

Technical Notes

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Application of a Composition-Explicit Distillation Curve Metrology to Mixtures of Jet-A and S-8

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I. Introduction

ONE of the most important and informative properties that is measured for complex fluid mixtures is the distillation (or boiling) curve [1–3]. Distillation curves are commonly used in the design, operation, and specification of liquid fuels such as gasoline, diesel fuel, rocket propellant, and gas turbine fuel. In previous work, several significant improvements in the measurement of distillation curves for complex fluids were introduced [4–8]. The modifications to the classical measurement (embodied in [9]) provide for 1) a composition-explicit data channel for each distillate fraction (for both qualitative and quantitative analysis); 2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state; 3) temperature, volume, and pressure measurements of low uncertainty that are suitable for equation-of-state development; 4) consistency with a century of historical data; 5) an assessment of the energy content of each distillate fraction; 6) trace-chemical analysis of each distillate fraction; and 7) corrosivity assessment of each distillate fraction, in addition to the usual temperature–volume relationship. We have applied this advanced approach to the distillation curve to a variety of mixtures that include simple n-alkanes, gas turbine fuels, gasolines, diesel fuels, and rocket propellant [10–12]. In this Note, we report the application of the advanced distillation curve approach to mixtures of the gas turbine fuel Jet-A with a synthetic fuel.

Environmental concerns, and the potential of disruptions in supply, have led to the development of new aviation fuels based on the Fischer–Tropsch process. One such fuel made from natural gas is designated as S-8 (CAS no. 437986-20-4).[‡] It is clear that initial applications of S-8 will be in formulations mixed with either JP-8 or Jet-A. Indeed, early flights performed in a B-52 testbed were done with such mixtures [13]. The basic property needed for the specification of such mixed fuels is the composite fuel volatility as represented by the distillation curve.

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II. Experimental

Samples of Jet-A were obtained from Wright Laboratory's Aero Propulsion and Power Directorate at Wright–Patterson Air Force Base. The sample of S-8 was also obtained from this source, but was produced by Syntroleum Corporation of Tulsa, OK.[§] Jet-A was a composite of numerous available batches (from multiple manufacturers) of Jet-A, mixed in approximately equal volume aliquots. It is therefore considered to be representative of typical Jet-A in terms of chemical, physical, and engineering properties. The sample of S-8 had a lower viscosity and density than that of Jet-A. Each of the samples was analyzed by gas chromatography and mass spectrometry (GC-MS) [6]. As a result of the analyses by GC-MS, a typical composition suite was determined for both S-8 and Jet-A, presented in Tables 1 and 2. These analyses focus on the most abundant components (in excess of 1%) and are based on the uncalibrated area response on the total ion chromatogram obtained by GC-MS.

The mixtures discussed in this Note were composed of Jet-A and S-8 in three different volume ratios: 25/75, 50/50, and 75/25% (vol/vol) of S-8/Jet-A, respectively. The mixtures were prepared with volumetric pipettes at 25°C. The uncertainty in the volume measurement was 0.05 ml. The hexane used as a solvent in this work was obtained from a commercial supplier and was analyzed by gas chromatography. It was used without further purification.

The composition-explicit distillation curve apparatus and approach has been described in detail elsewhere [5,7]. The required fluid for the distillation curve measurement (in each case, 200 ml) was placed into the boiling flask with a 200-ml volumetric pipette. The thermocouples were then inserted into the proper locations to monitor T_k , the temperature in the fluid, and T_h , the temperature at the bottom of the takeoff position in the distillation head. Enclosure heating was then commenced with a four-step program based upon a previously measured distillation curve. Volume measurements were made in the level-stabilized receiver, and sample aliquots were collected at the receiver adapter hammock.

Because the measurements of the distillation curve were performed at ambient atmospheric pressure measured with an electronic barometer, temperature readings were corrected for what should have been obtained at standard atmospheric pressure. This was done with the modified Sidney Young equation, in which the constant term was assigned a value of 0.000109 [14–16].

III. Results and Discussion

A. Initial Boiling Temperatures

During the initial heating of each sample in the distillation flask, the behavior of the fluid was observed. Typically, during the early stages of a measurement, the first bubbles will appear intermittently, and this action will quell if the stirrer is stopped momentarily. Sustained vapor bubbling is then observed. In the context of the

[§]Data available online at <http://www.syntroleum.com/MSDS/S-8Jet-Fuel.pdf>.

[‡]To describe materials and experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturers' names or labels. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular product or equipment is necessarily the best available for the purpose.

Table 1 The approximate composition determined for S-8^a

Name	CAS no.	Area percentage	Name	CAS no.	Area percentage
2-methyl heptane	592-27-8	0.323	n-undecane	1120-21-4	2.420
3-methyl heptane	589-81-1	0.437	x-methyl undecane	NA	1.590
1,2,3-trimethyl cyclopentane	15890-40-1	0.965	3-methyl undecane	1002-43-3	1.15
2,5-dimethyl heptane	2216-30-0	1.131	5-methyl undecane	1632-70-8	1.696
4-methyl octane	2216-34-4	2.506	4-methyl undecane	2980-69-0	1.045
3-methyl octane	2216-33-3	1.323	2-methyl undecane	7045-71-8	1.072
n-nonane	111-84-2	1.623	2,3-dimethyl undecane	17312-77-5	1.213
3,5-dimethyl octane	15869-96-9	1.035	n-dodecane	112-40-3	2.595
2,6-dimethyl octane	2051-30-1	0.756	4-methyl dodecane	6117-97-1	0.929
4-ethyl octane	15869-86-0	1.032	x-methyl dodecane	NA	0.744
4-methyl nonane	17301-94-9	1.904	2-methyl dodecane	1560-97-0	1.293
2-methyl nonane	871-83-0	1.019	x-methyl dodecane	NA	1.281
3-methyl nonane	5911-04-6	1.385	n-tridecane	629-50-5	1.739
n-decane	124-18-5	2.050	4-methyl tridecane	26730-12-1	0.836
2-5-dimethyl nonane	17302-27-1	1.175	6-propyl tridecane	55045-10-8	1.052
5-ethyl-2-methyl octane	62016-18-6	1.015	x-methyl tridecane	NA	1.066
5-methyl decane	13151-35-4	1.315	n-tetradecane	629-59-4	1.562
4-methyl decane	2847-72-5	1.134	x-methyl tetradecane	NA	1.198
2-methyl decane	6975-98-0	1.529	5-methyl tetradecane	25117-32-2	0.720
3-methyl decane	13151-34-3	1.583	n-pentadecane	629-62-9	1.032
			x-methyl tetradecane	NA	0.727

^aWhen ambiguity exists regarding isomerization, the substituent position is indicated as a general variable x.

Table 2 The approximate composition determined for Jet-A^a

Name	CAS no.	Area percentage	Name	CAS no.	Area percentage
n-heptane	142-82-5	0.125	2,3-dimethyl decane	17312-44-6	0.681
ethyl cyclohexane	108-87-2	0.198	1-ethyl-2,2,6-trimethyl cyclohexane	71186-27-1	0.364
2-methyl heptane	592-27-8	0.202	1-methyl-3-propyl benzene	1074-43-7	0.569
toluene	108-88-3	0.320	aromatic	NA	0.625
cis-1,3-dimethyl cyclohexane	638-04-0	0.161	5-methyl decane	13151-35-4	0.795
n-octane	111-65-9	0.386	2-methyl decane	6975-98-0	0.686
1,2,4-trimethyl cyclohexane	2234-75-5	0.189	3-methyl decane	13151-34-3	0.969
4-methyl octane	2216-34-4	0.318	aromatic	NA	0.540
1,2-dimethyl benzene	95-47-6	0.575	aromatic	NA	0.599
n-nonane	111-84-2	1.030	1-methyl-(4-methylethyl) benzene	99-87-6	0.650
x-methyl nonane	NA	0.597	n-undecane	1120-21-4	2.560
4-methyl nonane	17301-94-9	0.754	x-methyl undecane	NA	1.086
1-ethyl-3-methyl benzene	620-14-4	1.296	1-ethyl-2,3-dimethyl benzene	933-98-2	1.694
2,6-dimethyl octane	2051-30-1	0.749	n-dodecane	112-40-3	3.336
1-methyl-3-(2-methylpropyl) cyclopentane	29053-04-1	0.285	2,6-dimethyl undecane	17301-23-4	1.257
1-ethyl-4-methyl benzene	622-96-8	0.359	n-tridecane	629-50-5	3.998
1-methyl-2-propyl cyclohexane	4291-79-6	0.370	1,2,3,4-tetrahydro-2,7-dimethyl naphthalene	13065-07-1	0.850
1,2,4-trimethyl benzene	95-63-6	1.115	2,3-dimethyl dodecane	6117-98-2	0.657
n-decane	124-18-5	1.67	2,6,10-trimethyl dodecane	3891-98-3	0.821
1-methyl-2-propyl benzene	1074-17-5	0.367	x-methyl tridecane	NA	0.919
4-methyl decane	2847-72-5	0.657	x-methyl tridecane	NA	0.756
1,3,5-trimethyl benzene	108-67-8	0.949	n-tetradecane	629-59-4	1.905
x-methyl decane	NA	0.613	n-pentadecane	629-62-9	1.345

^aWhen ambiguity exists regarding isomerization, the substituent position is indicated as a general variable x.

advanced distillation curve measurement, sustained bubbling is also somewhat intermittent, but it is observable even when the stirrer is momentarily stopped. Finally, the temperature at which vapor is first observed to rise into the distillation head is recorded. This is termed the vapor rise temperature. The observation of the vapor rise temperatures of complex fluids is important

because these are the initial boiling temperatures of each fluid. Moreover, these temperatures can be modeled theoretically, for example, with an equation of state. The initial temperature observations for a representative measurement are summarized in Table 3; the measurement uncertainty is discussed in detail elsewhere [5,6].

Table 3 A summary of the initial behavior of the three mixtures of Jet-A and S-8, along with the initial behaviors of the starting fluids

Observed temperature, °C	S-8	75/25 S-8 and Jet-A	50/50 S-8 and Jet-A	25/75 S-8 and Jet-A	Jet-A 4658
Onset	163.0	160.9	154.9	161.8	139.9
Sustained	168.6	182.3	178.6	178.9	185.6
Vapor rising	181.9	184.8	186.6	189.1	190.5

Table 4 Representative distillation curve data for the three mixtures of S-8 and Jet-A measured in this work

Distillate volume fraction, %	S-8 ^a		75/25 S-8 and Jet-A		50/50 S-8 and Jet-A		25/75 S-8 and Jet-A		Jet-A 4658 ^a	
	T_k , °C	T_h , °C	T_k , °C	T_h , °C	T_k , °C	T_h , °C	T_k , °C	T_h , °C	T_k , °C	T_h , °C
5	183.6	169.2	187.8	176.2	190.2	171.0	193.3	174.7	195.4	174.7
10	185.0	173.9	190.4	180.8	192.8	177.6	196.4	183.2	198.5	183.3
15	187.7	179.1	193.4	184.2	196.4	183.6	199.9	189.3	201.5	187.0
20	190.2	173.6	196.3	182.6	199.9	188.9	202.9	192.5	204.7	189.1
25	193.0	175.5	199.8	187.5	203.5	184.8	206.6	189.6	208.1	190.6
30	196.2	181.9	202.8	191.1	206.3	192.7	209.6	193.1	211.3	192.8
35	199.5	187.7	206.3	194.5	209.9	193.3	212.7	196.5	214.3	194.6
40	202.9	192.0	209.9	197.5	213.3	193.8	216.4	198.4	217.6	199.1
45	207.1	196.2	213.7	198.1	217.1	196.6	219.7	200.8	220.7	202.6
50	211.0	200.3	218.2	205.8	221.1	201.8	223.6	207.2	224.2	205.4
55	215.3	205.2	222.4	210.4	225.1	206.9	227.5	211.3	227.6	208.6
60	219.6	209.3	226.6	214.6	228.8	208.1	231.0	215.3	231.2	212.4
65	224.2	213.6	231.6	219.4	233.3	213.1	235.0	219.9	234.7	214.9
70	229.4	219.1	236.4	225.8	237.2	220.0	238.9	221.2	239.4	216.6
75	235.2	224.3	241.8	229.2	242.3	221.1	243.7	226.5	243.3	218.7
80	240.1	231.4	247.5	233.9	247.2	225.8	248.8	233.2	247.9	220.8
85	246.8	236.8	255.4	240.7	254.4	231.5	255.7	235.5	253.6	224.1

^aThe data for the individual components S-8 and Jet-A 4658 are provided for reference; these data are plotted in Fig. 1.

B. Distillation Curves

Representative distillation curve data for the three mixtures of Jet-A with S-8, along with data for the starting materials, are presented in Table 4. In this table, we provide both T_k and T_h . The T_k value is a true thermodynamic state point that can be modeled theoretically, whereas the T_h data allow comparison with earlier measurements made with typical distillation curve instrumentation. In this table, the estimated uncertainty in the temperatures (with a coverage factor $k = 2$) is 0.1 °C [17]. The uncertainty in the volume measurement that is used to obtain the distillate volume fraction is 0.05 ml in each case.

The distillation curves based on the data from Table 4 are presented in Fig. 1. The shapes of all of the curves are of the subtle sigmoid type that one would expect for a highly complex fluid with many components, distributed over a large range of relative molecular masses. There is no indication of the presence of azeotropy among the constituents, because there is an absence of multiple inflections and curve flattening.

C. Composition Channel Information

Although the gross examination of the distillation curves is instructive and valuable for many design purposes, the composition channel of the advanced approach can provide even greater understanding and information content. One can sample and examine the individual fractions as they emerge from the condenser, as discussed in the Introduction. Following the analytical procedure described, samples were collected and prepared for analysis. Chemical analyses of each fraction were done by gas

chromatography with flame ionization detection and mass spectrometric detection. Representative chromatograms for aviation fuels have been presented previously [6].

D. Hydrocarbon Type Classification

The distillate fractions of the three Jet-A and S-8 mixtures, along with the starting fluids Jet-A and S-8, were examined for hydrocarbon types by use of a mass spectrometric classification method summarized in [18]. In this method, one uses mass spectrometry (or gas chromatography and mass spectrometry) to characterize hydrocarbon samples into six types. The six types or families are paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes (or aromatics), indanes, and tetralins (grouped as one classification), and naphthalenes. The procedure and uncertainty of this method and the potential pitfalls were treated earlier [10].

The results of these hydrocarbon type analyses are presented in Tables 5–9 and plotted in Fig. 2. The first row in each of the tables reports the results of the analysis as applied to the entire sample (called the composite) rather than to distillate fractions. The residue is the heavy undistilled fluid left behind in the distillation flask.

The distribution of hydrocarbon type as a function of distillate fraction is instructive among the different turbine fuel mixtures. Mixtures that have a high concentration of S-8 are seen to have a very high paraffin content, as expected. This approximate concentration ranges from more than 75% for the mixture that contains 75% S-8, to more than 55% for the mixture that only contains 25% S-8. For each mixture, the alkylaromatic content decreases markedly as a function of distillate fraction; this is especially notable for the mixtures that are rich in Jet-A. For the 75/25 S-8/Jet-A mixture, the alkylaromatic concentration shows a great deal of scatter that results from the very low concentration of such components in mixtures rich in S-8. The concentrations of the indanes and tetralins and the naphthalenic compounds increase with distillate fraction; this increase is especially pronounced in the mixtures that are rich in Jet-A.

IV. Conclusions

The use of the advanced distillation curve method can provide extremely useful insights into the properties of aviation fuels (and mixtures thereof) and allow a more technically sound approach to be taken when formulating advanced mixtures. This was illustrated by the potential of a chemical analysis of each distillate cut as a function

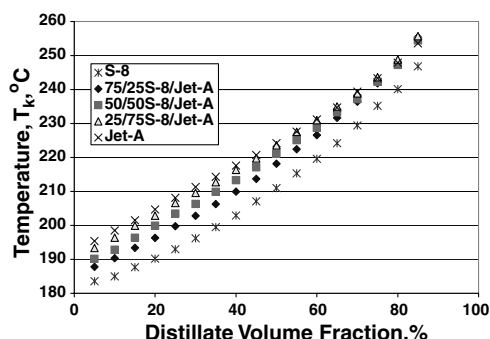


Fig. 1 Representative distillation curves for each of the three mixtures of S-8 and Jet-A with the curves for the individual components, S-8 and Jet-A, also provided.

Table 5 Summary of the results of hydrocarbon family calculations based on the method of [18] for 75/25 S-8/Jet-A

Distillate volume fraction, %	Paraffins vol %	Monocycloparaffins vol %	Dicycloparaffins vol %	Alkylaromatics vol %	Indanes and tetralins vol %	Naphthalenes vol %
<i>Composite</i>	75.3	22.0	0.4	1.2	0.2	0.9
0.025	74.1	22.2	0.2	3.2	0.0	0.3
10	77.9	19.1	0.1	2.6	0.0	0.3
20	76.7	19.9	0.1	2.9	0.0	0.4
30	76.6	20.0	0.1	2.9	0.0	0.5
35	77.6	19.2	0.1	2.7	0.0	0.4
40	75.9	20.1	0.3	3.0	0.2	0.6
45	81.5	16.3	0.0	1.9	0.0	0.2
50	78.1	18.9	0.2	2.3	0.1	0.5
60	78.9	18.4	0.1	1.7	0.1	0.7
70	72.3	21.6	1.4	2.3	0.8	1.6
80	84.1	15.2	0.0	0.1	0.0	0.6
Residue	83.1	16.5	0.0	0.0	0.0	0.4

Table 6 Summary of the results of hydrocarbon family calculations based on the method of [18] for 50/50 S-8/Jet-A

Distillate volume fraction, %	Paraffins vol %	Monocycloparaffins vol %	Dicycloparaffins vol %	Alkylaromatics vol %	Indanes and tetralins vol %	Naphthalenes vol %
<i>Composite</i>	65.4	23.5	6.1	8.8	3.0	2.3
0.025	66.7	22.9	0.4	9.6	0.0	0.3
10	67.9	23.3	0.5	7.8	0.2	0.4
20	68.9	22.3	0.5	7.7	0.2	0.4
30	70.6	20.9	0.3	7.4	0.3	0.5
35	70.8	20.9	0.4	7.1	0.3	0.4
40	71.3	20.5	0.4	6.8	0.4	0.6
45	73.2	19.3	0.3	6.4	0.3	0.5
50	71.9	20.0	0.4	6.2	0.8	0.8
60	70.4	21.7	0.6	5.2	1.1	1.0
70	73.1	20.9	0.4	3.4	1.0	1.2
80	76.9	19.4	0.1	1.5	0.9	1.2
Residue	72.3	25.9	0.3	0.2	0.1	1.2

Table 7 Summary of the results of hydrocarbon family calculations based on the method of [18] for 25/75 S-8/Jet-A

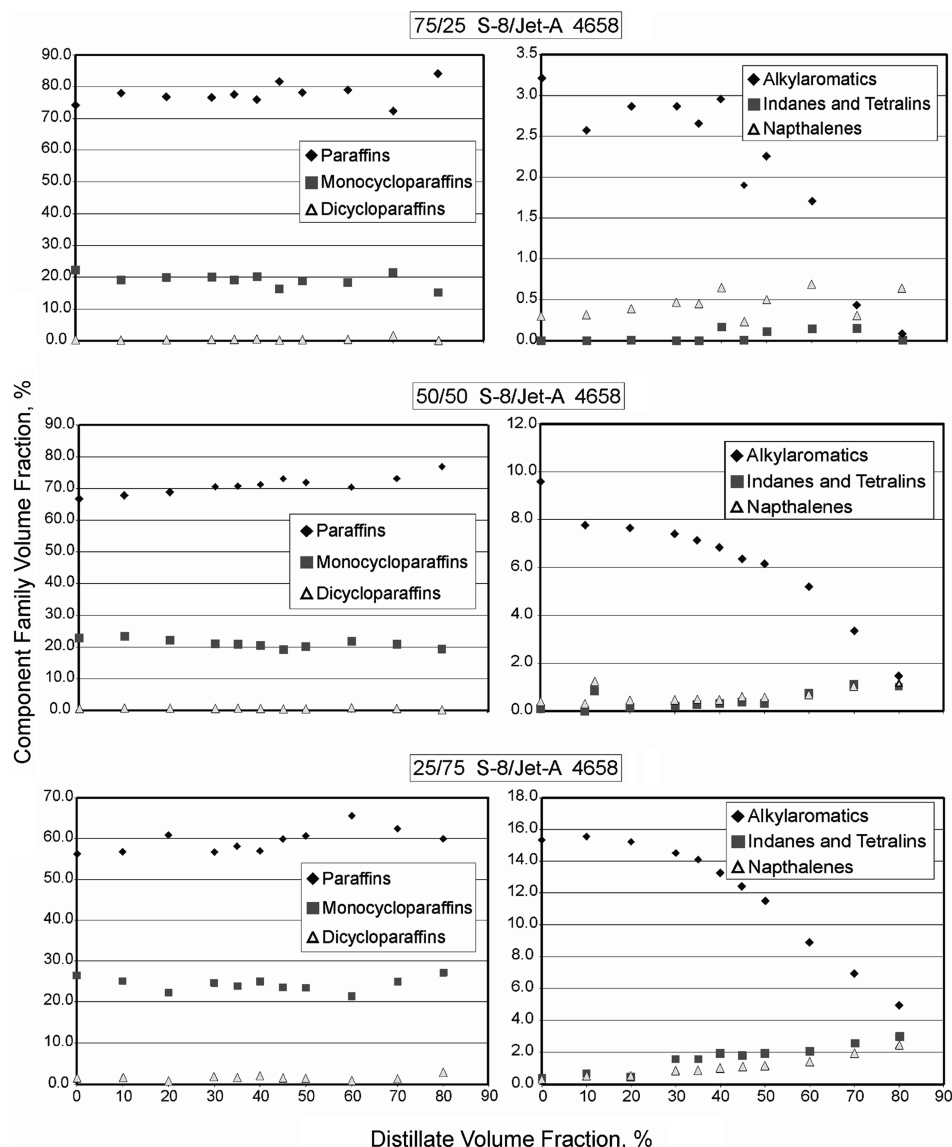
Distillate volume fraction, %	Paraffins vol %	Monocycloparaffins vol %	Dicycloparaffins vol %	Alkylaromatics vol %	Indanes and tetralins vol %	Naphthalenes vol %
<i>Composite</i>	48.1	25.6	8.5	11.3	4.2	2.5
0.025	56.2	26.5	1.3	15.3	0.4	0.3
10	56.7	25.1	1.5	15.5	0.7	0.5
20	60.9	22.3	0.7	15.2	0.5	0.5
30	56.7	24.6	1.8	14.5	1.6	0.8
35	58.1	23.9	1.5	14.1	1.6	0.8
40	57.0	24.9	1.9	13.3	1.9	1.0
45	59.9	23.6	1.2	12.4	1.8	1.1
50	60.7	23.4	1.3	11.5	1.9	1.2
60	65.5	21.5	0.6	8.9	2.1	1.4
70	62.4	24.9	1.3	6.9	2.6	1.9
80	59.9	27.1	2.7	4.9	3.0	2.4

Table 8 Summary of the results of hydrocarbon family calculations based on the method of [18] for Jet-A

Distillate volume fraction, %	Paraffins vol %	Monocycloparaffins vol %	Dicycloparaffins vol %	Alkylaromatics vol %	Indanes and tetralins vol %	Naphthalenes vol %
<i>Composite</i>	46.5	22.5	5.4	18.4	4.5	2.4
0.025	40.4	27.3	3.4	27.3	1.2	0.5
10	39.8	25.1	4.5	27.2	2.6	0.8
20	41.2	24.6	4.4	25.6	3.1	1.1
30	40.9	25.2	5.8	22.1	4.3	1.6
35	43.2	24.5	4.3	21.9	4.2	1.8
40	43.3	25.3	4.8	20.0	4.6	2.0
45	41.7	25.9	6.4	18.7	5.0	2.3
50	42.9	25.8	5.6	18.1	5.1	2.4
60	43.1	26.4	6.7	15.0	5.9	2.9
70	43.8	27.1	7.4	11.8	6.3	3.6
80	48.7	29.9	7.0	6.3	4.6	3.3
Residue	49.7	31.9	7.0	3.4	3.4	4.5

Table 9 Summary of the results of hydrocarbon family calculations based on the method of [18] for S-8

Distillate volume fraction, %	Paraffins vol %	Monocycloparaffins vol %	Dicycloparaffins vol %	Alkylaromatics vol %	Indanes and tetralins vol %	Naphthalenes vol %
<i>Composite</i>	80.0	17.3	0.9	0.1	0	1.9
0.025	79.1	18.4	0.1	1.8	0.0	0.6
10	81.2	16.4	0.0	1.9	0.0	0.5
20	81.0	18.0	0.1	0.0	0.0	0.9
30	80.8	17.9	0.3	0.0	0.0	1.1
35	82.0	16.8	0.1	0.0	0.0	1.1
40	85.8	13.7	0.0	0.0	0.0	0.5
45	87.8	11.9	0.0	0.0	0.0	0.3
50	85.3	13.8	0.0	0.0	0.0	0.9
60	85.1	13.9	0.0	0.0	0.0	1.1
70	85.1	13.7	0.0	0.0	0.0	1.2
80	83.6	15.0	0.0	0.0	0.0	1.4
Residue	84.8	14.7	0.0	0.0	0.0	0.5

**Fig. 2** A plot of the hydrocarbon types resulting from the [18] analysis for three mixtures of Jet-A and S-8.

of fuel mixture. As we have shown, any applicable analytical technique can be applied to individual cuts. This results in information that not only explains the structure of individual distillation curves, but forms the basis for a more informed design and specification process.

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