

Assessment of the Compositional Variability of RP-1 and RP-2 with the Advanced Distillation Curve Approach

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RP-1 is a long-established hydrocarbon fuel that continues to be widely used as the kerosene component in rocket propulsion systems. The desire in recent years to use rocket engines many times, rather than a single time, has led to reformulations of RP-1 and to the formulation of RP-2. In terms of processing, increased hydro-treating of the component feedstock fluids used in the manufacture of RP-1 can lower the sulfur, olefin, and aromatic content significantly. The resulting fuels have demonstrably lower metal corrosion effects and are thus more amenable to multiple use rocket engines. In recent years, the reformulated RP-1 mixtures have been extensively studied in terms of thermophysical properties, combustion processes and kinetics, and performance. Still unknown is how compositional variability resulting from the various blending strategies affects both the properties and our ability to correctly predict the fluid behavior with mathematical models. To address this question, we have obtained 11 batches of RP-1 that were prepared to represent the range of formulation recipes. For each of these representative formulations, we have assessed the compositional variability with the advanced distillation curve (ADC) metrology. This method is an improvement of classical boiling curve techniques. It features (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 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 this paper, we will employ all applicable data channels of the ADC to show the compositional variability and also discuss how the variability will impact predictive modeling. We use these data to conclude that the variabilities of RP-1 and RP-2 are significant and perhaps higher than expected.

Introduction

Modern rocket engines can operate on either a liquid or a solid fuel package, although the liquid fuel package is the more easily controlled and the more flexible of these two classifications.¹ Indeed, Goddard's initial 1926 rocket flight tests used a liquid fuel package consisting of oxygen and gasoline. Since that time, the major practical liquid fuel packages have been those based either on oxygen + hydrogen or oxygen + kerosene. While the oxygen + hydrogen mixture is the highest performing practical propellant mixture commonly used in terms of specific impulse (actually hydrogen + fluorine is higher but is not practical), it has significant limitations, which include the complexity and cost of cryogen use (temperatures in the range of 20 K), the hazards associated with liquid hydrogen, and very low density (when compared to a hydrocarbon mixture such as kerosene). The initial oxygen + kerosene propellant mixtures that were developed utilized turbine aviation fuels as the kerosene component, starting with the kerosene-like fluid JP-4. The aviation fuels were not produced with a set of sufficiently tight specifications

(in terms of physical properties such as density, volatility, chemical components, enthalpy of combustion, etc.) to be effective rocket propellants, however.

This limitation led to the development of RP-1 (for rocket propellant 1) in the mid 1950s.² This fluid, produced as MIL-P-25576, has a much narrower allowable density range (0.801–0.815 g/mL) and volatility range (185–210 °C) and a much lower allowable sulfur (< 500 ppm, mass/mass), olefin (< 1.0%, vol/vol), and aromatic (< 5.0%, vol/vol) content than the common turbine aviation fuels.³ RP-1 is now a long-established hydrocarbon fuel that continues to be widely used in propulsion systems. Distillates from crude oil that are high in naphthalene content are generally used for RP-1 production in order to meet the specifications for density, heat of combustion, and aromatic content.³ Previous analysis of RP-1 has shown the fuel to be a complex mixture of compounds including paraffins, olefins, and aromatics.⁴ Although the sulfur concentration specification for RP-1 was set at 500 ppm (mass/mass), the typical as-delivered lot was much

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lower, at 30 ppm (mass/mass). Historically, the formulation of RP-1 has been formulated by mixing separate blending stocks according to “recipes” that are known to produce fluids that are within specification. The recipes varied depending upon availability, economics, and logistics. This practice is still employed with present formulations.

The desire in recent years to use rocket engines many times, rather than a single time, has led to reformulations of the kerosene component of liquid rocket propellants. In terms of processing, increased hydro-treating of fluids such as RP-1 can lower the sulfur, olefin, and aromatic content significantly. The resulting fuels have demonstrably lower metal corrosion effects and are thus more amenable to multiple use rocket engines. Three grades of RP-1 were originally considered for specification with the ultimate goal of decreasing the sulfur concentration specification: TS-30 (with a total sulfur specification < 30 ppm, mass/mass, similar to typical as-delivered RP-1), TS-5 (total sulfur specification of < 5 ppm, mass/mass), and UL (ultralow sulfur, < 100 ppb, mass/mass). Testing showed that ultralow sulfur RP-1 (ultralow RP-1, sometimes simply called ultra) provided significant performance benefits over TS-5 with only marginally greater costs, so the sulfur content of this fuel was chosen as the specification limit for what became RP-2. The RP-1 sulfur limit was lowered from 500 to 30 ppm (mass/mass), more closely reflecting the as-delivered material. We note that the specification for RP-1 and RP-2 aromatic content is the same; however, one commonly finds a lower aromatic content in RP-2.^{5,6}

As a result of the reformulations described above, it has been necessary to measure many of the chemical and thermophysical properties of both RP-1 and RP-2.^{4,7–10} These properties have included the chemical composition, chemical stability, volatility, density, viscosity, speed of sound, and thermal conductivity, many of which have been measured at NIST. From these data, we have developed surrogate mixture models to represent the thermophysical and transport properties. These surrogate models were implemented within the framework of the NIST Refprop computer program.¹¹

A weakness of this body of work is that the measurements were performed on only one sample or batch, each, of RP-1

and RP-2. Only a single batch of RP-1 was used because of the two that were available to us at the time, one was known to be unusual and, in fact, out of specification.^{12,13} Only a single batch or formulation of RP-2 was used because at the time the measurements were made, the formulator had produced only one batch of this fluid. The limitations caused by these limited sample availabilities were clear even during the model development process and were in fact discussed in detail upon release of the models.¹⁴

We recognize that the specifications for RP-1 and RP-2 are stringent when compared to those of mass commodity fuels such as Jet-A or JP-8.¹⁵ Moreover, the potential for radical departures (within the specifications) may well be low, given the desire on the part of formulators to deviate little from successful recipes. Despite this, there have been indications that some unexpected variability has been encountered by launch contractors.¹⁴ In an effort to evaluate what the range and effect of compositional variability might be, we have undertaken in this work an evaluation of the possible range of composition, derived from different recipes. We have obtained for this evaluation what we consider to be orthogonal batches (that is, mutually exclusive, independently prepared batches that are uncorrelated with one another) of rocket kerosene. These batches are distinct from batches that might sequentially be added to a storage tank, where batch to batch carryover will correlate samples. Orthogonal samples are free of all such effects. These batches were intentionally prepared to reflect a significant range of possible variability and are not necessarily to be construed as the typical range of variability that the user might encounter.¹⁶

In this paper, we report our initial evaluations with detailed chemical analyses and our findings as determined by the advanced distillation curve (ADC) approach. Additional evaluations of the thermophysical property measurements (density, viscosity, and speed of sound) and theoretical model implications will be presented in the future.

Advanced Distillation Curve Metrology. Simply stated, the distillation curve is a graphical depiction of the boiling temperature of a fluid or fluid mixture plotted against the volume fraction distilled.^{17–19} The most common presentation of the distillation curve is a plot of the boiling temperature (at ambient pressure) against volume fraction. The standard test method, ASTM D-86, provides the usual approach to measurement.²⁰ The data obtained with ASTM D-86 are the initial boiling point, the temperature at predetermined distillate volume fractions, and the final boiling point. The ASTM D-86 test suffers from several drawbacks, including large uncertainties in temperature measurements and little theoretical significance.²¹

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Table 1. Listing by Retention Time (RT) of the Components of RP-1 Identified with GC–MS for the 11 Blends of RP-1 Formulated for the Variability Study and for the Earlier Sample of RP-1 (RP-1-4572)^a

peak no.	RT (min)	compound	CAS no.	area %											RP-1-4572
				blend 1	blend 2	blend 3	blend 4	blend 5	blend 6	blend 7	blend 8	blend 9	blend 10	blend 11	
1	0.697	2-methylbutane	78-78-4	0	0.003	0.001	0.004	0.004	0	0	0	0	0.001	0	0.01
2	0.723	acetone	67-64-1	0.02	0	0.001	0.003	0	0.005	0.009	0.017	0.003	0.012	0.023	0.004
3	0.827	<i>n</i> -hexane	110-54-3	0.004	0	0	0	0.004	0.002	0	0.001	0.001	0.005	0	0.005
4	0.886	methylcyclopentane	96-37-7	0	0	0	0	0	0	0	0	tr	0.002	0	0.006
5	0.969	cyclohexane	110-82-7	0	0	0	0	0	0	0	0	0.001	0.002	0.005	0.02
6	1.03	2,2-dimethylhexane	590-73-8	0	0.001	0	0	0	0	0.003	0.003	0.002	0.003	0.006	0.025
7	1.07	<i>n</i> -heptane	142-82-5	0	0	0	0	0	0	0	0	0.001	0	0	0.016
8	1.19	methylcyclohexane	108-87-2	0	0	0	0	0	0.003	0	0.003	0.002	0	0	0.052
9	1.401	toluene	108-88-3	0	0.004	0.02	0	0	0	0.01	0.007	0.006	0.006	0.011	0.07
10	1.83	1a,3a,5b-trimethylcyclohexane	1795-27-3	0	0.018	0.016	0	0	0	0	0	0.002	0	0	0
11	1.9	1,3,5-trimethylcyclohexane	1839-63-0	0.024	0.036	0.041	0.06	0.018	0	0.063	0.056	0.027	0.038	0.073	0.075
12	2.05	1a,2a,4b-trimethylcyclohexane	7667-60-9	0.002	0.033	0.028	0	0	0	0	0	0	0	0	0
13	2.122	1a,2b,4b-trimethylcyclohexane	7667-60-9	0.032	0.08	0.094	0.064	0.023	0.046	0.17	0.032	0.064	0.085	0.169	0.15
14	2.16	1a,3a,5b-trimethylcyclohexane	1795-26-2	0.15	0.016	0.02	0.032	0.01	0.02	0.027	0.026	0.013	0.016	0.028	0.044
15	2.23	ethylbenzene	100-41-4	0	0	0	0	0	0	0	0	0.009	0	0	0.021
16	2.3	<i>o</i> -xylene	95-47-6	0	0	0	0	0	0	0.006	0	0.019	0.004	0.004	0.1
17	2.33	1a,2b,3a-trimethylcyclohexane	1678-81-5	0	0.026	0.013	0	0	0	0	0	0	0	0	0
18	2.4	1a,2b,4a-trimethylcyclohexane	N/A	0	0.091	0.008	0.017	0	0.017	0.079	0.102	0	0	0.088	0.06
19	2.42	1,2,4-trimethylcyclohexane	2234-75-5	0.02	0.064	0.113	0.028	0.018	0.023	0.031	0.064	0.047	0.061	0.033	0.046
20	2.47	1,2,3-trimethylcyclohexane	1678-97-3	0.057	0.033	0.107	0.12	0.044	0.09	0.068	0.037	0.029	0.037	0.077	0.14
21	2.51	1-ethyl-4-methylcyclohexane trans	6236-88-0	0.013	0.011	0.052	0.04	0.016	0.02	0.036	0.067	0.017	0.027	0.051	0.057
22	2.556	1-ethyl-4-methylcyclohexane	3728-56-1	0	0.041	0.035	0.039	0.028	0	0.065	0.029	0	0.041	0.081	0.083
23	2.582	1-ethyl-4-methylcyclohexane	4926-78-1	0.034	0.014	0.014	0.04	0.051	0.039	0.029	0.006	0.045	0.02	0	0.036
24	2.654	<i>p</i> -xylene	106-42-3	0	0	0	0	0	0	0.005	0	0.007	0	0	0.051
25	2.726	1a,2a,3b-trimethylcyclohexane	7667-55-2	0	0.015	0.039	0	0	0	0	0.023	0	0	0	0
26	2.76	1a,2a,3a-trimethylcyclohexane	1839-88-9	0	0.024	0	0.029	0	0	0.027	0.058	0.019	0	0.019	0
27	2.8	<i>x,y,z</i> -trimethylcyclohexane	N/A	0	0.044	0.049	0.075	0	0	0.066	0.059	0.028	0	0.063	0.068
28	2.82	1,2,3-trimethylcyclohexane	1678-97-3	0	0.052	0.08	0.047	0	0.029	0	0.055	0.027	0.031	0.072	0.117
29	2.85	1-ethyl- <i>x</i> -methylcyclohexane	N/A	0.089	0.029	0.03	0.052	0.066	0.072	0	0.021	0.026	0.016	0.075	0.072
30	2.9	1-ethyl- <i>x</i> -methylcyclohexane	N/A	0.013	0.014	0.012	0.023	0.01	0.018	0.019	0.007	0.008	0.002	0.023	0.032
31	3.432	1-ethyl-2,3-dimethylcyclohexane	7667-60-9	0.08	0.013	0.2	0.15	0.086	0.11	0.18	0.148	0.077	0.086	0.187	0.22
32	4.248	2-ethyl-1,3-dimethylcyclohexane	61142-69-6	0.06	0.09	0.15	0.123	0.054	0.092	0.11	0.103	0.059	0.025	0.125	0.2
33	4.355	1-methyl- <i>x</i> -propylcyclohexane	N/A	0.21	0	0.43	0.35	0.167	0.29	0.38	0.359	0.2	0.17	0.418	0.42
34	4.661	1,2,3-trimethylbenzene	526-73-8	0.3	tr	0	0	0	0	tr	0	tr	0	0	0.22
35	5.379	2-methylbutyl cyclopentane	53366-38-4	0.53	0.39	0.9	0.267	0.32	0.36	0.22	0.371	0	0.4	0.423	0.51
36	5.45	2,6-dimethylnonane	17302-28-2	0.56	0.54	1.81	0.683	0.539	0.63	0.58	0.708	0.45	0.45	0.7	0.94
37	5.615	butylcyclohexane	1678-93-9	0.71	0.9	1.23	0.851	0.654	0.78	0.62	0.701	0.54	0.6	0.81	0.99
38	6.195	<i>trans</i> -decalin	493-02-7	1.46	1.6	1.91	0.951	1.375	1.51	1.23	0.971	0.98	1.06	1.53	1.26
39	6.51	5-methyldecane	2216-32-2	0.77	0.72	1.02	0.8	0.71	0.76	0.58	0.77	0.68	0.7	0.79	0.66
40	6.727	2-methyldecane	6975-98-0	1.08	1	1.41	1.062	1.256	1.03	0.74	0.982	1.13	0.98	1.05	1.2
41	6.93	3-methyldecane	13151-34-3	1.02	1.1	1.4	1.08	0.98	1.04	0.78	1.09	0.92	0.98	1.08	1.2
42	7.015	adamantane	281-23-2	0.45	0.44	0.57	0.409	0.351	0.41	0.43	2.18	0.25	0.226	0.311	0.44
43	7.244	3-butylcyclohexanone	39178-69-3	0.92	0.8	1.01	0.89	0.824	0.87	0.58	0.842	0.62	0.6	0.71	1.07
44	7.582	<i>cis</i> -decalin	42588-37-2	1.77	1.5	1.72	1.617	1.663	1.51	1.04	0.98	1.05	0.78	1	0.95
45	7.9	<i>n</i> -undecane	1120-12-4	1.03	0.2	1.6	0.4	0.338	0.5	0.5	1.454	2.7	3.5	0.8	1.58
46	7.992	<i>trans</i> -2-methyl decalin	100015-24-7	1.3	1.6	1.6	1.98	1.726	1.1	0.9	1.02	0.5	0.2	1.4	0.83
47	8.554	2-methyl decalin	2958-76-1	2.34	2.4	2.65	2.377	2.61	2.33	1.62	2.3	1.7	1.71	2.31	1.84
48	9.021	pentyl cyclohexane	4292-92-6	1.24	1	1.13	1.25	1.12	1.25	0.76	0.939	0.85	0.77	0.92	0.98
49	9.37	2- <i>syn</i> -methyl- <i>cis</i> -decalin	100015-58-5	1.22	1.2	1.11	1.8	1.33	1.73	0.53	0.648	0.74	0.55	0.64	0.97
50	9.543	1-methyl-4-(1-methylbutyl)cyclohexane	54411-00-6	1.23	1	0.99	0.987	1.084	1.31	0.35	0.83	0.79	0.67	0.82	1
51	10.016	5-methylundecane	1632-70-8	2.06	1.8	1.92	2.01	1.87	2.18	1.38	1.7	1.73	1.6	1.74	1.52
52	10.189	4-methylundecane	2980-69-0	1.65	1.4	1.35	2.015	1.55	1.89	0.91	1.08	1.19	1.09	1.13	1.24
53	10.351	2-methylundecane	7045-71-8	2.42	1.9	1.96	2.352	2.083	2.36	1.49	1.76	1.78	1.56	1.71	1.66
54	10.595	3-methylundecane	1002-43-4	2	1.6	1.5	2	1.702	1.88	1.52	1.41	2.08	1.37	1.51	1.52
55	11.182	2,6-dimethyl decalin	1618-22-0	1.58	1.5	1.36	1.95	1.5	1.91	1.17	1.29	1.21	1.06	1.31	1.42
56	11.421	1,3-dimethyladamantane	702-79-4	0.8	0.88	1	1.331	0.924	1.27	0.63	0.561	0.78	0.476	0.21	0.77
57	11.805	<i>n</i> -dodecane	112-40-3	4.02	2	2	2.4118	1.7	2.31	2.84	1.43	4.38	2.92	2	2.75
58	12.379	2,6-dimethylundecane	17301-23-4	2.95	3	2.47	3.752	3.221	3.53	2.33	2.59	2.21	2.09	2.42	2.38
59	13.127	hexylcyclohexane	4292-75-5	1.46	1.7	1.38	1.584	1.56	2	1.38	1.311	1.31	1.36	1.41	1.43
60	13.943	<i>x,y</i> -dimethylundecane	N/A	1.05	1.1	1.02	1.31	1.05	1.19	0.94	0.971	1.14	0.91	0.79	1.03
61	14.2	4-methyldodecane	N/A	0.93	1.3	0.82	1.283	1.18	1.59	0.91	0.892	0.88	1.09	0.92	1.06
62	14.375	2,10-dimethylundecane	17301-27-8	1.6	1.9	1.47	2.061	1.73	1.92	1.68	1.58	1.57	1.61	1.55	1.68
63	14.604	<i>x,y</i> -dimethylundecane	N/A	1.05	1.4	1.07	0.939	1.26	1.41	1.22	2.02	1.17	1.2	1.2	0.78
64	14.71	2,3,6-trimethyloctane	62016-33-5	1.87	2.2	1.76	2.596	2.21	2.35	1.94	0.53	1.7	1.83	1.79	1.73
65	14.924	2-methylnaphthalene	91-57-6	1.12	0.7	0.6	0.752	0.676	0.78	1.24	0.59	1.25	0.15	0.19	1.1
66	15.288	1,1'-bicyclohexyl	92-51--3	0.72	1.1	0.95	1.452	1.385	1.41	1.08	0.922	0.88	1.06	1.07	0.85
67	15.477	1-methylnaphthalene	90-12-0	0.64	0.72	0.57	0.716	0.607	0.684	0.79	0	0.7	0.19	0.21	1.1
68	15.654	<i>n</i> -tridecane	629-50-5	2.98	0.35	0.61	0.5	0.77	0.44	3.23	0.585	3	0.96	0.15	2.18
69	16.215	<i>x,y</i> -dimethyldodecane	N/A	0.86	1.1	0.93	1.114	1.245	1.05	1.18	1.13	1.02	1.16	1.12	1.04

Table 1. Continued

peak no.	RT (min)	compound	CAS no.	area %											RP-1-4572
				blend 1	blend 2	blend 3	blend 4	blend 5	blend 6	blend 7	blend 8	blend 9	blend 10	blend 11	
70	17.225	6-methyltridecane	13287-21-3	0.61	0.9	0.72	0.729	1	0.72	0.85	0.9	0.8	1.03	0.81	0.77
71	17.439	4-methyltridecane	26730-12-1	0.75	1.03	0.9	0.837	1.38	0.86	1.11	1.16	1.06	1.36	1.06	0.85
72	17.59	3-methyltridecane	6418-41-3	1.27	1.5	1.33	1.191	1.72	1.23	1.52	1.69	1.74	1.73	1.59	1.39
73	17.772	2-methyltridecane	1560-96-9	0.54	0.81	0.73	0.624	1	0.65	0.87	0.96	0.85	1.09	1.17	0.74
74	17.945	2,y,z-trimethyl dodecane	N/A	1.18	1.6	1.45	1.25	2.23	1.21	1.85	2.18	1.85	0.85	1.75	1.36
75	18.594	n-tetradecane	629-59-4	3.55	1.8	0.96	0.2	0.492	0.25	2.03	1.1	2.25	1.38	1	0.83
76	18.789	4,4,8,9,10-pentamethyl decalin	80655-44-3	0.68	0.72	0.63	0.309	0.77	0.57	1.21	0.92	1.17	1.12	0.89	0.62
77	19.152	1,4-dimethylnaphthalene	571-58-4	0.39	0	0	0	0	0	0.79	0	0.84	0	0	0
78	19.545	1,6-dimethylnaphthalene	575-43-9	0.19	0	0	0	0	0	0.36	0	0.43	0	0	0
79	20.159	2,6,10,15-tetramethylheptadecane or 2,6,10-trimethyltetradecane	54833-48-6	0.59	1.2	1.19	0.385	1.68	0.42	1.94	2.18	1.64	2.26	1.98	0.96
80	20.442	x-methyl 1,1'-biphenyl	N/A	0.09	0	0	0	0	0	0.17	0	0.242	0	0	0
81	20.835	x,y,z-trimethylnaphthalene	N/A	0.07	0.28	0	0	0	0	0.36	0	0.433	0	0	0
82	21.049	n-pentadecane	629-62-9	0.6	0.19	0.15	0.03	1.5	0.03	0.8	0.263	0.96	0.33	0.28	0.48
83	23.087	tert-hexadecanethiol	25360-09-2	0	0.095	0.02	0	0.093	0	0.154	0.158	0.147	0.187	0.052	0
84	23.241	n-hexadecane	544-76-3	0.08	0.08	0.02	0	0.06	0	0.15	0.085	0.2	0.111	0	0.08
85	23.38	tetratetracontane	7098-22-8	0	0.102	0	0	0.049	0	0.017	0.087	0.178	0.106	0.078	0
86	24.2	2,6,10-trimethylpentadecane	3892-00-0	0	0.12	0.066	0	0.238	0	0.13	0.299	0.18	0.275	0.166	0.13
87	25.358	2,6,10-trimethylhexadecane	55000-52-7	0	0.03	0.034	0	0.132	0	0.04	0	0.055	0.061	0.061	0.036
88	25.743	methyl tetradecanoate	124-10-7	0.021	0.04	0.013	0	0	0	0	0	0	0	0	0

^aThe area counts are uncalibrated and are intended only as a rough guide to the relative composition of the sample. In some cases, additional notation is included to indicate the position and orientation of the side chain, where 1a is a side chain at the 1st carbon in the cis configuration and 2b is a side chain at the 2nd carbon in the trans configuration.

In an effort to remedy the shortcomings of the standard distillation method described above and to develop a performance based test method, we have reported in detail an improved distillation method and apparatus. Improvements to the traditional distillation apparatus include (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 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.^{21–26} The most important advantage presented by the advanced distillation curve metrology is the ability to sample the fluid during the course of the distillation. Sampling very small volumes of the distillate (5–25 μ L) yields nearly instantaneous composition measurements to accompany the temperature data grid. Chemical analysis of the distillate fractions allows for some understanding of how the composition of the fluid varies with volume fraction and distillation temperature, even for complex fluids. The fraction-by-fraction chemical analysis coupled with the distillation curve (which can be used to approximate vapor–liquid equilibrium of complex mixtures) presents a more complete picture of the fluid under study. All inflections and slopes of the distillation

curve are the result of the changing composition, and this feature (the fraction-by-fraction chemical analysis) provides an avenue to measure this changing composition.

This improved distillation method also provides important advantages over other methods such as the simulated distillation method embodied in procedures such as ASTM D-2887.²⁷ In that method, for example, one uses the gas chromatographic behavior of a suite of compounds as a frame of comparison with a fuel. A significant advantage offered by the metrology discussed in this paper is the ability to develop a thermodynamic model of the distillation curve with an equation of state.^{11,21–25,28–30} In addition, when designing a fuel surrogate, it is critical to know what components are actually present with relation to the fuel volatility. This aspect permits a physically authentic surrogate to be derived.

The composition-explicit data channel of the advanced distillation curve metrology allows for a detailed fraction-by-fraction chemical analysis of the composition of the fluid under study. Some suitable analytical techniques include gas chromatography with either flame ionization detection (GC–FID) or mass spectral detection (GC–MS), element specific detection (such as gas chromatography with sulfur or nitrogen chemiluminescence detection, GC–SCD or GC–NCD), two-dimensional GC (GC \times GC), Fourier transform infrared spectrophotometry (FTIR), or nuclear magnetic resonance spectroscopy (NMR). We have applied the advanced distillation curve method to a wide variety of mixtures, including

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Table 2. Listing by Retention Time (RT) of the Components of the RP-2 Sample Identified with GC–MS.^a

peak no.	RT (min)	compound	CAS no.	area %
				RP-2- 5433
1	1.9	1,3,5-trimethylcyclohexane	1839-63-0	0.098
2	2.122	1a,2b,4b-trimethylcyclohexane	7667-60-9	0.187
3	2.16	1a,3a,5b-trimethylcyclohexane	1795-26-2	0.047
4	2.4	1a,2b,4a-trimethylcyclohexane	N/A	0.06
5	2.42	1,2,4-trimethylcyclohexane	2234-75-5	0.06
6	2.47	1,2,3-trimethylcyclohexane	1678-97-3	0.119
7	2.51	1-ethyl-4-methylcyclohexane trans	6236-88-0	0.072
8	2.556	1-ethyl-4-methylcyclohexane	3728-56-1	0.038
9	2.726	1a,2a,3b-trimethylcyclohexane	7667-55-2	0.074
10	2.76	1a,2a,3a-trimethylcyclohexane	1839-88-9	0.098
11	2.8	x,y,z-trimethylcyclohexane	N/A	0.074
12	2.85	1-ethyl-x-methylcyclohexane	N/A	0.024
13	3.432	1-ethyl-2,3-dimethylcyclohexane	7667-60-9	0.215
14	4.248	2-ethyl-1,3-dimethylcyclohexane	61142-69-6	0.134
15	4.355	1-methyl-x-propylcyclohexane	N/A	0.416
16	5.45	2,6-dimethylnonane	17302-28-2	0.837
17	5.615	butylcyclohexane	1678-93-9	0.965
18	6.195	trans-decalin	493-02-7	1.62
19	6.51	5-methyldecane	2216-32-2	0.9
20	6.727	2-methyldecane	6975-98-0	1.5
21	6.93	3-methyldecane	13151-34-3	1.15
22	7.015	adamantane	281-23-2	0.083
23	7.244	3-butylcyclohexanone	39178-69-3	0.77
24	7.582	cis-decalin	42588-37-2	1.05
25	7.9	n-undecane	1120-12-4	1.28
26	7.992	trans-2-methyl decalin	100015-24-7	1.28
27	8.554	2-methyl decalin	2958-76-1	2.43
28	9.021	pentyl cyclohexane	4292-92-6	0.972
29	9.37	2-syn-methyl-cis-decalin	100015-58-5	0.927
30	9.543	1-methyl-4-(1-methylbutyl) cyclohexane	54411-00-6	0.425
31	10.016	5-methylundecane	1632-70-8	1.83
32	10.189	4-methylundecane	2980-69-0	1.23
33	10.351	2-methylundecane	7045-71-8	1.75
34	10.595	3-methylundecane	1002-43-4	1.58
35	11.182	2,6-dimethyl decalin	1618-22-0	1.26
36	11.421	1,3-dimethyladamantane	702-79-4	0.527
37	11.805	n-dodecane	112-40-3	2.15
38	12.379	2,6-dimethylundecane	17301-23-4	2.45
39	13.127	hexylcyclohexane	4292-75-5	1.43
40	13.943	x,y-dimethylundecane	N/A	1.01
41	14.2	4-methyldodecane	N/A	1.1
42	14.375	2,10-dimethylundecane	17301-27-8	1.57
43	14.604	x,y-dimethylundecane	N/A	0.83
44	14.71	2,3,6-trimethyloctane	62016-33-5	1.96
45	14.924	2-methylnaphthalene	91-57-6	0.625
46	15.288	1,1'-bicyclohexyl	92-51-3	1.22
47	15.477	1-methylnaphthalene	90-12-0	0.615
48	15.654	n-tridecane	629-50-5	0.526
49	16.215	x,y-dimethyldodecane	N/A	1.1
50	17.225	6-methyltridecane	13287-21-3	0.874
51	17.439	4-methyltridecane	26730-12-1	1.15
52	17.59	3-methyltridecane	6418-41-3	1.61
53	17.772	2-methyltridecane	1560-96-9	0.903
54	17.945	2,y,z-trimethyldodecane	N/A	1.89
55	18.594	n-tetradecane	629-59-4	0.413
56	18.789	4,4,8,9,10-pentamethyl decalin	80655-44-3	0.826
57	20.159	2,6,10,15-tetramethylheptadecane or 2,6,10-trimethyltetradecane	N/A	1.59
58	23.087	tert-hexadecanethiol	25360-09-2	0.02
59	24.2	2,6,10-trimethylpentadecane	3892-00-0	0.193
60	25.358	2,6,10-trimethylhexadecane	55000-52-7	0.124
61	25.743	methyl tetradecanoate	124-10-7	0.048

^aThe area counts are uncalibrated and are intended only as a rough guide to the relative composition of the sample. In some cases, additional notation is included to indicate the position and orientation of the side chain, where 1a is a side chain at the 1st carbon in the cis configuration and 2b is a side chain at the 2nd carbon in the trans configuration.

gasoline, diesel fuel, and rocket and aviation kerosene, and crude oils.^{6,31–54}

Experimental Section

For this work, 11 separate and orthogonal (independently prepared with no correlation or interrelation) samples of RP-1

were obtained from the formulator, each prepared with a somewhat different recipe, yet all meeting the specification for the fluid, along with the sample of the currently supplied RP-1. In addition to these samples, we also were in possession of the earlier sample of RP-1, upon which all of the thermophysical and transport property measurements were made pursuant to the

Table 3. Sulfur Concentration in Parts Per Million (ppm) Determined with GC with Sulfur Chemiluminescence Detection (SCD) for Each of the 11 Blends of RP-1 Formulated for the Variability Study and for the Earlier Sample of RP-1 (RP-1-4572)^a

blend no.	sulfur concentration (ppm)
1	24.1
2	12.6
3	<1
4	2.5
5	10.6
6	6.2
7	18.3
8	6.3
9	18.8
10	5.4
11	4.7
4572	19.9

^aUncertainties are discussed in the text.

development of the Refprop based model (RP-1-4572).^{11,12} The samples were all pink in color because of the presence of a dye, azobenzene-4-azo-2-naphthol. The samples were subjected to

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Table 4. Initial Boiling Behavior for the 11 Blends of RP-1 Formulated for the Variability Study and for the Earlier Sample of RP-1 (RP-1-4572)^a

blend (pressure)	sustained boiling (°C)	vapor rise (°C)
1 (83.0 kPa)	208.0	211.2
2 (83.5 kPa)	207.6	210.3
3 (84.0 kPa)	204.5	207.3
4 (83.6 kPa)	206.5	208.6
5 (84.1 kPa)	210.2	212.8
6 (83.5 kPa)	205.5	207.7
7 (82.9 kPa)	212.1	214.0
8 (81.9 kPa)	206.1	208.9
9 (81.7 kPa)	209.3	211.0
10 (81.8 kPa)	211.1	213.6
11 (80.8 kPa)	206.3	208.9
4572 (83.7 kPa)	201.5	203.9

^aThe measurements in this table have been adjusted to standard atmospheric pressure with the Sydney Young equation. The pressures at which the measurements were made are provided so that the actual measured temperatures may be recovered. Uncertainties are discussed in the text.

Table 5. Initial Boiling Behavior for an RP-2 Sample and for the Earlier RP-2 Sample (RP-2-EAFB)^a

blend (pressure)	sustained boiling (°C)	vapor rise (°C)
EAFB (82.7 kPa)	202.9	206.4
5433 (83.1 kPa)	214.3	216.5

^aThe measurements in this table have been adjusted to standard atmospheric pressure with the Sydney Young equation. The pressures at which the measurements were made are provided so that the actual measured temperatures may be recovered. Uncertainties are discussed in the text.

chemical analysis before the measurement of the distillation curve. They were analyzed with gas chromatography–mass spectrometry (GC–MS) with a 30 m capillary column with a 1 μm coating of the stationary phase, 5% phenyl dimethyl polysiloxane.⁵⁵ Samples were injected with a syringe into a split/splitless injector set with a 50 to 1 split ratio. The injector was operated at a temperature of 325 °C and a constant head pressure of 82.7 kPa (12 psig). A temperature program of 50 °C followed by a temperature ramp of 3 °C per minute to 90 °C and then a temperature ramp of 6 °C per minute to 170 °C was used. Mass spectra were collected for each peak from 32 to 550 relative

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Table 6. Representative Distillation Curve Data for the 11 Blends of RP-1 Formulated for the Variability Study and for the Earlier Sample of RP-1 (RP-1-4572)^a

volume fraction %	blend 1 °C, 83.0 kPa	blend 2 °C, 83.5 kPa	blend 3 °C, 84.0 kPa	blend 4 °C, 83.6 kPa	blend 5 °C, 84.1 kPa	blend 6 °C, 83.5 kPa	blend 7 °C, 82.9 kPa	blend 8 °C, 81.9 kPa	blend 9 °C, 81.7 kPa	blend 10 °C, 81.8 kPa	blend 11 °C, 80.8 kPa	RP-1-4572 °C, 83.7 kPa
0.025	211.1	210.3	207.2	208.5	212.6	207.5	213.8	208.8	210.9	213.5	208.8	202.6
5	211.9	211.8	208.7	209.5	213.6	208.4	215.6	210.3	212.2	214.9	210.2	204.0
10	212.6	212.8	209.5	210.1	214.4	209.0	216.7	211.3	213.1	215.8	211.2	205.6
15	213.4	213.9	210.7	210.9	215.4	209.9	218.1	212.5	214.2	217.2	212.6	207.2
20	214.3	215.1	211.8	211.9	216.7	210.7	219.7	214.0	215.5	218.6	214.0	208.6
25	215.2	216.3	213.4	212.9	217.6	211.6	221.4	215.6	216.6	220.0	215.7	210.1
30	216.2	217.7	214.5	214.0	218.7	212.6	223.0	217.2	218.0	221.6	217.3	212.1
35	217.2	219.1	215.7	214.9	219.6	213.6	224.7	218.7	219.1	223.0	218.9	213.7
40	218.4	220.4	217.5	216.1	221.0	214.7	226.4	220.6	220.8	225.0	220.8	215.6
45	219.5	222.0	219.1	217.3	222.5	215.8	228.2	222.3	222.2	226.8	222.5	217.3
50	220.7	223.8	220.7	218.7	224.0	217.1	230.3	224.2	223.7	228.8	224.6	219.4
55	222.0	225.7	222.7	219.8	225.7	218.6	232.3	226.4	225.5	231.0	226.8	221.6
60	223.8	227.6	224.8	221.4	227.7	220.0	234.3	228.9	227.4	233.5	229.1	224.0
65	225.4	229.8	227.3	223.1	230.0	221.5	237.0	231.8	229.8	236.3	231.9	226.5
70	227.2	232.0	229.7	224.8	232.3	223.3	239.4	234.9	232.4	239.3	234.7	229.0
75	229.4	234.6	233.0	226.9	235.3	225.4	242.3	238.4	235.6	242.8	238.3	232.2
80	232.1	237.9	236.1	229.4	238.9	227.6	245.5	242.9	239.3	246.8	242.4	235.7
85	235.4	241.7	240.6	232.2	243.7	230.9	249.9	248.6	244.5	252.0	247.8	241.3
90	239.8	247.1	246.9	235.9	249.6	235.1	255.4	255.7	250.9	258.1	254.6	

^aThe measurements in this table have been adjusted to what would be obtained at standard atmospheric pressure with the Sydney Young equation. The pressures at which the measurements were made are provided so that the actual measured temperatures may be recovered. Uncertainties are discussed in the text.

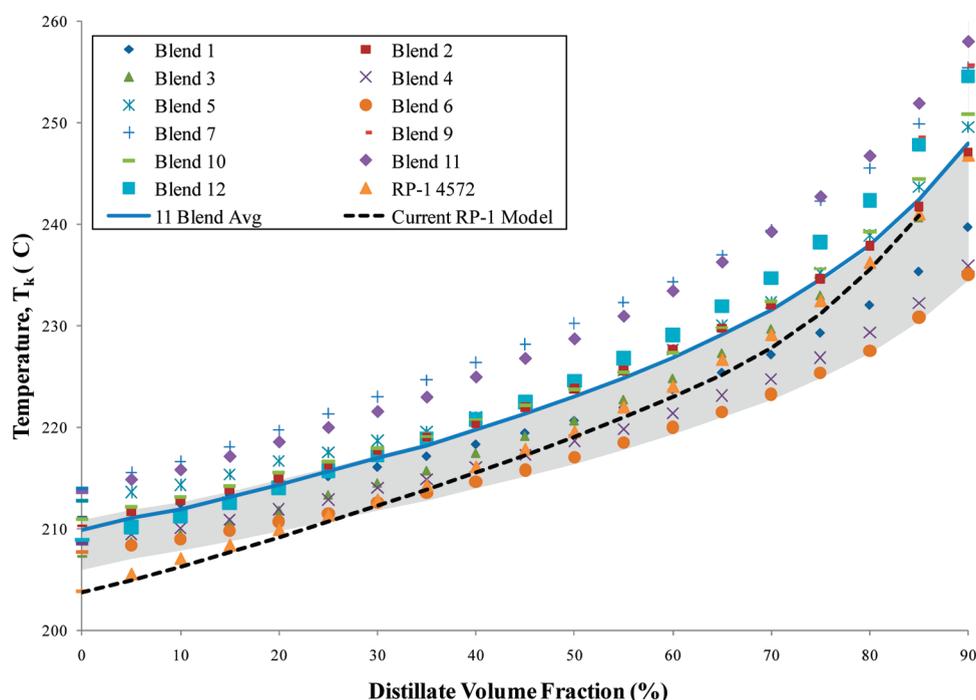


Figure 1. Graphical representation of the distillation curves of the 11 orthogonal samples of RP-1 measured in this work. In addition, we plot the measurements of RP-1-4572 that were used to develop the Refprop model and the predictions of the model itself as the dashed line. The solid line represents the mean temperature, and the shaded area represents the standard deviation of the mean for all 12 measurements. The measurements have been adjusted to what would be obtained at atmospheric pressure by use of the modified Sydney Young equation.

molecular mass (RMM) units. Peaks were identified with guidance from the NIST/EPA/NIH Mass Spectral Database, and also on the basis of retention indices.^{56,57} The total sulfur concentration in each RP-1 sample was analyzed on a commercially

available GC–SCD.⁵⁸ The total sulfur concentration in each vial was calculated with external calibration with carbon disulfide.^{22,46,59}

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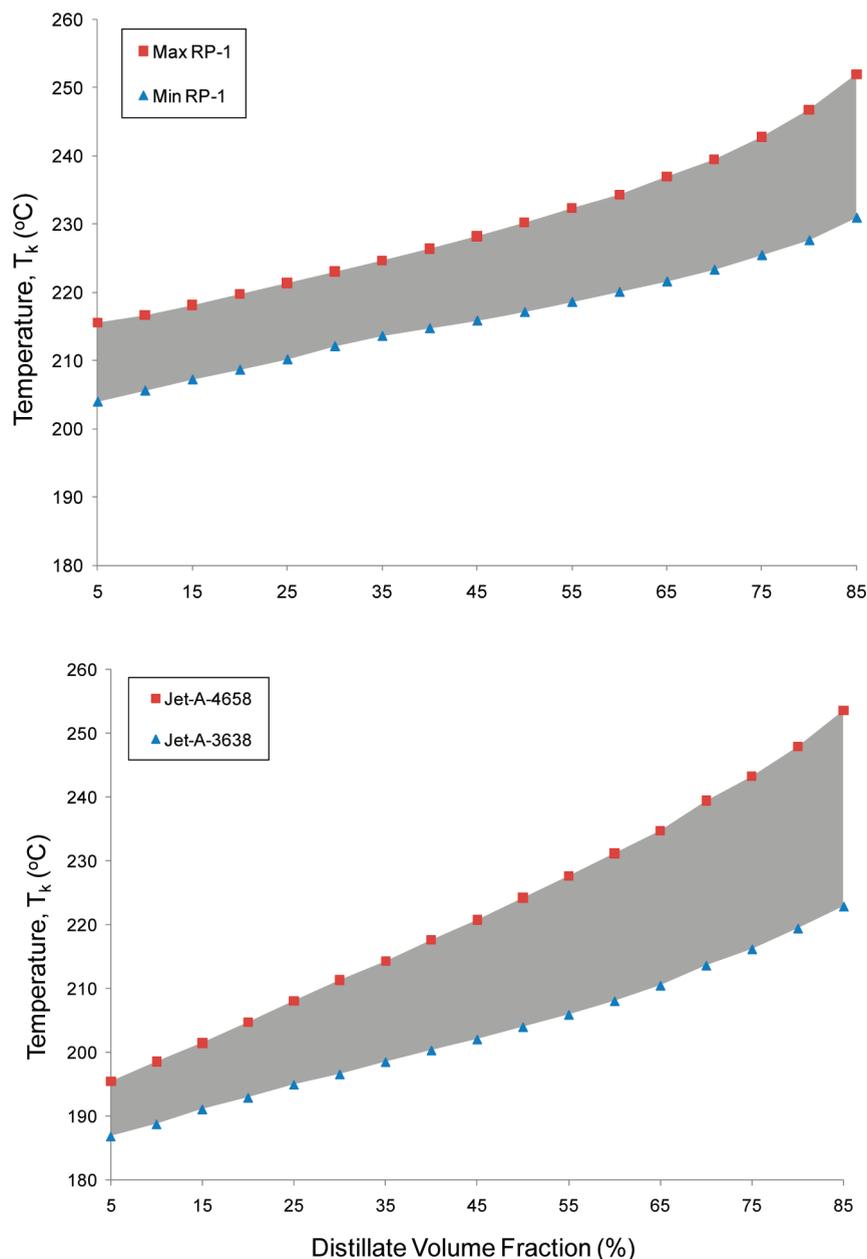


Figure 2. A graphical representation of the variability of the 12 blends of RP-1 measured in this work and the 4 blends of Jet-A and JP-8 measured previously in other work on aviation kerosene. These data are presented on the same temperature scale, thus the shaded areas compare the variability of these two fluids. The measurements have been adjusted to what would be obtained at atmospheric pressure by use of the modified Sydney Young equation.

Two RP-2 samples from different batches made approximately 4 years apart and that were not intended to display variability were available for this evaluation. The earlier sample of RP-2 is the fluid, upon which all of the thermophysical and transport property measurements were made pursuant to the development of the Refprop based model (RP-2-EAFB). The samples were clear and colorless (no dye is added to this fuel). RP-2 was also analyzed by GC–MS with the method above. Peaks were identified with guidance from the NIST/EPA/NIH Mass Spectral Database and also on the basis of retention indices.^{56,57}

The *n*-hexane used as a solvent in this work was obtained from a commercial supplier and was analyzed by gas chromatography (30 m capillary column of 5%-phenyl-95%-dimethyl polysiloxane having a thickness of 1 μm , temperature program of 50 °C followed by a temperature ramp of 5 °C/min to 170 °C) with flame ionization detection and mass spectrometric detection. These

analyses revealed the purity to be approximately 99%, and the fluid was used without further purification.

The method and apparatus for the distillation curve measurement have been reviewed in a number of sources (see the references cited above), so additional general description will not be provided here. For each distillation curve measurement, two temperature channels were measured: T_k , the temperature measured directly in the fluid (kettle), and T_h , the temperature measured at the bottom of the takeoff position in the distillation head. The required amount of fluid for the distillation curve measurement (in each case, 200 mL) was placed into the boiling flask with a 200 mL volumetric pipet. The thermocouples were then inserted into the proper locations to monitor T_k and T_h . 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.

Since the measurements of the distillation curve are performed at ambient atmospheric pressure (measured with an electronic barometer), temperature readings were adjusted for what should be obtained at standard atmospheric pressure. This adjustment was done with the modified Sydney Young equation, in which the constant term was assigned a value of 0.000 109.^{60–63} The magnitude of the adjustment is of course dependent upon the extent of deviation from standard atmospheric pressure. The location of the laboratory in which the measurements reported herein were performed is approximately 1650 m above sea level, resulting in a typical temperature adjustment of 7–8 °C.

Results and Discussion

Chemical Composition. The chemical compositions of 11 separate and orthogonal samples of RP-1 along with the earlier sample of RP-1 were determined with GC–MS. The component list in Table 1 includes all peaks (listed with the retention time (RT) in min and the CAS registry number) with an uncalibrated area percent greater than 1% in at least 1 of the 11 blends of RP-1 formulated for the variability study. The component list in Table 1 also includes some additional peaks that represent both the “light” components (with an RT less than 5 min) and the “heavy” components (with an RT greater than 22 min) that were present in trace quantities and other interesting components that were present in minor (less than 1%) peak areas. These are included to aid in any future modeling efforts, specifically to facilitate representing the properties at the compositional extremes. In some cases, a component was detectable at a low level but above the minimum detectable quantity. Instead of an area % value, the quantity is denoted as tr, for “trace”. There are several instances in which the substituent positions could not be determined on the basis of the mass spectrum, and the chemical name is listed with *x*, *y*, or *z*, instead of the position index. In these cases, no CAS registry number is provided. The chemical composition for the previously measured RP-1 (RP-1-4572), upon which all of the thermophysical and transport property measurements were made pursuant to the development of the Refprop based model, is also presented for comparison. The fluids were composed primarily of linear and branched paraffins, cycloparaffins, alkenes, and some aromatics.

The chemical composition of the RP-2 sample was also identified with GC–MS. Table 2 presents the component list for all peaks that were present with an uncalibrated area percent greater than 1% and also includes some additional peaks that represent both the “light” and the “heavy” components and other interesting components that were present in minor (much less than 1%) peak areas. The RP-2 fluid was also composed primarily of linear and branched paraffins, cycloparaffins, alkenes, and some aromatics. The influence of the compositional differences exhibited by the 12 RP-1 blends and the 2 RP-2 samples on the initial boiling behaviors and distillation curves will be discussed below.

Total Sulfur Concentration. The total sulfur content of each RP-1 blend was determined with GC–SCD. Table 3

Table 7. Representative Distillation Curve Data for an RP-2 Sample and for the Earlier RP-2 Sample (RP-2-EAFB)^a

volume fraction, %	EAFB °C (82.7 kPa)	RP-2-5433 °C (83.1 kPa)
0.025	206.1	
5	207.7	217.8
10	208.6	219.1
15	209.8	220.4
20	211.3	221.8
25	212.7	223.2
30	214.2	225.1
35	215.8	226.8
40	217.6	228.9
45	219.4	231.0
50	221.4	233.3
55	223.6	236.0
60	225.9	238.6
65	228.5	241.6
70	231.4	244.7
75	234.8	248.0
80	238.8	250.7
85	243.9	254.0
90	250.2	257.4

^aThe measurements in this table have been adjusted to what would be obtained at standard atmospheric pressure with the Sydney Young equation. The pressures at which the measurements were made are provided so that the actual measured temperatures may be recovered. Uncertainties are discussed in the text.

shows that the total sulfur concentration of each blend was less than 30 ppm. The sources of uncertainty in evaluating the total sulfur concentration are twofold: there is uncertainty in the area quantitation and in the calibration. The overall uncertainty (with a coverage factor $k = 2$), associated with the recovered sulfur content, was determined to be 3% at the low concentrations encountered in this work.

Initial Boiling Behavior. The initial boiling behaviors of each of the 11 orthogonal blends of RP-1, along with the earlier sample of RP-1, and the two samples of RP-2 were measured. Typically, during the earlier stages of measurements, the first bubbles will appear intermittently and are rather small.²¹ These bubbles cease if the stirrer is stopped momentarily. The temperature at which this intermittent bubbling is observed is called the onset temperature and typically corresponds to the departure of air and other dissolved light gases. Sustained bubbling, which occurs subsequent to onset, is characterized by larger, more vigorous bubbles and is still observed when the stirring is briefly stopped. Eventually, vapor is observed to rise upward into the distillation head, causing an immediate response on the T_h thermocouple. We have shown that this temperature, called the vapor rise temperature, is actually the initial boiling temperature (IBT) of the mixture. This temperature is of low uncertainty and thermodynamically consistent and, therefore, can be modeled theoretically with an equation of state.

The initial temperature observations for each of the 12 RP-1 blends are summarized in Table 4. These values are the average of two separate measurements done for each blend. The uncertainty (with a coverage factor $k = 2$)⁴³ of these measurements has been discussed in detail in previous papers and is approximately 2 °C in the sustained bubbling temperatures and approximately 0.2 °C in the vapor rise temperature. We will confine our comments to the vapor rise temperature because of its significance to theory; the onset and sustained bubbling temperatures are used merely as diagnostics. We note that the vapor rise temperature for the 12 blends ranges from 203.9 to 214.0 °C, with a spread of

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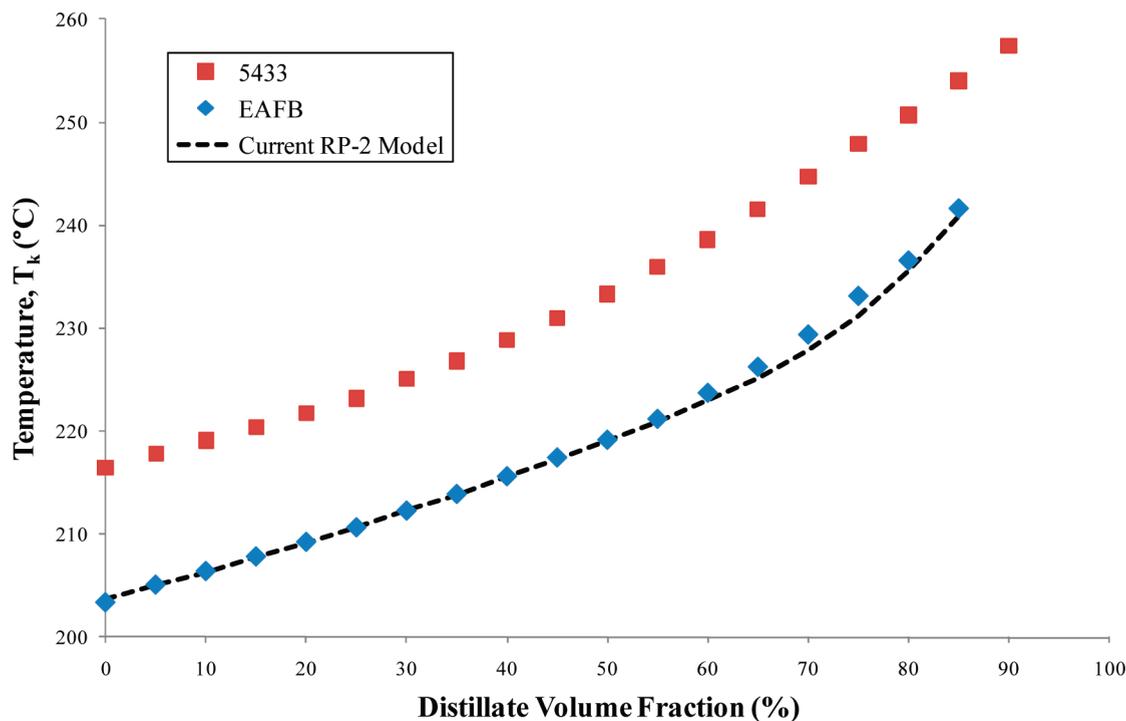


Figure 3. Representative distillation curves for an RP-2 sample and for the earlier RP-2 sample (RP-2-EAFB). The predictions made with the Refprop model are also presented. The measurements have been adjusted to what would be obtained at atmospheric pressure by use of the modified Sydney Young equation.

10.1 °C. The range in the vapor rise temperatures is due to the different chemical compositions for the RP-1 blends (see Table 1). For example, the significantly lower boiling temperatures for RP-1-4572 are due to the relatively higher concentrations of light components (2.4%) in RP-1-4572 compared to those of the other 11 RP-1 blends (0.6%–1.6%). While the spread is due to the different chemical compositions of each blend, the significance of this spread is somewhat difficult to interpret, given the fact that the batches formulated for this work were intended to be variable. Moreover, no such study has been undertaken in the past to form the basis of a comparison.

Perhaps a relevant comparison can be made with several different blends of Jet-A/JP-8. These fuels are commodity aviation kerosenes that are formulated according to wide specification parameters to ensure an adequate supply for military and civilian aviation. Thousands of individual batches of Jet-A/JP-8 have been produced since the 1950s. In prior work, we extensively measured thermophysical properties of four of these fluids.²⁵ Despite the relatively small sample number, we will use this study for comparison because the samples were in fact chosen to represent Jet-A/JP-8 variability. One of the samples considered in that earlier work was a composite Jet-A fluid prepared by mixing approximately equal volumes of five individual batches of Jet-A. This composite sample was prepared at the Air Force Research Laboratory and was provided for many research projects in the aviation fuel community to represent what might be considered a typical Jet-A fluid.⁶⁴ Another sample was known to be unusual in that it showed a remarkably high volatility, an unusually low aromatic content and density, while still meeting all of the specifications for Jet-A. This

fluid was acceptable for use in aviation, but it was nevertheless understood to be unusual. The third sample was simply a typical Jet-A fuel chosen essentially at random from a collection of Jet-A fuels, and the fourth sample was of JP-8, taken directly from the flight line at Wright Patterson Air Force Base. Among those four samples of Jet-A, the range in the vapor rise temperature was 184.2 to 190.5 °C. This range of 6.3 °C is considerably less than what was measured for the RP-1 samples discussed above. Even though the 11 RP-1 blends were made variable intentionally, the specifications for Jet-A are less stringent than those for RP-1 and, thus, we expected to see a smaller range of boiling temperatures for the RP-1 samples.

The onset temperatures for the two samples of RP-2 that we have measured are provided in Table 5. We note that the variability is essentially the same as that for RP-1, with a range of 10.1 °C. It is not clear what conclusions can be drawn from these observations at this time because there are only two samples currently available for evaluation. However, once again, we were surprised to observe a range in boiling temperatures considerably more than what was measured for Jet-A, especially since the RP-2 samples are from different batches that were not intended to display variability.

Distillation Curves. The distillation curve data, presented in T_k , for all 12 RP-1 blends are provided in Table 6. These data include the 11 orthogonal blends studied and also the earlier measurement upon which the Refprop model was formulated (RP-1-4572). We do not list the T_h data in the table because it was mainly used as a diagnostic measurement in this work and not for data analysis/comparison. The temperature data were found to be highly reproducible and comparable to repeatability achieved in our previous work with the ADC. The average standard deviation for replicate temperatures averaged for the complete distillation curves of

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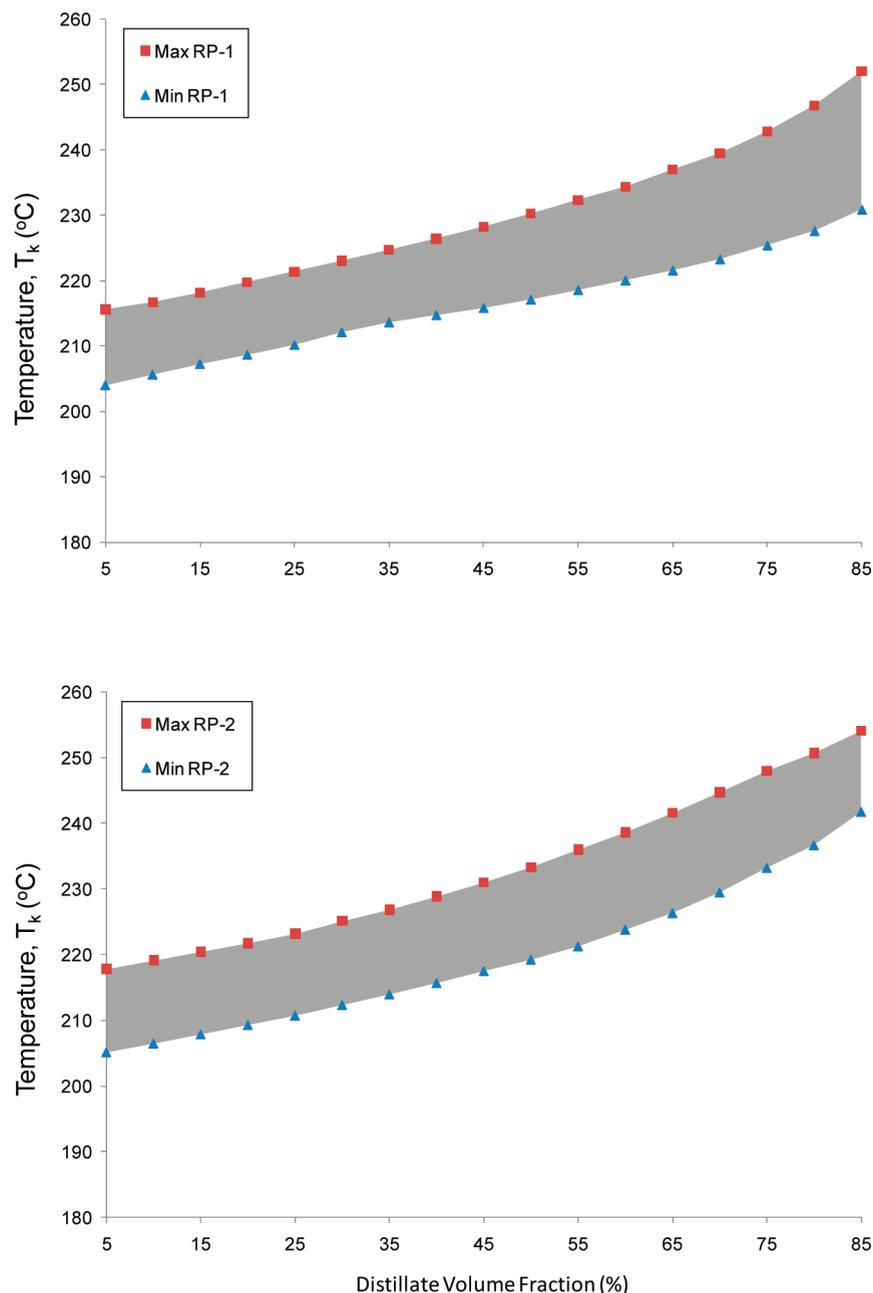


Figure 4. A graphical representation of the variability of the two RP-2 samples and the 11 orthogonal RP-1 blends along with the earlier sample of RP-1. These data are presented on the same temperature scale, thus the shaded areas compare the variability of these two fluids. The measurements have been adjusted to what would be obtained at atmospheric pressure by use of the modified Sydney Young equation.

all 12 RP-1 samples was 0.26 °C. The uncertainty in the volume measurement that was used to obtain the distillate fraction was 0.05 mL in each case. The uncertainty in the measured atmospheric pressure was 0.003 kPa.

In Figure 1, we present the data of Table 6 graphically. In addition, we show on the plot a line that represents the mean temperature at each distillate volume fraction. The standard deviation of this mean value is indicated by the shaded region that surrounds the mean line. The variability among these samples is, at first glance, somewhat surprising because RP-1 is a fluid whose specifications are relatively tightly controlled, especially compared with mass commodity fluids such as aviation turbine kerosene and diesel fuel. As mentioned earlier, however, the blends formulated for this work were intended to be variable and cover the range that might reasonably be encountered.

We also present in Figure 1 the distillation curve data of the sample used for the Refprop model development and the predictions generated from that model (the dashed line).¹¹ Two problems are immediately apparent. First, we can see that the model lies below most of the temperatures measured in the present work. It is only after approximately the 50% distillate volume fraction of the distillation curves where the model merges with the curves measured here. The second problem is with the shape of the modeled curve. The slope of the modeled curve increases far too steeply in the late stages of the curve, compared with the curves measured in this work. We note that the model represents the behavior of RP-1-4572 (the fluid that was used in its development) very well. This agreement is indicative of the precision with which we can target specific mixtures, but it is also indicative of the limitations

Table 8. Results Following a Hydrocarbon Classification ASTM 2789 Analysis for Each of the 11 Blends of RP-1 Formulated for the Variability Study and for the Earlier Sample of RP-1 (RP-1-4572)^a

blend number	paraffins vol %	monocyclo-paraffins vol %	dicyclo-paraffins vol %	alkylbenzenes vol %	indanes, tetralins vol %	naphthalenes vol %
1	35.1	34.2	21.3	5.8	1.3	2.2
2	31.9	38.4	24.8	4.0	0.3	0.6
3	33.7	37.6	23.7	4.1	0.3	0.6
4	34.1	38.6	22.3	4.1	0.4	0.5
5	34.0	38.9	22.7	3.3	0.6	0.6
6	35.0	39.8	21.4	2.8	0.4	0.6
7	36.8	35.9	18.4	5.3	1.4	2.1
8	34.0	39.6	21.6	4.0	0.3	0.5
9	39.0	34.8	16.9	5.2	1.6	2.5
10	37.0	36.9	21.0	4.1	0.3	0.7
11	34.4	38.7	22.0	4.1	0.2	0.6
4572	35.7	35.9	19.7	6.2	1.2	1.3

^aUncertainties are discussed in the text.

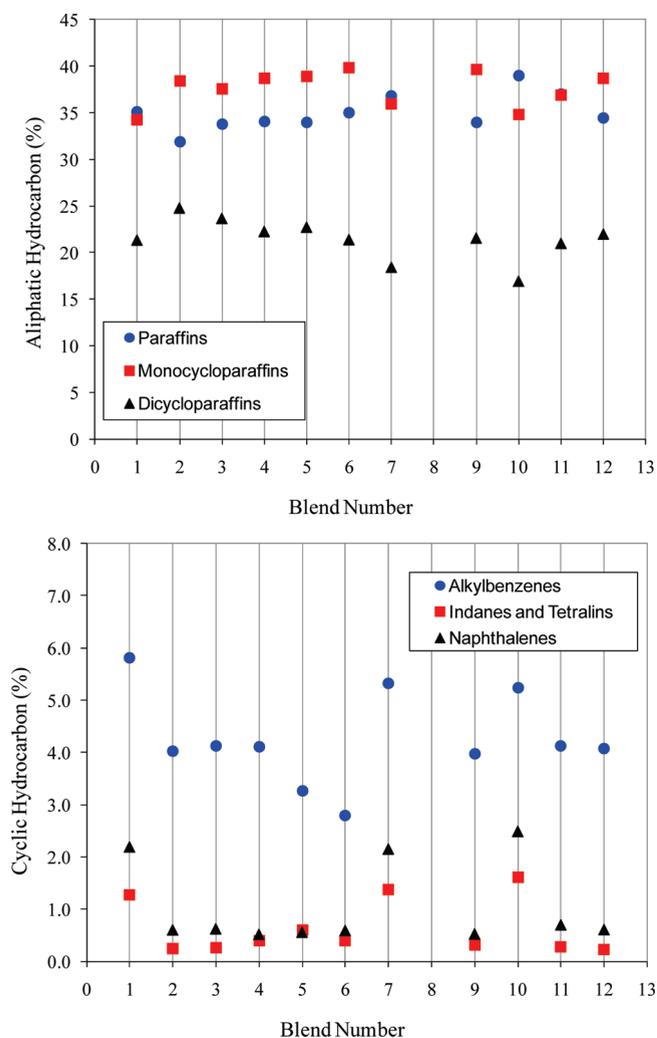


Figure 5. Plots showing the distribution of chemical families present in the 12 blends of RP-1, as determined by GC–MS and the ASTM 2789 analysis. Blend 12 is the RP-1-4572 blend.

encountered when the actual extent of compositional variability is unknown.

We can return to our comparison with aviation turbine kerosenes in Figure 2, in which we compare the spread of aviation kerosene (Jet-A/JP-8) with the spread of the RP-1 blends that we have measured in this work.^{22,51} These data are presented on the same temperature scale, thus the shaded

areas compare the variability of these two fluids. Figure 2 shows that the difference between the high and low temperatures increases during the distillation for both Jet-A and RP-1. For example, the difference for RP-1's distillation temperatures is 11.1 °C at the 10% distillate volume fraction, 13.2 °C at the 50% distillate volume fraction, and 21.1 °C at the 85% distillate volume fraction. The difference for the Jet-A distillation temperatures is 9.8 °C at the 10% distillate volume fraction, 20.2 °C at the 50% distillate volume fraction, and 30.7 °C at the 85% distillate volume fraction. The variability of both Jet-A and RP-1, as indicated on this figure, is striking.

The distillation curve data for the two currently available RP-2 samples are provided in Table 7. These data are also presented graphically in Figure 3. We also show the prediction of the Refprop model for RP-2. This model was developed from measurements performed on the sample labeled RP-2-EAFB. We again note that the Refprop model represents the behavior of this sample very well, yet failing to capture the variability. In Figure 4, we present the variability with the shading diagram similar to that provided for RP-1. The difference for the RP-2 distillation temperatures is 12.7 °C at the 10% distillate volume fraction, 14.2 °C at the 50% distillate volume fraction, and 12.3 °C at the 85% distillate volume fraction. Although it is difficult to draw conclusions based on only two samples, it appears that the variability of RP-2 is similar to that of Jet-A and RP-1 throughout the distillation. The observed variability is significant and should be investigated further by the examination of orthogonal blends of this fuel as well.

Hydrocarbon Classification. Another analytical technique that complements the above analyses examines the 11 orthogonal blends of RP-1 along with the earlier sample of RP-1 for hydrocarbon types by use of a mass spectrometric classification method similar to that summarized in ASTM D-2789.²⁷ In this method, one uses GC–MS to characterize hydrocarbon samples into six types. The six types or families include the following: paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes (arenes or aromatics), indanes and tetralins (grouped as one classification), and naphthalenes. 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.⁶⁵ The uncertainty of this method and the potential pitfalls were discussed earlier.²⁴ The hydrocarbon classification analysis was done on neat samples from each of

the 12 RP-1 blends. Note that while we often apply this to individual fractions, here that would be too much detail.

The results of the hydrocarbon classification for the 12 RP-1 blends are presented in Table 8 and illustrated in Figure 5. All 12 blends are similar in their hydrocarbon classification and are composed of mostly aliphatic hydrocarbons (~94%) with small amounts of aromatics (~4%). The hydrocarbon classification method is not able to distinguish the variability of the RP-1 samples. The ADC method, which measures the volatility and approximates the vapor liquid equilibrium of a complex mixture, is very capable of distinguishing the variability of the RP-1 samples. The volatility measurement is a sensitive method to evaluate compositional variability because even minor changes in composition can affect the volatility strongly. In fact, we have shown with aviation kerosenes that other properties such as density, speed of sound, heat capacity, and most other thermophysical properties are not sufficiently sensitive enough to be used as a metric for the compositional variability.^{66,67}

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Conclusions

In this paper, we have presented experimental work on 12 blends of RP-1 (11 orthogonal blends specially prepared and a mixture used for model development earlier) and on two samples of RP-2 from different batches made approximately 4 years apart and that were not intended to display variability. The earlier RP-2 sample was used for model development earlier. The results were compared on the basis of detailed compositional analyses and the temperature grid measurements with the advanced distillation curve approach. This series of measurements is part of a larger study in which the distillation results and the chemical component analyses will be augmented by measurements of density, viscosity, and speed of sound and a comparison with thermodynamic and transport model predictions. The observations made on the basis of the distillation results and the component analyses are nevertheless of concern; it is clear that the model developed to represent “RP-1” may not in fact represent (1) all the variability that might be expected and (2) the correct change in volatility at higher temperatures. This conclusion would not have been realized without these measurements on the 11 new blends. We will likely have to develop a more general model and potentially make other revisions.

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