by mass (0.06 M) of the relaxation agent chromium(III) acetylacetonate

(Cr(acac)₃). Therefore, the final concentration of Cr(acac)₃ in the NMR sample was 0.03 M, which is comparable to concentrations conventionally used.⁴⁴ The samples were maintained at 30 °C for all of the NMR measurements. ^1H NMR spectra were referenced to the TMS peak at 0.0 ppm, and ^{13}C NMR spectra were referenced to the solvent peak at 77.0 ppm.

Quantitative ^1H NMR spectra were obtained with a 30° flip angle and a long pulse repetition time (a 10.0 s data acquisition time plus a 10.0 s waiting time). The dwell time was 41.6 μs . The 90° pulse width for ^1H was 15 μs . A sweep width of 12019.23 Hz (–4 to +16 ppm) was used. Spectral processing was done without zero filling and with exponential line broadening of 0.3 Hz. After 64 scans, the spectra had signal-to-noise ratios of approximately 3×10^4 (based on the tallest peak).

Quantitative $^{13}\text{C}\{^1\text{H}\}$ spectra were obtained with a 30° flip angle, a long pulse repetition time (a 0.909 s data acquisition time plus a 10.0 s waiting time), inverse-gated WALTZ-16 proton decoupling, and a relaxation agent (see above).⁴⁵ The dwell time was 13.867 μs . The 90° pulse width for ^{13}C was 12 μs . A sweep width of 36057.69 Hz (–20 to +220 ppm) was used. Spectral processing was done without zero filling and with exponential line broadening of 1 Hz. After 512 scans, the spectra had signal-to-noise ratios of approximately 3000 (based on the tallest peak). The effectiveness of these parameters for producing quantitative ^{13}C spectra was verified by collecting spectra for three test compounds under the same conditions. For the test compound isocetane (2,2,4,4,6,8,8-heptamethylnonane), integral areas within 3% of predicted values were produced for the quaternary carbons, and integral areas within 2% of predicted values were produced for the other types of carbon. For the test compound tetralin (1,2,3,4-tetrahydronaphthalene), integral areas within 7% of predicted values were produced for the quaternary aromatic carbons, integral areas within 6% of predicted values were produced for the aromatic CH carbons, and integral areas within 1% of predicted values were produced for the CH₂ carbons. For the test compound 1-methylnaphthalene, integral areas within 8% of predicted values were produced for the quaternary aromatic carbons and integral areas within 7% of predicted values were produced for the aromatic CH carbons.

For each neat fuel (but not for the distillate fractions), we also obtained ^{13}C DEPT-90 and ^{13}C DEPT-135 spectra. For the DEPT (distortionless enhancement by polarization transfer) experiments, a coupling constant ($J_{\text{C-H}}$) of 140 Hz was used, as recommended for hydrocarbon fuels with both aromatic and aliphatic components.⁴⁶ A sweep width of 29761.9 Hz (–10 to +190 ppm) was used. Other acquisition parameters for the DEPT experiments included an acquisition time of 1.10 s, a relaxation delay of 2.0 s, and a total of 512 scans. The DEPT spectra were used to determine the number of hydrogen atoms bonded to each type of carbon; that is, they were used to identify ^{13}C types, not to quantitate the different types of carbon.

The relative amounts of various types of hydrogen and carbon were determined by the integration of spectral regions following literature methods, such as those used by Dettman et al.^{38,40} Some minor changes in the previously reported integral regions were made for these gas turbine fuel samples. First, integral regions were sometimes truncated so as not to include large sections of baseline with no peaks. That is, the integral regions reported in the tables are the maximum intervals; the actual intervals integrated may be smaller (this was done to minimize the contribution of baseline drift to the integral value). Second, for the ^{13}C spectra, the cutoff between quaternary aromatic carbons and aromatic CH carbons was changed to 131.2 ppm (instead of 129.0 ppm). This change was based on the results of DEPT spectra for these samples, which showed a clear break between the two types of carbon at 131.2 ppm. Third, for the ^1H spectra, the solvent peaks for acetone- d_6 and water were cut out of their respective integral regions by removing the intervals 2.0–2.1 ppm and 2.75–2.78 ppm, respectively. Fourth, for the ^1H spectra, the cutoff between the paraffinic CH₂ and paraffinic CH₃ regions was changed to 1.02 ppm (instead of 1.09 ppm) to correspond to the observed spectral minimum. Fifth, for the ^1H spectra, the two alkenic CH₂ regions were combined.

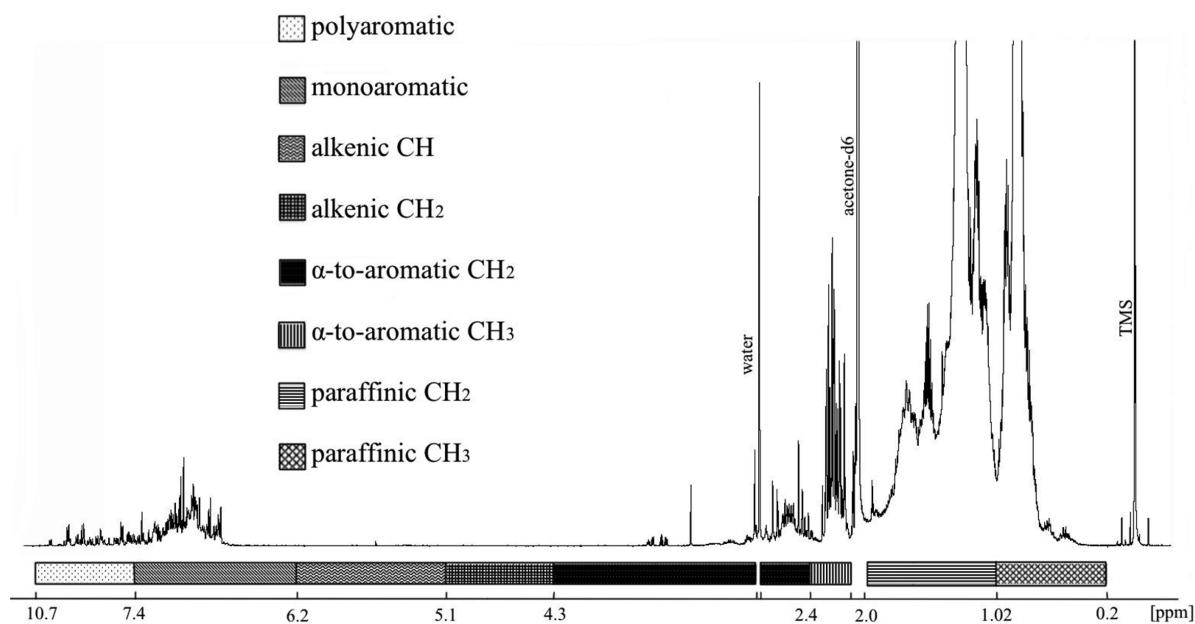


Figure 1. ^1H NMR spectrum of Jet-A-LMO with integral regions shown. The y-axis has been expanded such that some peaks are off-scale.

Four sources of uncertainty were considered for the peak integrals reported herein: incomplete relaxation and residual nuclear Overhauser effects (NOE), which are significant only for the ^{13}C NMR spectra; repeatability in the distillation; baseline drift; and peak overlap. The magnitude of the influence of incomplete relaxation and residual NOE was determined from the spectra of test compounds (see above). For aromatic carbons, the relative integral areas were found to be as much as 8% lower than the areas for CH_2 or CH_3 carbons in the same molecule. The repeatability of the distillation was determined from replicate distillations of the Jet-A-LMO sample. The relative standard deviation (rsd) for a particular integral region was calculated for each distillate fraction of Jet-A-LMO. Then the average rsd for that integral region was used for all of the fuel samples. The rsd for ^1H integral regions for Jet-A-LMO ranged from 0.2% to 3%, except for the very small alkene integrals (where values of rsd were, not surprisingly, higher). The rsd for ^{13}C integral regions for Jet-A-LMO ranged from 0.6% to 12%. The contribution of baseline drift to the uncertainty of integration was determined by the integration of regions of noise in the spectra. For the ^1H NMR spectra, the relative standard uncertainty due to baseline drift ranged from 0.04% to 3% (except for the very small alkene integrals). For the ^{13}C NMR spectra, the relative standard uncertainty due to baseline drift ranged from 0.3% to 13% depending on the size and width of the integral. Peak overlap was only important for cases where individual peaks are integrated, such as for the determination of the extent of branching. The estimated values for these sources of uncertainty were added in quadrature to arrive at the combined standard uncertainties that are reported in the [Results and Discussion](#).

The time and effort required to analyze fuels by NMR spectroscopy is comparable to the time and effort required for GC-MS or GC-FID. The ^1H and ^{13}C spectra took 22 and 94 min, respectively, of instrument time. Integration of spectral regions is easy to automate, and only took a couple minutes operator time for each spectrum (to manually phase the spectrum, crop integral regions, and so forth). The analysis of branching is more complex. To begin with, it requires that at least two DEPT spectra be collected for each sample (each DEPT spectrum took 27 min of instrument time). Also, integration of individual peaks is best done by hand. In total, the data analysis for branching took about 30 min of operator time per sample.

RESULTS AND DISCUSSION

Eight independent gas turbine fuel samples were analyzed by quantitative ^1H and ^{13}C NMR spectroscopy. Along with the neat fuel, five distillate fractions were analyzed: the first 0.5 mL, then after 10 vol %, 50 vol %, 80 vol %, and the residue in the kettle after 90% of the volume had distilled. Our primary approach for the NMR analysis was based on a literature method^{38,40} in which regions of each spectrum are integrated and compared (see the [Experimental Section](#) for details of some minor modifications that were made to the literature method). The advantage of this approach is that it allows for a simple, rapid comparison of different fuels and distillate fractions.^{38,40,46,47} The disadvantage of this approach is that some of the integral regions actually contain more than one type of hydrogen or carbon (see below).

We used a different approach for the analysis of paraffinic branching. In this case, individual peaks were integrated instead of integrating spectral regions. This is necessary because of the manner in which the relevant peaks are scattered throughout the spectrum. The mole fraction of unbranched paraffins (i.e., linear alkanes) was determined from five large peaks in the ^{13}C NMR spectrum, which are easily identifiable by comparison with literature data. The mole fraction of branch points was determined by identifying CH peaks in the paraffinic region of the spectrum with ^{13}C DEPT NMR, then the larger peaks were identified by comparison to literature data.

An important advantage of ^1H NMR spectroscopy is that high signal-to-noise spectra can be obtained rapidly with only a few milligrams of sample. Achieving quantitative peak integrals is also straightforward because ^1H relaxation times are short, and decoupling is not necessary. The combination of these two advantages leads to relatively small uncertainties for ^1H peak integrals. ^1H NMR spectroscopy also distinguishes certain structural categories that have overlapping peak ranges in ^{13}C NMR spectra, specifically polyaromatics versus monoaromatics and alkenes versus aromatics, which makes ^1H NMR spectroscopy particularly useful for analysis of the unsaturated fraction of the fuel.^{38,40} On the basis of a comparison with

Table 1. Comparison of the Integral Values for ^1H Spectral Regions for All of the Neat Jet Fuels

δ (ppm)	proton type	JP-8-6169 (mol % ^1H)	JP-5-4810 (mol % ^1H)	Jet-A-WBU (mol % ^1H)	Jet-A-LMO ^c (mol % ^1H)	Jet-A-5237 (mol % ^1H)	Jet-A-4877 (mol % ^1H)	Jet-A-4599 (mol % ^1H)	Jet-A-4598 (mol % ^1H)	rel. uncertainty ^d (%)
10.7–7.4	polyaromatic CH	0.38	0.52	0.26	0.50	0.09	0.13	0.38	0.36	4.1
7.4–6.2	monoaromatic CH	2.74	2.12	3.52	2.37	3.31	3.39	3.50	2.78	1.2
6.2–5.1	alkenic CH	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	
5.1–4.3	alkenic CH_2	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	
4.3–2.4 ^a	α -to-aromatic CH_2	2.11	1.80	2.54	1.98	2.45	2.54	2.81	2.64	3.4
2.4–2.1	α -to-aromatic CH_3	3.64	2.98	3.97	2.99	4.21	4.29	4.47	3.74	1.2
2.0–1.02	paraffinic CH_2	56.75	56.98	55.35	57.46	57.21	57.04	55.16	54.57	0.2
1.02–0.2	paraffinic CH_3	34.37	35.60	34.36	34.68	32.70	32.62	33.69	35.92	0.4

^aThe water signal at ~ 2.8 ppm was excluded from the integral. ^bThe integral value was $\leq 0.02\%$, which is the detection limit. ^cThese are the averaged values from three separate samples of the same lot of fuel. ^dThis is the relative combined standard uncertainty in the integral values.

literature spectra, the cutoff between polyaromatic and monoaromatic resonances is quite good, but not perfect. It is not uncommon for polyaromatic peaks to tail into the monoaromatic region or for monoaromatic peaks to tail into the polyaromatic region. In rare cases, an entire peak may be located in the “wrong” integral region. The uncertainty caused by “impure” spectral regions is difficult to estimate and was not included in the uncertainty analysis (see the [Experimental Section](#)). On the other hand, ^1H NMR spectroscopy has two major drawbacks. First, because of the small chemical shift range, peak overlap in the spectra of complex mixtures can be a limiting factor. This is particularly true in the aliphatic region of the spectrum, which represents the majority of a gas turbine fuel sample. Second, some structural moieties do not have a defined number of hydrogen atoms. For example, for a polyaromatic molecule the number of aromatic hydrogen atoms depends on the number of alkyl side-chains and the number of bridgehead carbons. Therefore, some types of quantitative comparisons of ^1H integral areas require an assumption about the average number of protons in a structural moiety.

^{13}C NMR spectroscopy has two important advantages for the analysis of complex mixtures like gas turbine fuels. First, it has a broader chemical shift range, which means that many different types of carbon can be distinguished. This is particularly important for analysis of the aliphatic region of hydrocarbon mixtures. Additionally, structural moieties generally have a defined number of carbon atoms, which simplifies the comparison of integral areas. A related advantage for hydrocarbon mixtures is that carbon makes up the majority of the mass of such samples, so the integral areas, which are proportional to the mole fraction of carbon in the sample, also approximate mass fraction. On the other hand, ^{13}C NMR spectroscopy has two major disadvantages. First, it is much less sensitive than ^1H NMR. Therefore, even with relatively concentrated spectroscopic samples and long experiment times, ^{13}C NMR spectra have relatively low signal-to-noise. Second, long relaxation times and the need to decouple ^1H , make it more difficult to ensure that integral areas are quantitative. Both effects lead to relatively larger uncertainties in the integral values from ^{13}C NMR spectra.

Composition and Variability of the Neat Gas Turbine Fuels by ^1H NMR Spectroscopy. Figure 1 shows a ^1H NMR spectrum of Jet-A-LMO with the spectral regions indicated. Table 1 shows a comparison of the integral values for ^1H NMR spectral regions for all of the neat gas turbine fuels. The integrals in Table 1 have not been normalized for the relative number of hydrogen atoms per carbon. That is, the integrals in

Table 1 still reflect the fact that a paraffinic CH_3 group has 3 times the signal intensity that an aromatic CH will have. It is also important to note that Table 1 lacks a category for paraffinic CH, because peaks for this type of proton are not well separated from the other spectral regions. From the ^{13}C DEPT spectra, it is clear that paraffinic CH exists in all the gas turbine fuels. The CH peaks are expected to be mostly subsumed into the large paraffinic CH_2 integral,³⁷ where their relative effect is minimized.

Several general observations about the gas turbine fuel samples can be made directly from the data in Table 1. First, the aromatic fraction of the gas turbine fuels is mostly monoaromatic, although the ratio (monoaromatic CH)/(polyaromatic CH) ranges broadly from 4.1 to 37. Second, all of these samples contained very few alkenes (≤ 0.02 mol % alkenic hydrogen). Third, the aromatic rings tend to be heavily substituted in all of the gas turbine fuels, as explained below. Fourth, and not surprisingly, paraffinic CH_2 and paraffinic CH_3 make up the large majority of the protons in all of the samples.

Some simple calculations allow the estimation of other useful ratios.⁴⁷ For example, one can estimate the mole percent of aromatic carbon in each gas turbine fuel sample in the following way. First, the ^1H integral values are normalized by dividing by the number of hydrogen atoms attached to each carbon (i.e., CH integrals are divided by 1, CH_2 integrals are divided by 2, and CH_3 integrals are divided by 3). Then, the sum of the (normalized) integrals for aromatic hydrogens and α -to-aromatic hydrogens is divided by the sum of all the (normalized) integrals. This calculation shows that the approximate mol % of aromatic carbon in the gas turbine fuels ranges from 10.1% (for JP-5-4810) to 14.9% (for Jet-A-4599). It is also simple to estimate the number of side-chains on the aromatic rings from the ^1H spectra. One can simply compare the sum of the integrals for aromatic CH to the sum of the (normalized) integrals for α -to-aromatic CH_2 and α -to-aromatic CH_3 . (It should be noted that the integral region given as α -to-aromatic CH_2 likely contains some amount of α -to-aromatic CH and α -to-aromatic CH_3 .⁴⁷) One can readily see that for all of the neat gas turbine fuels, the ratio of aromatic methyl side-chains to larger aromatic side-chains, which include aliphatic rings, is approximately one to one. The ratio of aromatic side-chains to aromatic protons ranges from 0.7 to 0.8. Hence, an average monoaromatic ring would have two or three side-chains, with approximately equal amounts of methyl groups and longer alkyl groups.

Analysis of the Gas Turbine Fuel Distillate Volume Fractions by ^1H NMR Spectroscopy. Each of the gas turbine fuels listed in Table 1 was distilled by the ADC method.

Table 2. Comparison of the Integral Values for ¹H Spectral Regions for the Composition Explicit Data Channel of the Advanced Distillation Curve Method for Jet-A-LMO

δ (ppm)	proton type	Jet-A-LMO distillate fractions ^a						rel. uncertainty ^d (%)
		first drop (mol % ¹ H)	10 vol % (mol % ¹ H)	50 vol % (mol % ¹ H)	80 vol % (mol % ¹ H)	residue (mol % ¹ H)	neat fuel (mol % ¹ H)	
10.7–7.4	polyaromatic	0.08	0.18	0.46	0.75	1.04	0.50	4.1
7.4–6.2	monoaromatic	3.32	3.06	2.21	1.95	1.94	2.37	1.2
6.2–5.1	alkenic CH	0.10	^c	^c	^c	^c	^c	31
5.1–4.3	alkenic CH ₂	0.03	^c	^c	^c	^c	^c	54
4.3–2.4 ^b	α-to-aromatic CH ₂	1.20	1.60	1.92	2.26	2.99	1.98	3.4
2.4–2.1	α-to-aromatic CH ₃	3.63	4.08	2.93	2.27	2.00	2.99	1.2
2.0–1.02	paraffinic CH ₂	52.26	54.12	57.86	59.46	60.98	57.46	0.2
1.02–0.2	paraffinic CH ₃	39.38	36.94	34.59	33.31	31.03	34.68	0.4

^aThese are the averaged values from three separate distillations of the same lot of fuel. ^bThe water signal at ~2.8 ppm was excluded from the integral.

^cThe integral value was ≤0.02%, which is the detection limit. ^dThis is the relative combined standard uncertainty in the integral values.

Although the gross examination of the distillation curves is instructive and valuable for many design purposes, the composition channel of ADC provides a great deal of additional information. For each fuel, samples of four distillate volume fractions (the first 0.5 mL, then after 10, 50, and 80 vol %) were taken as they emerged from the condenser. The remaining 10% undistilled liquid, or “residue,” was also sampled. Each distillate fraction was analyzed by ¹H NMR in a manner analogous to the neat fuels (see above).

Table 2 shows a comparison of the ¹H spectral regions for the distillate fractions of Jet-A-LMO (the analysis of the neat fuel is included in Table 2 for comparison). Similar data for the other gas turbine fuels are given in the Supporting Information (see Table S3). The integrals in Table 2 have not been normalized (i.e., they still reflect the fact that a CH₃ group has three times the signal intensity of a CH group). The distillation and analysis of Jet-A-LMO were done in triplicate to assess the repeatability of this type of measurement, and the integral values in Table 2 are the averages from all three distillations. The repeatability of the ¹H NMR measurement was excellent, with relative standard deviations for the integrals that ranged from 0.2% for the largest integral (paraffinic CH₂) to 3% for the smaller integrals. Not surprisingly, the very small alkene integrals in the first 0.5 mL of distillate had the largest relative standard deviations (~10%).

Analysis of the distillate fractions of Jet-A-LMO (Table 2) showed quantitatively how the lighter fractions differed from the heavier fractions. The most dramatic change was in the ratio (monoaromatic CH)/(polyaromatic CH), which was 43 in the first 0.5 mL of distillate but only 1.9 in the residue. Interestingly, the mol % of total aromatic protons changed little during the course of the distillation. The average number of side-chains on the aromatic rings increases for the heavier fractions; the ratio of aromatic side-chains to aromatic protons increases from 0.53 for the first drop of distillate to 0.73 for the residue. The size of the aromatic side-chains also increases for the heavier fractions; the ratio of aromatic methyl side-chains to larger aromatic side-chains changes from 2.0 for the first drop of distillate to 0.45 for the residue. The expected increase in the mol % of paraffinic CH₂ for the heavier fractions was also observed. This was accompanied by an expected decrease in the mol % of paraffinic CH₃ (i.e., end groups). Another interesting observation from Table 2 is that the first 0.5 mL of distillate contained a small, but detectable, amount of alkenic protons. Heavier fractions showed no detectable alkene. One of the

other gas turbine fuel samples (the JP-8-6169) showed the same type of result: light alkenes were detected in the first 0.5 mL of distillate. One possible explanation for these two results is that these two batches of gas turbine fuel were slightly contaminated with a lighter fuel fraction.

Composition and Variability of the Neat Gas Turbine Fuels by ¹³C NMR Spectroscopy. Figure 2 shows a ¹³C NMR spectrum of Jet-A-LMO with the spectral regions indicated. Table 3 shows a comparison of the integral values for the ¹³C NMR spectral regions for all of the neat gas turbine fuels. The analysis of Jet-A-LMO was done in triplicate to assess the repeatability of this type of measurement, and the integral values for this fuel (Table 3) are the averages. The repeatability of the ¹³C NMR measurement is not as good as the ¹H measurement because baseline drift is more important for the ¹³C NMR spectra (which have relatively low signal-to-noise ratios); there is additional uncertainty due to relaxation and residual NOE effects. Consequently, the integral values for the ¹³C NMR spectral regions have larger uncertainties.

Some general observations can be made directly from the data in Table 3. The mol % of aromatic carbons in the gas turbine fuels is simply the sum of the peak areas for the quaternary aromatic region and the aromatic CH region. It ranges from 8.0 mol % (for JP-5-4810) to 12.7 mol % (for Jet-A-4599). The ¹³C NMR analysis gives systematically lower values for the aromatic content of the fuel than the ¹H NMR analysis (see above). However, tests described in the Experimental Section show that, with our NMR experiment, aromatic carbons give integral values that are 6–8% lower than predicted, presumably as a result of incomplete relaxation. If this is taken into account, the aromatic content determined by ¹H or ¹³C NMR is the same within the combined standard uncertainties of the two measurements. One of the ¹³C NMR spectral regions in Table 3 is (primarily) due to cycloparaffin CH₂ groups. The amount of cycloparaffin does not vary much between the gas turbine fuel samples.

Other integral regions in Table 3 give information about the extent of paraffinic branching. However, for a closer look at paraffinic branching, it is useful to look at individual peaks. Long, unbranched, paraffinic chains can be observed directly from five peaks in the ¹³C spectra.^{29,39,40} In Figure 2, which shows the ¹³C NMR spectrum of Jet-A-LMO, the peaks due to long unbranched paraffinic chains are labeled as follows: the “chain α-CH₃” is the terminal methyl group, the “chain β-CH₂” peak is the methylene group attached to the terminal methyl,

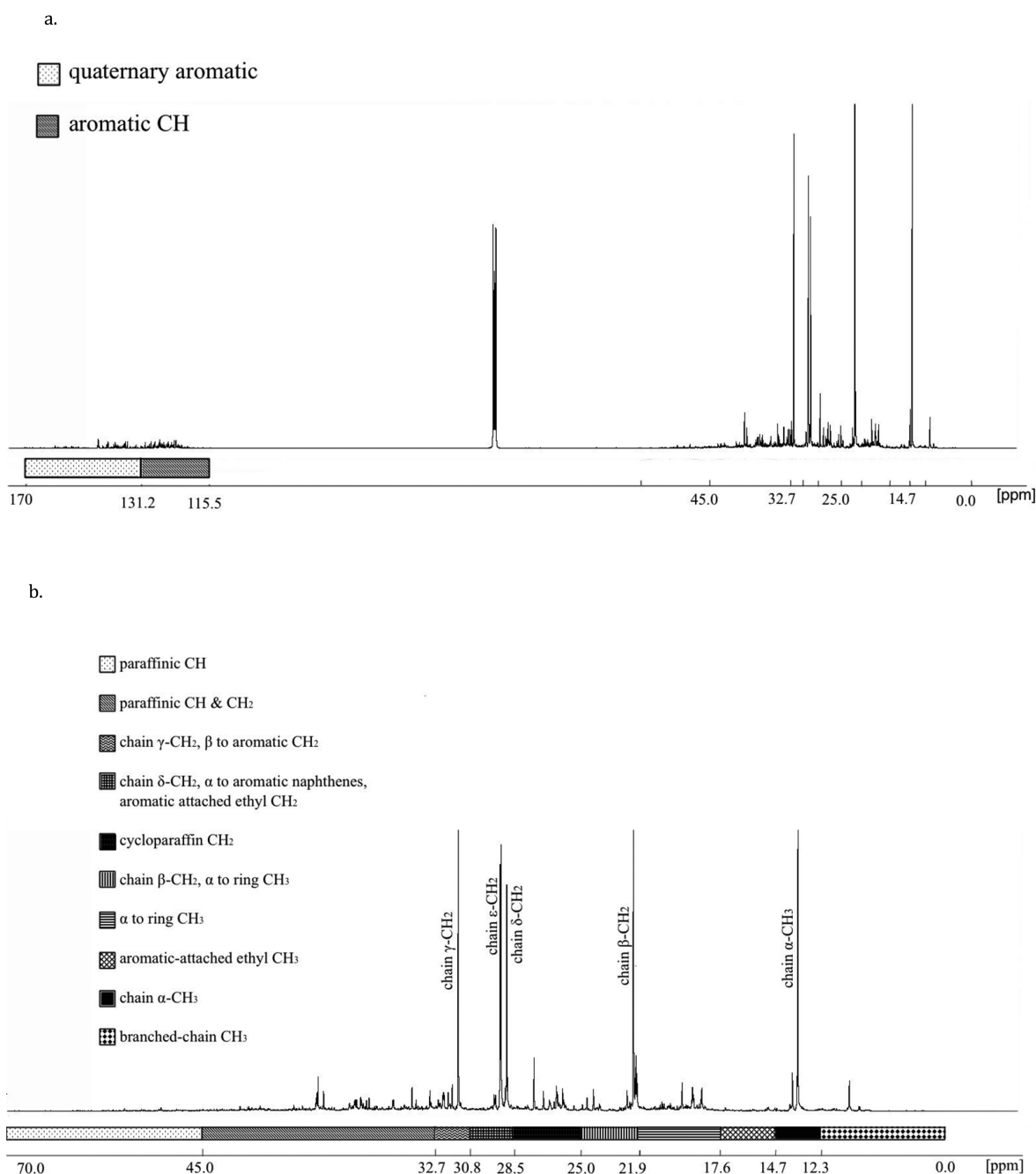


Figure 2. Quantitative ^{13}C spectrum for Jet-A-LMO that was obtained by use of inverse-gated WALTZ-16 proton decoupling and a relaxation agent (see text): 2a. the full spectrum, and 2b. an expanded view of the paraffinic region.

and so forth. Figure 2b shows an expanded view of the paraffinic region for clarity. The “chain $\epsilon\text{-CH}_2$ ” peak contains resonances for all of the carbons at the C5 position and higher. In prior reports^{28,37,38} the “chain $\epsilon\text{-CH}_2$ ” peak was indicated to be a single peak; however, in our NMR spectra it consisted of two poorly resolved peaks. By comparison with the spectra of pure alkanes under the same conditions, we identified the upfield (right) “chain $\epsilon\text{-CH}_2$ ” peak as C5 carbons and the downfield (left) peak as C6 and higher carbons. Table 4 shows the integral values of these five peaks; summing the peaks yields the total mole fraction of carbon atoms that are in long, unbranched, paraffinic chains in each sample. On average, carbon atoms of this type make up about a quarter of the carbon atoms in the gas turbine fuel samples, but there is

significant variability. It is important to note that long linear moieties in any type of hydrocarbon can contribute to the five linear alkane peaks shown in Figure 2 and Table 4. If the linear moiety is long enough, some of resonances will be indistinguishable from *n*-alkane resonances. For example, 4-methyldodecane contains a linear carbon chain that is 8 carbons long. Under the conditions of our NMR experiment, the resonances for the five carbon atoms farthest from the branch point are indistinguishable from the five “linear alkane” peaks. The contribution of such linear moieties explains the fact that, for a given fuel sample, the peaks for chain $\alpha\text{-CH}_3$, chain $\beta\text{-CH}_2$, chain $\gamma\text{-CH}_2$, and chain $\delta\text{-CH}_2$ do not all have the same intensity (Tables 4 and 7).

Table 3. Comparison of the Integral Values for ^{13}C Spectral Regions for All of the Neat (Undistilled) Jet Fuels

δ (ppm)	carbon type ^a	JP-8-6169 (mol % ^{13}C)	JP-5-4810 (mol % ^{13}C)	Jet-A-WBU (mol % ^{13}C)	Jet-A-LMO ^b (mol % ^{13}C)	Jet-A-5237 (mol % ^{13}C)	Jet-A-4877 (mol % ^{13}C)	Jet-A-4599 (mol % ^{13}C)	Jet-A-4598 (mol % ^{13}C)	rel. uncertainty ^c (%)
170– 131.2	quaternary aromatic	3.85	3.09	4.74	3.23	4.49	4.74	5.28	4.13	16.0
131.2– 115.5	aromatic CH	5.99	4.89	6.86	5.41	6.70	6.66	7.44	5.72	9.1
70.0– 45.0	paraffinic CH	1.41	2.46	2.45	1.89	2.00	1.51	1.64	2.93	18.0
45.0– 32.7	paraffinic CH and CH_2	17.81	21.84	20.47	19.48	17.04	16.13	18.98	21.66	3.7
32.7– 30.8	chain γ - CH_2 , β to aromatic CH_2	9.61	9.00	8.44	9.98	9.95	9.73	8.81	8.68	2.4
30.8– 28.5	chain δ - CH_2 , α to aromatic naphthenes, aromatic attached ethyl CH_2	17.90	15.95	15.23	17.03	18.24	18.52	15.52	14.07	2.1
28.5– 25.0	cycloparaffin CH_2	7.96	8.67	8.05	8.48	6.85	7.04	8.05	8.38	2.8
25.0– 21.9	chain β - CH_2 , α to ring CH_3	12.68	12.01	11.74	12.45	12.52	12.53	11.76	11.18	2.2
21.9– 17.6	α to ring CH_3	9.58	9.62	9.50	9.49	8.94	9.30	10.24	11.28	3.5
17.6– 14.7	aromatic-attached ethyl CH_3	1.18	1.51	1.72	1.38	1.47	1.39	1.32	1.81	5.9
14.7– 12.3	chain α - CH_3	9.53	8.52	8.30	8.76	9.70	10.13	8.59	7.45	2.7
12.3–0.0	branched-chain CH_3	2.49	2.43	2.49	2.42	2.09	2.31	2.38	2.71	12.7

^aThe alkene region from 115.5 to 100 ppm is not listed because peaks in this region were below the detection limit ($\leq 0.1\%$). ^bThese are the averaged values from three separate samples of the same lot of fuel. ^cThis is the relative combined standard uncertainty in the integral values.

Table 4. Comparison of Integral Values of the Five Peaks due to Long Unbranched Paraffinic Chains

δ (ppm)	carbon type	JP-8-6169 (mol % ^{13}C)	JP-5-4810 (mol % ^{13}C)	Jet-A-WBU (mol % ^{13}C)	Jet-A-LMO ^a (mol % ^{13}C)	Jet-A-5237 (mol % ^{13}C)	Jet-A-4877 (mol % ^{13}C)	Jet-A-4599 (mol % ^{13}C)	Jet-A-4598 (mol % ^{13}C)	rel. uncertainty ^b (%)
13.7	chain α - CH_3	5.64	4.92	4.81	5.36	5.85	6.12	4.69	3.80	5.8
22.4	chain β - CH_2	5.66	4.61	4.43	5.07	5.64	5.80	4.35	3.44	5.7
31.6	chain γ - CH_2	4.93	3.89	3.70	4.37	5.01	5.20	3.69	2.87	5.4
29.1	chain δ - CH_2	4.09	3.34	3.35	3.75	4.23	4.62	2.93	2.31	5.8
29.4 ^c	chain ε - CH_2	6.84	6.37	5.79	7.10	7.51	7.61	5.62	5.07	5.5
total		22.21	27.2	23.1	22.1	25.7	28.2	29.4	21.3	

^aThese are the averaged values from three separate distillations of the same lot of fuel. ^bThis is the relative combined standard uncertainty in the integral values. ^cThe ε - CH_2 peak actually represents two poorly resolved peaks (one peak is from C5 carbons and one is from carbons > C5).

Table 5. Comparison of Integral Values of Major Peaks that Correspond to Methyl Branching

δ (ppm)	CH at methyl branch point	JP-8-6169 (mol % ^{13}C)	JP-5-4810 (mol % ^{13}C)	Jet-A-WBU (mol % ^{13}C)	Jet-A-LMO ^a (mol % ^{13}C)	Jet-A-5237 (mol % ^{13}C)	Jet-A-4877 (mol % ^{13}C)	Jet-A-4599 (mol % ^{13}C)	Jet-A-4598 (mol % ^{13}C)	rel. uncertainty ^b (%)
27.6	β position	1.05	1.03	0.91	1.01	0.89	0.86	1.02	0.97	25
32.2	interior ^d	0.50	0.46	0.45	0.47	0.52	0.51	0.49	0.45	37
32.4 ^c	interior ^d	0.80	0.86	0.74	0.87	0.71	0.69	0.83	0.76	24
34.1	γ position	0.77	0.68	0.60	0.64	0.74	0.73	0.84	0.66	33
total		3.12	3.02	2.70	2.99	2.86	2.79	3.18	2.84	

^aThese are the averaged values from three separate distillations of the same lot of fuel. ^bThis is the relative combined standard uncertainty in the integral values. ^cThis row represents the sum of two poorly resolved CH peaks at 32.4 ppm. ^dThese peaks represent a methyl branch point ≥ 4 carbons atoms from the end of the chain.

Paraffinic branching has been studied in detail by ^{13}C NMR spectroscopy, and many individual peaks in the ^{13}C NMR spectrum of fluids such as gas turbine fuels can be identified.³⁹ One straightforward method for determining the extent of branching is to determine the number of protons attached to each type of carbon with ^{13}C DEPT experiments. As expected, ^{13}C DEPT spectra of the gas turbine fuel samples showed no detectable quaternary carbons in the aliphatic region,

suggesting that the fraction of branching points for the aliphatic fraction is equal to the fraction of CH carbons, which is simple to determine from a comparison of ^{13}C DEPT spectra. For every neat fuel sample, the largest CH peak in the spectrum resonates at 27.6 ppm (which, it should be noted, is in the spectral region designated as “cycloparaffin CH_2 ” in Tables 3 and 6). This peak corresponds to a methyl branch point at the β carbon of an aliphatic chain,³⁹ and it accounts for about 1 mol

Table 6. Comparison of the Integral Values for ^{13}C Spectral Regions for the Composition Explicit Data Channel of the Advanced Distillation Curve Method for Jet-A-LMO^a

δ (ppm)	carbon type ^b	Jet-A-LMO distillate fractions ^c						rel. uncertainty ^d (%)
		first drop (mol % ^{13}C)	10 vol % (mol % ^{13}C)	50 vol % (mol % ^{13}C)	80 vol % (mol % ^{13}C)	residue (mol % ^{13}C)	neat fuel (mol % ^{13}C)	
170–131.2	quaternary aromatic	2.78	3.45	3.09	3.03	3.56	3.23	16.0
131.2–115.5	aromatic CH	6.90	6.33	5.06	5.12	5.66	5.41	9.1
70.0–45.0	paraffinic CH	1.30	1.69	2.29	2.57	2.59	1.89	18.0
45.0–32.7	paraffinic CH and CH_2	19.14	19.46	20.33	20.78	19.79	19.48	3.7
32.7–30.8	chain γ - CH_2 , β to aromatic CH_2	10.16	10.08	9.87	9.72	9.05	9.98	2.4
30.8–28.5	chain δ - CH_2 , α to aromatic naphthenes, aromatic attached ethyl CH_2	11.52	14.42	17.16	18.46	20.01	17.03	2.1
28.5–25.0	cycloparaffin CH_2	10.21	8.62	8.28	8.18	8.12	8.48	2.8
25.0–21.9	chain β - CH_2 , α to ring CH_3	14.32	12.82	12.46	12.26	11.00	12.45	2.2
21.9–17.6	α to ring CH_3	10.09	10.02	9.02	8.54	9.04	9.49	3.5
17.6–14.7	aromatic-attached ethyl CH_3	1.38	1.53	1.40	1.23	1.34	1.38	5.9
14.7–12.3	chain α - CH_3	9.45	9.01	8.79	8.15	7.49	8.76	2.7
12.3–0.0	branched-chain CH_3	2.75	2.57	2.25	1.96	2.34	2.42	12.7

^aThe analysis of the neat fuel is included for comparison. ^bThe alkene region from 115.5 to 100 ppm is not listed because peaks in this region were below the detection limit ($\leq 0.1\%$). ^cThese are the averaged values from three separate distillations of the same lot of fuel. ^dThis is the relative combined standard uncertainty in the integral values.

Table 7. Comparison of Integral Values for the Five Peaks in the ^{13}C NMR Spectrum that Correspond to Long, Unbranched, Paraffinic Chains^a

δ (ppm)	carbon type	Jet-A-LMO distillate fractions ^b						rel. uncertainty ^d (%)
		first drop (mol % ^{13}C)	10 vol % (mol % ^{13}C)	50 vol % (mol % ^{13}C)	80 vol % (mol % ^{13}C)	residue (mol % ^{13}C)	neat fuel (mol % ^{13}C)	
13.7	chain α - CH_3	5.18	5.58	5.28	5.04	4.56	5.36	6
22.4	chain β - CH_2	4.73	5.40	5.31	5.07	4.42	5.07	6
31.6	chain γ - CH_2	3.41	4.56	4.59	4.39	3.97	4.37	5
29.1	chain δ - CH_2	2.54	3.80	4.02	3.83	3.48	3.75	6
29.4 ^c	chain ϵ - CH_2	2.94	4.76	7.61	8.79	10.52	7.10	5
total		18.81	24.10	26.81	27.13	26.94	25.66	

^aThe mol % of such carbon increases over the course of the distillation, and this is almost entirely due to the dramatic increase in the “chain ϵ - CH_2 ” peak. ^bThese are the averaged values from three separate distillations of the same lot of fuel. ^cThe ϵ - CH_2 peak actually represents two poorly resolved peaks (one peak is from C5 carbons and one is from carbons > C5). ^dThis is the relative combined standard uncertainty in the integral values.

% of the carbon in each fuel sample (Table 5). The other largest CH peaks are also listed in Table 5; they all correspond to other known³⁹ types of methyl branching. This preponderance of methyl branching for the aliphatic fraction was expected, and was also observed in the GC–MS analyses of the same gas turbine fuels. The list of CH peaks in Table 5 is not exhaustive, but it does account for the majority of the aliphatic CH carbons that were observed in the ^{13}C DEPT spectra of the gas turbine fuels. There are ~ 10 other CH peaks with enough intensity to be observed in the ^{13}C DEPT spectra, but the total intensity of those peaks is equal to only about 1.5 mol % of the carbon in the fuels. It should also be noted that these numbers correspond to a lower limit in the amount of branching in the gas turbine fuel samples. The region of the ^{13}C NMR spectrum where most of the paraffinic CH peaks appear (approximately 32–70 ppm) contains many small peaks; hence, peak overlap and detection limits likely obscure many small CH peaks. The smaller CH peaks could correspond to other types of branching such as larger alkyl side-chains or alkyl substitution of cycloparaffins.

Analysis of the Gas Turbine Fuel Distillate Volume Fractions by ^{13}C NMR Spectroscopy. The same distillate

volume fractions that were analyzed by ^1H NMR were also analyzed by ^{13}C NMR, although separate, more concentrated, samples were prepared (see the Experimental section for details). Each distillate fraction was analyzed by ^{13}C NMR in a manner analogous to the neat fuels. Table 6 shows a comparison of the ^{13}C NMR spectral regions for the distillate fractions of Jet-A-LMO (the analysis of the neat fuel is included for comparison). Similar data for the other jet fuels are given in the Supporting Information (see Table S4). The distillation and analysis of Jet-A-LMO was done in triplicate to assess the repeatability of this type of measurement, and the integral values in Table 6 are the averages from all three distillations. The most dramatic trend in Table 6 is the near doubling, over the course of the distillation, in the peak integral for the region from 28.5 to 30.8 ppm (which contains resonances from longer-chain linear aliphatics and heavier aromatic molecules).

The extent of paraffinic branching in the distillate fractions was also studied. Table 7 gives mole percentages for the five peaks in the ^{13}C NMR spectrum that correspond to long, unbranched, paraffinic chains. The total mole percentage of these carbons increases over the course of the distillation, and this is almost entirely due to the dramatic increase in the chain

Table 8. Comparison of the Relative Abundance of the Most Common Types of Aliphatic Branching

δ (ppm)	CH at methyl branch point	Jet-A-LMO distillate fractions ^a						rel. uncertainty ^d (%)
		first drop (mol % ¹³ C)	10 vol % (mol % ¹³ C)	50 vol % (mol % ¹³ C)	80 vol % (mol % ¹³ C)	residue (mol % ¹³ C)	neat fuel (mol % ¹³ C)	
27.6	β position	0.93	0.97	0.97	1.04	0.98	1.01	25
32.2	interior ^c	0.25	0.38	0.45	0.39	0.44	0.47	37
32.4 ^b	interior ^c	0.56	0.58	0.81	0.96	1.02	0.87	24
34.1	γ position	0.39	0.59	0.63	0.61	0.62	0.64	33
total		2.14	2.52	2.86	3.00	3.05	2.99	

^aThese are the averaged values from three separate distillations of the same lot of fuel. ^bThis row represents the sum of two poorly resolved CH peaks at 32.4 ppm. ^cThese peaks represent a methyl branch point ≥ 4 carbons atoms from the end of the chain. ^dThis is the relative combined standard uncertainty in the integral values.

ϵ -CH₂ peak, which increases from 2.94 ± 0.15 to 10.52 ± 0.53 mol % over the course of the distillation, which shows that the fraction of long linear aliphatic chains increases upon distillation. Table 8 shows the relative abundance of the most common types of aliphatic branching (compare with Table 5). The abundance of branch points at the β position of aliphatic chains changes little for the various distillate fractions; however, branching on the interior of the aliphatic chains approximately doubles over the course of the distillation. For the heavier fractions of the fuel, interior branching becomes as important as branching at the β and γ positions.

Comparison of Gas Turbine Fuel Analysis by NMR Spectroscopy with the Mass Spectral Analysis Described in ASTM D-2789. It is instructive to compare the results of ¹H and ¹³C NMR analyses with the results of other analytical methods. As mentioned in the Introduction, the fuel samples studied herein were analyzed previously¹⁵ by use of a mass spectrometric classification method based on ASTM D-2789.¹⁹ With this method, which we refer to as the “2789 analysis”, MS or GC-MS is used to classify the components of a hydrocarbon fuel into six types: paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes, indanes and tetralins (grouped as one classification), and naphthalenes. This method uses the measurement of a global mass spectrum for the sample and then the compares the intensity of characteristic ion fragments (m/z , defined as the ratio of ion mass to ion charge) for the determination of hydrocarbon types, see Table S5 of the Supporting Information for m/z ions whose intensities are used in the calculation. Although the method is specified only for application to low olefinic gasoline and has significant limitations, it is of practical relevance to many complex fluid analyses and is often applied to gas turbine fuels, rocket propellants, and missile fuels.⁴⁸ The exact methods and uncertainties associated with this type of analysis are presented elsewhere and will not be repeated here.¹³

One difficulty in comparing the NMR spectral regions with the results of the 2789 analysis is that the two methods do not categorize compounds in the same way. For example, there are ¹³C NMR spectral regions for two types of aromatic carbons: quaternary carbons (i.e., bridgehead carbons or carbons with alkyl side-chains) and CH carbons. On the other hand, the 2789 analysis categorizes the aromatic fraction into alkylbenzenes, indanes and tetralins, and naphthalenes. Consequently, direct, quantitative comparison of individual spectral regions is not always clear between the two methods. A more subtle difficulty is that, with the 2789 method, only characteristic m/z fragment ions are used to classify the hydrocarbon type, which means that all other m/z ions are ignored. In addition, a

molecule may produce multiple fragments that contribute to more than one hydrocarbon type. On the other hand, classification by the NMR method is based on atomic assignments (not molecular fragments). For example, only the aromatic carbon atoms or aromatic hydrogen atoms are included in the spectral region for aromatics; any other types of atoms in the molecule are found (and counted) in other spectral regions.

With these difficulties in mind, it is instructive to compare the results of the 2789 analysis to the results from NMR analysis. The aromatic fraction provides some of the best comparisons. As discussed above, the mole percentage of total aromatic carbon can be directly determined from the ¹³C NMR spectra without assumptions (given the absence of alkenes in these samples). A range from 8.0 to 12.7 mol % was observed for the neat gas turbine fuels studied herein. With the 2789 analysis, the total mole percent of aromatic ions (i.e., the sum of characteristic ions produced by alkylbenzenes, indanes and tetralins, and naphthalenes) ranged from 20.1 to 32.1 mol %, which is more than double the range that was obtained by ¹³C NMR. Some, but not all, of the discrepancy is due to the types of fragments that are counted by the 2789 method, which include benzene and naphthalene rings with nonaromatic side chains still attached. That is, some of the carbon in a fragment that is classified as “aromatic” by the 2789 method may be in a nonaromatic moiety. In principle, it is possible to subtract the nonaromatic moieties from the characteristic aromatic fragments used by the 2789 analysis, but it is easier and more reliable to simply determine total aromatic carbon with ¹³C NMR.

Another case in which a quantitative comparison is possible is for the ratio of monocyclic aromatic compounds to polycyclic aromatic compounds. As discussed above, ¹H NMR shows that the ratio of (monocyclic aromatic CH)/(polycyclic aromatic CH) ranges from 4.1 to 37 for the neat fuels. With the 2789 method, the monocyclic aromatic compounds were assumed to be equal to the alkylbenzenes plus the indanes and tetralins. The polycyclic aromatic compounds were assumed to be equal to the naphthalenes. In this way, the 2789 analysis determined the ratio of (monocyclic aromatic ions)/(polycyclic aromatic ions) to range from 4.8 to 14 for the neat fuels. The ratios from the two methods were in excellent agreement when the ratio was relatively small; for example, for Jet-A-LMO, ¹H NMR analysis gave a ratio of 4.7 and the 2789 analysis gave a ratio of 5.1. For larger ratios, the agreement was not as good. The poorest agreement was for Jet-A-5237 where ¹H NMR gave a ratio of 37 and the 2789 analysis gave a ratio of 14. A similar comparison can be made for the distillate fractions. As noted

earlier, ^1H NMR shows a dramatic decrease in the ratio of (monocyclic aromatic CH)/(polycyclic aromatic CH) over the course of a distillation. For example, for Jet-A-LMO, ^1H NMR gave a ratio of 17 for the 10 vol % fraction and a ratio of 2.6 for the 80 vol % fraction (Table 2). Similar changes were also observed with the 2789 analysis (see Table S8); for Jet-A-LMO, the ratio of (monocyclic aromatic ions)/(polycyclic aromatic ions) changed from 10 for the 10 vol % fraction to 3.4 for the 80 vol % fraction. The 2789 analysis shows that these changes were mostly driven by an increase in naphthalenes (which approximately tripled over the course of the distillation) and a decrease of alkylbenzenes (which typically decreased by about 50% over the course of the distillation). In this case, it is not clear which method is more accurate because it is hard to determine the “purity” of the two spectral regions from the ^1H NMR (which were assigned by comparison of a collection of literature spectra), and one must also make the assumption that the fraction of quaternary carbons is the same for both monocyclic aromatic species and polycyclic aromatic species.

A couple of additional observations will be noted. First, the sum of the aromatic components from the 2789 analyses changed little over the course of the distillation, which was also observed for the NMR analyses (i.e., the mol % of total aromatic protons and carbons changed little during the course of the distillation). Second, the 2789 analysis showed that the concentration of tetralins increased in the heavier distillate fractions. This could account for the observation from NMR spectroscopy that the size of aliphatic side-chains on aromatic rings increases in the heavier distillate volume fractions.

Comparison of the Extent of Branching in the Gas Turbine Fuel Components as Determined by NMR or by GC–MS/FID. The extent of branching in the gas turbine fuels was studied by ^1H and ^{13}C NMR, as described above. Previously published results¹⁵ from the GC–MS/FID method make for a particularly good comparison with the ^{13}C NMR data because both methods generate peaks that are proportional to the mole fractions of carbon atoms. For each fuel sample, GC–MS/FID was used to generate a list of components that made up at least 1% of the fuel (i.e., GC–FID peaks that accounted for less than 1% of the total peak integral were ignored).^{13,14,49} Tables of data for all of the neat fuels and for the distillate fractions have been reproduced in the Supporting Information for the convenience of the reader (see Tables S9 and S10). The information obtained from the GC–MS/FID method is useful in a number of ways. Besides identifying the major compounds, the list can be used to derive an approximation of average fuel properties such as energy content.^{13,14,20,41}

In any comparison of the GC–MS/FID approach to other methods, two important limitations need to be kept in mind. First, by design, the GC–MS/FID method ignores the less abundant components of the fuel. Second, peak overlap in the chromatograms of gas turbine fuels is problematic because the major components are usually located in the unresolved “kerosene hump”. Few, if any, of the peak integrals in this region of the chromatogram represent a single compound. This means that the concentrations of identified compounds are likely to be overestimated because all of the intensity in each peak is assigned to a single (predominant) compound.

One can make a quantitative comparison between GC–MS/FID and ^{13}C NMR for the sum of unbranched paraffins (i.e., *n*-alkanes) in each fuel sample. These compounds give a limited number of large, easily identifiable peaks by both methods. As

determined by ^{13}C NMR, the total mol % of carbon atoms in linear paraffins is listed in Table 4 for the neat fuels and Table 7 for the distillate fractions of Jet-A-LMO. For the neat fuels, ^{13}C NMR indicated that the mol % of carbon from linear paraffins ranged from 17.5% to 29.4% (see the bottom line of Table 4). For the neat fuels, GC–MS/FID indicated that the mol % of carbon from linear paraffins was 31% for JP-8-6169, 28% for JP-5-4810, 28% for Jet-A-WBU, 32% for Jet-A-LMO, 28% for Jet-A-5237, 28% for Jet-A-4877, 21% for Jet-A-4599, and 21% for Jet-A-4598 (see Table S6 of the Supporting Information). The values obtained from GC–MS/FID are the same as, or higher than, those obtained from ^{13}C NMR, despite the fact that the ^{13}C NMR peaks include some contribution from long linear moieties in other classes of hydrocarbons (see the discussion of this issue above). Apparently, peak overlap in the GC–MS/FID method has, on average, a larger effect than the contribution of long linear moieties to ^{13}C NMR results.

Because GC–MS/FID purposefully ignores minor components in the sample, it is not possible to make a direct, quantitative comparison with the NMR analyses of branching types. Additionally, GC–MS does not always correctly identify skeletal isomers because major fragment ions are repeated between isomers.³⁷ Nevertheless, some trends observed in the GC–MS/FID analyses can be compared with the results of the NMR analyses. For example, from the list of major fuel components in Table S6 of the Supporting Information, it is clear that aromatic rings tend to be heavily substituted, which is consistent with the NMR analyses. It is also notable that methyl branching predominates in the paraffinic fraction, which is also consistent with the NMR analyses. Finally, ^1H NMR demonstrates that these gas turbine fuels contain very few alkenes. Though not designed for trace analysis, it is worth mentioning that alkenes are notably absent from the lists of major components that were generated by GC–MS/FID analysis.

■ CONCLUSIONS

Analysis of gas turbine fuels (and similar hydrocarbon mixtures) by quantitative NMR spectroscopy has some distinct advantages. Specifically, quantitative ^{13}C NMR spectroscopy provides a simple, accurate assessment of the total aromatic content and linear paraffin content in a fuel sample. With a little more effort, ^{13}C NMR can also provide an assessment of the types and the extent of branching in the paraffinic and aromatic fractions. Quantitative ^1H NMR spectroscopy is less powerful than quantitative ^{13}C NMR spectroscopy for hydrocarbon fuel analysis because of peak overlap in the paraffinic region and because assumptions are often required for data analysis. Nevertheless, ^1H NMR spectroscopy is still quite useful for the analysis of the unsaturated components in fuel samples. It is particularly useful for establishing the amount of alkene in such samples. On the other hand, unlike GC–MS methods, NMR spectroscopy cannot readily provide any information about the specific molecules that make up a complex mixture. In this regard, the combination of NMR spectroscopy and GC–MS is quite powerful. NMR spectroscopy can be used to establish the relative amounts of various classes of compounds in the sample and GC–MS/FID can be used to determine the identities of the major components in the mixture. This combination of information allows for the creation of robust thermophysical property models and realistic surrogate fuel mixtures.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.5b01035.

Average initial boiling behavior of jet fuels, representative distillation curve data, ^1H and ^{13}C spectral regions, hydrocarbon types delineated by ASTM D-2789, listing of major components found in neat (undistilled) samples of aviation fuels, listing of major components found in distillation volume fractions for Jet-A-LMO, table of the aliphatic hydrocarbon family types resulting from the ASTM D-2789 analysis performed on the jet fuels, comparison of integral values for the five peaks in the ^{13}C NMR spectrum that correspond to long, unbranched, paraffinic chains, comparison of the relative abundance of the most common types of aliphatic branching, distillation curves for measured jet fuels, representative DEPT135 and DEPT90 spectra of neat Jet-A-LMO, and representative ^1H and ^{13}C spectra with integral lines (including integrals of peak-free regions) of neat Jet-A-LMO (PDF).

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Notes

The authors declare no competing financial interest. Contribution of the United States government; not subject to copyright in the United States.

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■ NOMENCLATURE:

LMO = Vance Brand Airport, Longmont, CO
WBU = Boulder Municipal Airport, Boulder, CO

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