COMPARATIVE EVALUATION OF SEMI-SYNTHETIC JET FUELS

Addendum: Further Analysis of Hydrocarbons and Trace Materials To Support Dxxxx

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INTRODUCTION

Further analyses of the composition of the five synthetic paraffinic kerosenes (SPK) have been requested to support the proposed definition of SPK in the new ASTM Dxxxx Specification for Aviation Turbine Fuels Containing Synthesized Hydrocarbons, hereafter termed Dxxxx. Specifically, Table A1-2 of Dxxxx provides limits on the composition as provided here in Table 1.

Table 1. Other Detailed Requirements
(reproduced from Dxxxx Table A1-2)

Property	Limit		Test Method
Hydrocarbon Composition			
Cycloparaffins, mass %	max	15	D2425
Aromatics, mass %	max	0.5	D2425
Paraffins, mass %		Report	D2425
Carbon and hydrogen, mass %	min	99.5	D5291
Non-Hydrocarbon Composition			
Nitrogen, mg/kg	max	2	D4629
Water, mg/kg	max	75	D6304
Sulfur, mg/kg	max	15	D5453
Sulfur, mass %	max	0.0015	D2622
Metals (Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, P, Pb, Pd, Pt, Sn, Sr, Ti, V, Zn), mg/kg	max	0.1 per metal	UOP 389
Halogens, mg/kg	max	1	D7359

Of these, only sulfur and metals were reported in the original report evaluating the five synthetic paraffinic kerosenes (SPK). A different method, D4294, was used to analyze sulfur in the S-8, a method that is not sufficiently sensitive.

In the analysis for metals, the method used for the Shell GTL was not sufficiently sensitive, and the analysis of the Sasol IPK was incomplete. A new, more sensitive method has been recommended and proposed in the draft of Dxxxx. Also, several catalyst metals were added to the list specifically to address refinery operations. It should be noted that lithium was inadvertently left off of the slate of metals listed in Table A1-2 of Dxxxx. The engine OEMs have verified that lithium is a metal of concern and should be included. Discussions with UOP revealed that lithium can and will be included in the UOP389 method.

Nitrogen, water content, and halogens were not included in the original evaluation.

During the development of Dxxxx Table A1-2, there had been concern about the adequacy of method D2425 for analyzing low levels of aromatics in SPK type fuels. Two-dimensional gas chromatography (GCxGC) was suggested as a method against which to verify the D2425 results.

OBJECTIVE

This Addendum is provided in response to a request to reanalyze the five SPK fuels for the compositional properties listed in Table 1 to provide the following support of the ballot for Dxxxx:

1. Provide data on trace materials from sufficiently sensitive analyses common to all SPKs
2. Support the choice of method of analysis for hydrocarbons in the approval protocol
3. Provide a data base on trace materials for comparison of other alternative fuels and for management of change

NEW DATA

Table 2 presents the new compositional data on the same five SPK fuels previously evaluated.

All five fuels met the proposed limits for hydrocarbon analysis using ASTM D2425. Cyclo-paraffins were found in all five fuels; S-8 had the highest concentration at 9.0 m%. Aromatics were detected only in the Sasol GTL-2 fuel; the concentration of 0.3 m% was less than the proposed limit of 0.5 m%. In all five SPKs, the total paraffins, i.e., normal, iso-, and cyclo-, exceeded 99.5 m%.

The hydrogen and carbon analyses by D5291 confirmed that the five SPKs were at least 99.5 m% hydrocarbon as required.

Analyses were conducted for twenty-one metals. The level of detection varied with the individual metals, but all detection levels were below the proposed limit of 0.1 mg/kg. For the majority of metals, the detection level was 0.02 mg/kg or less; 0.07 mg/kg was the highest detection level. With only few exceptions, all of the metals were below the level of detection in all five fuels. Traces of calcium were found in all the fuels except the Shell GTL, aluminum was found in the two Sasol GTLs, and iron was found in the S-8 and Sasol GTL-1 samples. In all of these exceptions, the level was significantly below the proposed limit of 0.1 mg/kg.

The sulfur content in all five SPKS was less than 1 mg/kg, far less than the proposed limit of 15 mg/kg.

Nitrogen content was found to be at or below the proposed level of 2.0 mg/kg in all five fuels. The high JFTOT breakpoints of these fuels, as reported in the main report, verify that these levels of nitrogen will not affect the stability of SPK.

Water content ranged from 22 to 40 mg/kg, significantly less than the proposed limit of 75 mg/kg.

The method for halogens detects only fluorine and chlorine; the limit of detection for each is 0.1 mg/km, significantly lower than the proposed limit for halogens in Dxxxx of 1 mg/kg. Analysis for fluorine and chlorine are considered sufficient for “halogens” because their acids are commonly used in refinery processes, e.g., alkylation, whereas bromine and iodine are not.

Table 2. Compositional Analysis of Five SPK Fuels Compared to Proposed Dxxxx Limits

Property	Test Method	Proposed Dxxxx Limit	SPK Fuel				
			Sasol IPK	S-8	Shell GTL	Sasol GTL-1	Sasol GTL-2
Hydrocarbon Composition, mass %							
Aromatics	D2425	≤ 0.5	0.0	0.0	0.0	0.0	0.3
Cycloparaffins	D2425	≤ 15	2.6	9.0	4.0	2.6	7.7
Iso + n-paraffins[1]	D2425	report	97.4	91.0	96.0	97.4	92.0
Total paraffins[2]	D2425		100.0	100.0	100.0	100.0	99.7
Hydrogen and Carbon Content, mass %							
Hydrogen[2]	D5291		84.33	83.99	85.00	84.45	84.69
Carbon[2]	D5291		15.38	15.58	15.71	15.40	15.50
Hydrogen + Carbon	D5291	≥ 99.5	99.71	99.57	100.71	99.85	100.19
Non-Hydrocarbon Composition, mg/kg							
Nitrogen	D4629	≤ 2	2	<1	1	<1	2
Water	D6304	≤ 75	25	22	28	40	32
Sulfur	D5453	≤ 15	0.7	0.6	0.6	0.6	0.6
Halogens, total							
Chlorine	D7359	≤ 0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fluorine	D7359	≤ 0.1	0.1	<0.1	0.1	<0.1	<0.1
Metals Analysis, mg/kg							
Al (aluminum)	UOP389	≤ 0.1	<0.05	<0.05	<0.05	0.05	0.06
Ca (calcium)	UOP389	≤ 0.1	0.003	0.013	<0.003	0.009	0.039
Co (cobalt)	UOP389	≤ 0.1	<0.02	<0.02	<0.02	<0.02	<0.02
Cr (chromium)	UOP389	≤ 0.1	<0.02	<0.02	<0.02	<0.02	<0.02
Cu (copper)	UOP389	≤ 0.1	<0.02	<0.02	<0.02	<0.02	<0.02
Fe (iron)	UOP389	≤ 0.1	<0.02	0.02	<0.02	0.04	<0.02
K (potassium)	UOP389	≤ 0.1	<0.07	<0.07	<0.07	<0.07	<0.07
Li (lithium)	UOP839	≤ 0.1	<0.01	<0.01	<0.01	<0.01	<0.01
Mg (magnesium)	UOP389	≤ 0.1	<0.01	<0.01	<0.01	<0.01	<0.01
Mn (manganese)	UOP389	≤ 0.1	<0.02	<0.02	<0.02	<0.02	<0.02
Mo (molybdenum)	UOP389	≤ 0.1	<0.02	<0.02	<0.02	<0.02	<0.02
Na (sodium)	UOP389	≤ 0.1	<0.07	<0.07	<0.07	<0.07	<0.07
Ni (nickel)	UOP389	≤ 0.1	<0.02	<0.02	<0.02	<0.02	<0.02
P (phosphorus)	UOP389	≤ 0.1	<0.05	<0.05	<0.05	<0.05	<0.05
Pb (lead)	UOP389	≤ 0.1	<0.02	<0.02	<0.02	<0.02	<0.02
Pd (palladium)	UOP389	≤ 0.1	<0.02	<0.02	<0.02	<0.02	<0.02
Pt (platinum)	UOP389	≤ 0.1	<0.02	<0.02	<0.02	<0.02	<0.02
Sn (tin)	UOP389	≤ 0.1	<0.04	<0.04	<0.04	<0.04	<0.04
Sr (strontium)	UOP389	≤ 0.1	<0.005	<0.005	<0.005	<0.005	<0.005
Ti (titanium)	UOP389	≤ 0.1	<0.03	<0.03	<0.03	<0.03	<0.03
V (vanadium)	UOP389	≤ 0.1	<0.03	<0.03	<0.03	<0.03	<0.03
Zn (zinc)	UOP389	≤ 0.1	<0.05	<0.05	<0.05	<0.05	<0.05

Notes: 1. Termed "paraffins" in draft of Dxxxx; assumed to mean iso- plus normal paraffins from data provided
2. Not a part of the draft of Dxxxx; included here for information purposes and clarity

To address the questions raised concerning the adequacy of D2425 to measure low concentrations of aromatics, i.e., less than 0.5 m%, in paraffinic kerosene, four of the five SPKs were analyzed by two-dimensional gas chromatography, GCxGC, for composition by

hydrocarbon family. Table 3 presents the total concentrations of the aromatics, cyclo-paraffins, and iso- plus n-paraffins for the SPK fuels except for the S-8 for which GCxGC analysis has not been conducted. While GCxGC produces results for each family by carbon number, only the total is needed for comparison to the D2425 data listed in Table 2. The analyses of the three Sasol SPKs were provided by Sasol, and the analysis of the Shell GTL was provided by Shell. Figure 1 compares the results of the two methods for the four fuels analyzed by GCxGC. Both methods detected 0.3 m% aromatics in the sample of Sasol GTL-2. Although D2425 did not detect aromatics in Sasol GTL-1, the concentration detected by GCxGC was only 0.045 m%, so the agreement is still very good. Neither method detected aromatics in the other two fuels.

Table 3. Hydrocarbon Composition of SPK Fuels by GCxGC Methodology

Hydrocarbon Family	Sasol IPK	S-8	Shell GTL	Sasol GTL-1	Sasol GTL-2
Aromatics, m%	0	N.A.	0	0.045	0.3
Cycloparaffins, m%	7.32	N.A.	1	0.9	1
Iso- plus n-paraffins, m%	92.34	N.A.	98.9	98.9	98.7
Total paraffins, m%	99.66	N.A.	99.9	99.8	99.7

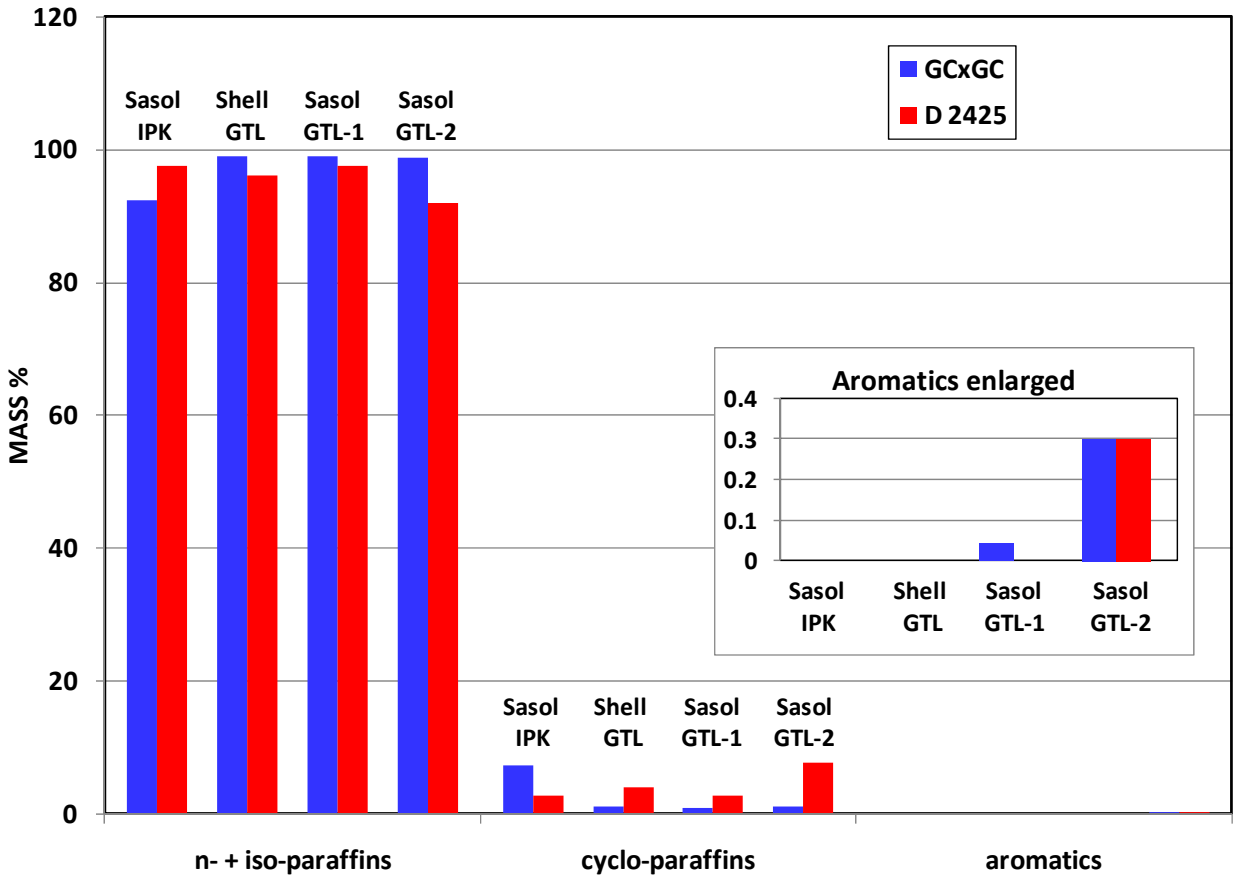

Figure 1. Comparison of D2425 and GCxGC Analyses of Hydrocarbons in SPKs

SUMMARY AND CONCLUSIONS

Additional analyses of the composition of the five available SPK fuels have been conducted to support the proposed requirements of Table A1-2 of Dxxxx. The samples of the fuels were the same as those used in the original analyses with the exception of the Sasol IPK. The sample used for IPK was a recent production sample. The IPK is the only SPK in production and analyses have shown it to be a very consistent product.

The analyses of all five SPKs met all of the proposed limits of Table A1-2.

The UOP 389 method for metals analysis was much more sensitive than the D7111 and D5385 methods used in the earlier evaluations, and it is now possible to say unequivocally that all analyzed metals are each less than 0.1 mg/kg in all the SPKs. Data on lithium has been included for completeness. It is recommended that lithium be added to Table A1-2 of Dxxxx to meet the needs of the engine OEMs.

Analysis of fluorine and chlorine are considered sufficient for halogen analysis because they are commonly used in some refining processes whereas bromine and iodine are not.

The hydrocarbon analysis for aromatics by D2425 was confirmed by the GCxGC analysis for the four SPKs analyzed by this method. The Sasol GTL-2 was found to contain 0.3 m% aromatics by both methods. Aromatics were found in only one other fuel by GCxGC at the very low level of 0.045 m%. Based on these results, it would appear that analysis by D2425 will provide an adequate control on aromatics.

Based on these results, it is concluded that the proposed methods and limits for these properties are appropriate for Dxxxx. SPK fuels meeting these limits will be typical of the 5 SPK fuels that have been produced.