FLAMMABILITY, IGNITION AND ELECTROSTATIC PROPERTIES OF NAVY FUELS DERIVED FROM COAL, TAR SANDS AND SHALE OIL

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INTRODUCTION

As part of the coordinated synthetic fuels research and development program of the Navy and other departments of the Department of Defense, National Aeronautic and Space Administration, Energy Research and Development Administration, Maritime Administration, and the Department of the Interior, the Naval Research Laboratory is investigating the flammability and related properties of JP-5 jet fuel derived from sources other than petroleum. NRL has also made a related study on ship propulsion fuels derived from coal, and these studies will be included in the last section of this paper.

Seven samples of turbine fuels from alternate sources were examined in this study, five from coal and one each from tar sands and shale oil. These materials were selected because they had been processed to have properties close to that of JP-5, the Navy's primary jet aircraft fuel. All five coal products were prepared by the Char Oil Energy Development (COED) process, followed by distillation and hydrogenation. The preparation and properties of coal-derived jet fuels are described in a Sun Oil Company report (1). Shale crude oil, made by the Paraho retort process, was converted to jet fuel (and other military fuels) by delayed coking, distillation, and hydrogenation (2). The tar sands fuel was produced by the Great Canadian Oil Sands Company (3). More details concerning the preparation of these fuels will be given in another paper of this Symposium (4). Two conventional JP-5 fuel samples (from petroleum) were included in the study for comparison. All of the JP-5 samples were supposed to meet the requirements of the military specifications of jet fuel (5), but some were not met.

FLAMMABILITY AND IGNITION PROPERTIES OF JP-5 JET FUELS FROM ALTERNATE SOURCES

This portion of the paper is concerned with the flammability and related properties of alternate jet fuels. Additional properties were also investigated and are reported in two other papers of this Symposium (4,6).

Flammability and Ignition Properties - Three flammability properties were included in this study: flash point, flammability index, and autoignition temperature. Flash points were determined by the Pensky-Martens Closed-Cup (PMCC) (7), Tag Closed-Cup (Tag) (8), or Seta Closed-Cup (Setaflash) flash point method (9). Flammability indices at several temperatures were determined by the NRL flame ionization detector method (10,11), and minimum autoignition temperatures (AIT) by ASTM D-2155 (12). Only the PMCC flash point determination is a specification requirement (60°C minimum), although the flammability index at 51.7°C is related to the "Explosiveness" requirement of the specification (5). The flash point and flammability index determinations are important since they are a measure of the tendency of a liquid fuel to form a flammable mixture with air at a given temperature. The significance of autoignition temperature is that it is a measure of the likelihood that spontaneous or autoignition might occur if the fuel contacts a hot surface, such as by leakage onto a steam pipe.

Results - Flammability index, flash point, and autoignition data are shown in Tables I - III. It is seen that the first three fuels in Table I (tar sands, shale oil, and COED 5) did not meet the 60°C minimum flash point (PMCC) requirement of the specification (5). On the other hand, the other coal samples had PMCC flash points which are considerably above that of the specification requirement. As is usually the case for fuels in the JP-5 flash point range, the Tag flash points are lower (average ≈2°) than those obtained by PMCC. Both the flash point and flammability index data for the petroleum JP-5 samples fell within the range found for the alternate fuel samples.

Flammability Index - Flammability index (E) is defined as the ratio of the vapor concentration in air (C, %v/v) to that at the lower flammability limit (L, %v/v), so that E = C/L. Flammability index may be expressed as a decimal or as percent. If E is less than 1 (100%), the vapor-air mixture is nonflammable, and if E is equal to or greater than unity, the mixture is flammable (10). In the case of liquids, the flammability index refers to the vapor-air mixture which is in equilibrium with the liquid at a given temperature. The flammability indices of all the fuels were determined at several temperatures, and are plotted in Figure 1. The flammability indices at 51.7°C (125°F) are shown in Table I. Flammability index, which is a vapor pressure function, has been shown to vary exponentially with temperature for hydrocarbons and their mixtures according to the following relationship (11):

$$\text{Log } E = m/(T\ ^\circ C + 230) + k \qquad 1)$$

where T is temperature (°C), and m and k are constants. As is shown in Figure 1, a plot of Log E vs reciprocal temperature is linear with slope m, and intercept k. Slopes and intercepts are included in the table.

If we let E = 100% in Equation 1, and solve for T, a value is obtained (T_E) which is related to flash point. T_E is that temperature at which the concentration of the vapor in equilibrium with the liquid fuel is equal to that at the lower flammability limit. T_E may also be obtained graphically by noting the temperatures at which the curves intersect the horizontal line at %E = 100%. In Figure 1, the small triangles are actual flash points (Tag) and it is seen that they lie close to the intersection points. A comparison of T_E and Tag flash points are shown in the table. The slopes (m) and intercepts (k), as in the case of flammability index, are dependent on fuel composition. In general, the slopes (negative) of the alternate fuel samples (1554 to 1906) are lower than that of the petroleum samples (1917 and 1994). Similarly, the intercepts (5.46 to 6.14) are lower than that of the petroleum fuels (6.65 and 6.84), so that it can be concluded that there are differences in composition between the alternate fuels and that of the petroleum fuel. Previous unpublished NRL work with six conventional JP-5 fuels gave a range of 1917 to 2076 (average = 1987) for slopes, and 6.65 to 7.19 (average = 6.88) for the intercepts.

Effect of Fuel System Icing Inhibitor Additive on Flash Point - Ethylene glycol monomethyl ether (EGME) is presently used as a fuel system icing inhibitor additive in JP-5 (5). It has been shown that at use concentrations (0.1 to 0.15%), EGME additive lowers the flash point of JP-5 3 to 4°C (13). This effect complicates the burden on refiners in meeting the minum flash point requirement of the specification. The question of whether this problem might also exist with JP-5 from alternate sources was also investigated and results are shown in Table II. A pure hydrocarbon is also included in the table for comparison. It will be seen in the table that the flash point depression at 0.15% EGME ranges from 2 to 5°C with the greatest effects occurring at the higher flash points. From this data, we conclude that the problem of flash point depression by EGME for petroleum fuels also exists for the fuels from alternate sources.

Autoignition Temperatures - Autoignition temperatures (AIT) for the JP-5 fuels are shown in Table III. The AIT data by the standard ASTM method (12) are shown under "hot flames" in the table. These temperatures represent the lowest temperatures at which visible ignition occurs in the standard 200-ml ASTM flask without the aid of an external ignition source. Observations were made in total darkness and with the aid of a thermocouple-recorder arrangement for monitoring the internal gas temperature inside of the flask. Cool flame ignitions were observed in the case of four of the coal samples, and one of the petroleum samples. It will be noted that the cool flame ignitions occurred at lower temperatures than that of the hot flame ignitions. From the point of view of safety, it is desirable to be able to determine a true minimum AIT. Since cool flames are precursors of hot flame ignitions, either type of ignition should be considered as a "positive" ignition. The differences in the table range from 4 to 14°C. If we pay attention to the lower values in all cases (cool flame or hot flame), the AIT values for the alternate fuel samples range from 241 to 247°C and these values are in the same range as that of the petroleum fuel samples.

Conclusions - The tar sands, shale oil, and one of the coal samples had flash points which were below that of the 60°C specification requirement. The remaining fuels from coal had flash points which were higher than specification requirements and also higher than those of the usual run of petroleum JP-5.

Flammability indices and flammability-temperature relationships of the alternate fuels were also measured, and found to differ somewhat from that of the petroleum fuels. Autoignition temperatures of the alternate fuels were similar to that of petroleum derived fuels.

In general, the flammability properties fo the JP-5 from alternate sources were not significantly different from that of JP-5 from petroleum. If the alternate fuels were refined to more closely agree with the flash point requirement, the other observed differences would probably be diminished.

ELECTROSTATIC PROPERTIES OF JP-5 JET FUELS FROM ALTERNATE SOURCES

Although neither electrical conductivity nor charging tendency are part of the present specifications for turbine fuels, both properties are useful in predicting whether an electrostatic ignition hazard exists in handling such products. Therefore these properties were measured on the alternate fuels to determine if these fuels posed a lesser or greater hazard than their petroleum-derived counterparts.

Determination of Electrostatic Properties - Electrical conductivity was determined by the ASTM method (14) and charging tendency with the EXXON Mini-Static Tester (15). The latter method measures the amount of electrical charge generated by flowing a fuel sample through a paper filter. Since the two methods were used to evaluate samples taken in a recent survey of jet fuels from ten commercial airports and three military bases (16), the results of the present study can be directly related to actual field experience.

Results and Conclusions - The electrical conductivity and charging tendency of the JP-5 samples derived from coal, tar sands and shale are summarized in Table IV. Conductivity is expressed in terms of picosiemens/meter (pS/m) and charging tendency as the density of charge in the fuel in microcoulombs/meter^3 ($\mu C/m^3$). The results of the present study are compared with the data obtained for various turbine fuels (Jet A, JP-4 and JP-5) in Figures 2 and 3. The data show that, with the exception of the JP-5 from shale oil, the conductivity and charging tendency of the alternate fuels are well within the ranges of the petroleum-derived Jet A samples but somewhat lower than the values obtained for the petroleum-derived JP-4 fuels. Since the total number of JP-5 samples in the fuel conductivity survey was quite small (18 samples from only one Naval Air Station vs 338 samples of Jet A from ten airports), it is better perhaps to restrict the comparison of the present data to the survey data for Jet A.

The JP-5 derived from shale oil was an exception. This fuel was an off-specification product containinga sediment which clogged the filter of the charging tendency apparatus making it impossible to obtain a charge density measurement. After this sample was filtered through a 0.45μ Millipore filter, a charge density of 7035

$\mu C/m^3$ was obtained, a value somewhat above the maximum observed in the study on petroleum derived jet fuels. However, in this case, the high charge density is of no concern since the conductivity of the JP-5 fuel derived from shale oil was sufficiently high (215 pS/m) that most of the charge generated in the filter decays in less than one second and hence does not constitute a hazard. In view of the rather low conductivities and charging tendencies exhibited by the other alternate fuels, no greater electrostatic hazard is envisoned in the handling of these products than their petroleum derived counterparts.

FLAMMABILITY AND IGNITION PROPERTIES OF SHIP PROPULSION FUELS DERIVED FROM COAL

The Navy has also been exploring the feasibility of burning fuel oil derived from coal in ships' propulsion systems (17). One fuel for this purpose was prepared from Illinois No. 6 coal by the COED process at FMC Corporation, Princeton, New Jersey under a contract with the Office of Coal Research, Department of the Interior (17). The crude COED product possessed a wide boiling range and, hence, a low flash point, $14^{o}C$. Therefore this product was distilled to remove the light fractions (17) and raise the flash point above $60^{o}C$, the minimum acceptable for ship propulsion fuel (18-20).

Results and Conclusions - The flammability and ignition properties of the processed COED fuel (SP-4) are compared in Table V with the properties of three petroleum derived fuels. These latter fuels include the current Navy ship propulsion fuel, Diesel Fuel Marine (DFM), and two obsolete types, Navy Distillate (ND) and Navy Special Fuel Oil (NSFO). The flash point of the COED fuel is slightly lower than that of the petroleum fuels and the flammability index is seen to be near the average of the three petroleum fuels. The autoignition temperature was somewhat higher than that of the three petroleum fuels.

A plot of flammability index vs reciprocal temperature for the processed COED fuel along with similar plots for typical petroleum derived ship fuels are shown in Figure 4. As in the case of the JP-5 data (Figure 1), the graphs are linear and intersect the horizontal E = 100% line relatively close to the flash point temperature.

The single sample of processed COED ship propulsion fuel (SP-4) which was investigated is not necessarily representative of synthetic fuel derived from coal. However, the data on this sample indicate that coal derived fuels will be satisfactory for ship propulsion use, at least from the viewpoint of flammability hazards.

SUMMARY AND CONCLUSIONS

The flammability, ignition, and electrostatic properties of JP-5 jet fuel from alternate sources and a ship propulsion fuel derived from coal were investigated. Flash points, flammability indices, autoignition temperatures, electrical conductivities and electrostatic charging tendencies were measured. In general, the properties of the alternate fuels were not significantly different from similar fuels derived from petroleum. These differences could probably be diminished by altering the production process and by observing care in meeting specification requirements.

ACKNOWLEDGMENT

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Table I - Flammability Index vs Temperature and Flash Point for JP-5 From Alternate Sources

Source	Flam. Index at 51.7°C (%)	Slope[a] ($^-$m)	Intercept[a] (k)	T_E(°C)[b]	Flash Point (°C)	
					Tag[c]	PMCC[d]
Tar sands	91.0	1554	5.48	54	55	57
Shale oil	87.8	1559	5.46	56	57	58
COED 5	86.0	1710	5.97	56	58	59
COED 3	31.5	-	-	-	76	77
COED 4	30.2	1828	5.97	76	76	78
COED 1	22.8	-	-	-	78	79
COED 2	21.9	1906	6.14	81	79	83
Petroleum 1	56.0	1994	6.84	62	61	62
Petroleum 2	62.0	1917	6.65	58	61	65

a - $\text{Log } E = m/(T^\circ C + 230) + k$.
b - $T_E(^\circ C) = -m/k - 230$.
c - ASTM D-56.
d - ASTM D-93

Table II - Effect of EGME* Icing Inhibitor Additive on Flash Points of JP-5 From Alternate Sources

Source	Flash Point (°C)**					Flash Point Depression (0.15% EGME) (°C)
	%EGME					
	0	0.10	0.15	0.30	0.50%	
Tar Sands	55	54	53	--	49	2
Shale Oil	57	-	54	53	-	3
COED 5	58	-	55	53	-	3
COED 3	76	73	71	--	62	5
COED 4	76	72	71	--	64	5
COED 1	78	74	73	--	63	5
COED 2	79	76	74	--	65	5
Petroleum 2	61	58	57	--	52	4
n-Undecane	66	63	62	--	56	4
EGME	41					

*Ethylene glycol monomethyl ether
** Tag Closed Cup, ASTM D-56

Table III - Autoignition Temperatures of JP-5 from Alternate Sources

SOURCE	Autoignition Temperature (°C)		
	Hot Flame*	Cool Flame**	Difference
Shale oil	241	-	-
Tar sands	248	-	-
COED 4	248	-	-
COED 1	252	248	4
COED 3	253	243	10
COED 5	253	249	4
COED 2	254	245	9
Petroleum 1	243	-	-
Petroleum 2	254	240	14

*ASTM D-2155

** "Spike" in temperature-time trace and/or an observed cool flame.

Table IV - Electrostatic Properties of JP-5 Fuels from Alternate Sources

SOURCE	Conductivity, pS/m	Charging Tendency, μC/m³
Tar sands	0.271	170
COED 1	8.49	1274
COED 2	0.964	418
COED 3	0.371	575
COED 4	0.288	584
COED 5	4.55	2705
Shale oil, as received	246	(*)
Shale oil, filtered thru 0.45μ millipore	215	7035

*Fuel contained a sediment which clogged the filter of the charging tendency apparatus.

Table V - Average Flammability and Ignition Properties of Ship Propulsion Fuels

Fuel	Flash Point (°C)*	Flammability Index (E_s%) **	Autoignition Temperature (°C)
Diesel Fuel, Marine(DFM)	79	36	240
Navy Distillate (ND) *	79	41	238
Navy Special Fuel Oil** (NSFO)	85	30	259
Processed COED Fuel (SP-4)	73	35	266

*Pensky-Martens closed cup.

** %E at 51.7° C

***Single sample.

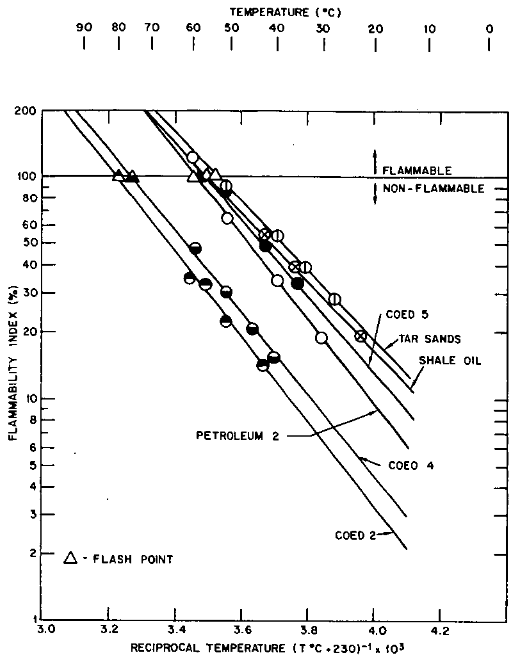

Figure 1. Flammability Index vs Temperature for Jet Fuels

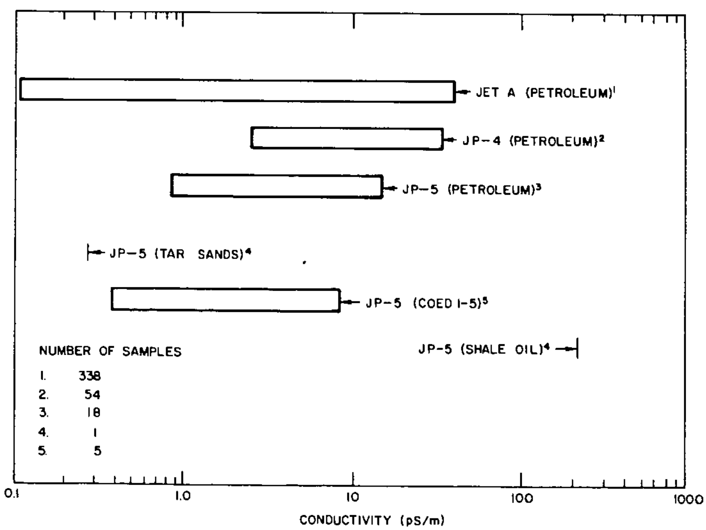

Figure 2. Ranges of Electrical Conductivities of Jet Fuels

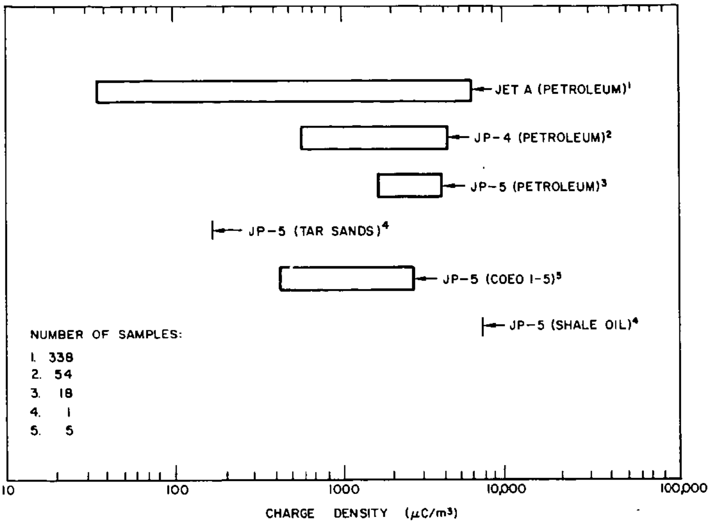

Figure 3 Ranges of Electrostatic Charge Densities of Jet Fuels

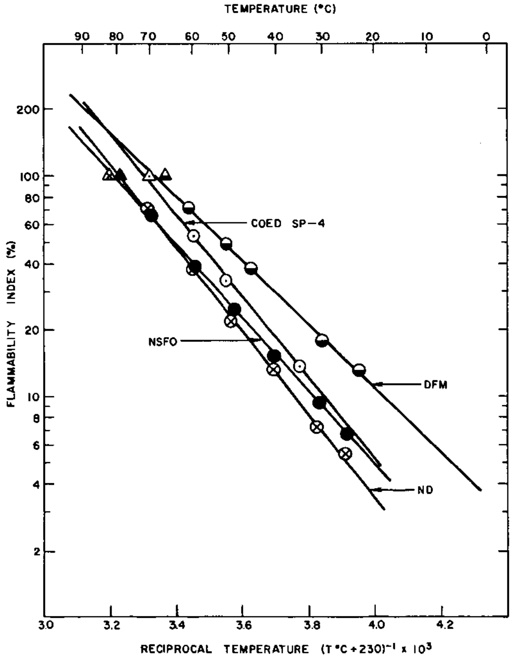

Figure 4 Flammability Index vs Temperature for Ship Propulsion Fuels