Flash Point and Chemical Composition of Aviation Kerosene (Jet A)

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Abstract

The relationship between chemical composition, flash point, and ignition energy was examined for eight samples of aviation kerosene (Jet A) with flash points between 29°C (84°F) and 74°C (165°F). We report the results of liquid characterization by two different laboratories. We use the results of headspace gas chromatography carried out by Woodrow and Seiber to characterize the vapor composition at liquid mass loading fractions of 3 and 400 kg/m^3. The composition data were analyzed to obtain analytical representations of vapor pressure and average molar mass as a function of temperature for each flash point fuel. The relationship between composition and flash point is examined by using two prediction methods. The first method is based on the notion of a critical value of fuel-air mass ratio at the flammability limit. The second method is based on Le Chatelier's rule for flammability limits. Both methods show a reasonable correlation between measured and predicted flash point. The relationship between flash point and ignition temperature threshold at a fixed spark ignition energy was examined for four fuels. A linear correlation was obtained for an ignition energy of 0.3 J. The effect of fuel weathering was examined by determining the flashpoints of seven fuel samples obtained from flight tests. The flash point increased about 8°C for fuel that had been exposed to 5 take-off, cruise, and landing cycles.

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1 Introduction

This study is a portion of the research program on aviation kerosene (Jet A) explosion hazards carried out by the Explosion Dynamics Laboratory at the California Institute of Technology (Caltech). This research was sponsored by the National Transportation Safety Board (NTSB) as part of the investigation into the TWA 800 accident on July 17, 1996.

Following this accident, the NTSB made safety recommendations (NTSB, 1996) aimed at reducing airplane fuel tank flammability and explosion hazard. These recommendations include minimizing potential ignition sources, reducing tank temperature, inerting the ullage, and possibly raising the fuel flash point. In response to these recommendations, the FAA (FAA, 1997) has asked the aviation industry (through the Aviation Regulatory Action Committee or ARAC) to consider a wide range of issues related to fuel tank flammability. The ARAC study (ARAC, 1998) included considering fuel flash point modification. The ARAC group concluded that a flash point increase to at least 140°F would be required to reduce the exposure level in center tanks to the level experienced now by wing tanks. Subsequently, the FAA has proposed new rules (FAA, 1999) governing fuel tank systems and a review of center fuel tank system design that includes "means to minimize development of flammable vapors in fuel tanks, or means to prevent catastrophic damage if ignition does occur."

As part of the ARAC study, fuel refiners considered the costs of various increments in flash point. However, this study was carried out in the absence of data on the effectiveness of changing flash point in reducing fuel tank flammability. There is an implicit assumption that an increase in flash point is, degree for degree, equivalent to decreasing the fuel temperature. There is no test data or analysis that supports this assumption. Indeed, the relationship between composition, flash point, and spark- or thermal-ignition hazard for a complex fuel such as aviation kerosene has never been explored in detail. This was the motivation for the present study.

The difficulty in establishing a relationship between fuel composition, flash point, and spark ignition hazard for a fuel like Jet A is due to a number of factors. Aviation kerosene fuels are complex mixtures, containing hundreds of species in varying amounts depending on the crude oil, refinement process and the time of the year. The vapor composition is different from that of the liquid and depends strongly on the temperature and to a lesser extent, the amount of liquid fuel in the fuel tank as measured by the mass loading, the ratio of liquid mass to total tank volume. Finally, the explosion hazard of fuel vapors depends on the nature of the ignition source. The petroleum industry and fuel safety analysts often rely on the measured flash point to rank the explosion hazards of different fuels. The relationship of flash point to spark or hot surface ignition is largerly unexplored for multi-component fuels. Moreover, flash point is an empirical fuel property specific to a particular pressure and mass loading.

The study reported here is a first step in understanding the relationship between the vapor composition of a particular set of Jet A fuels and flash point. The relationship between flash point and ignition energy is also briefly reported; details of the ignition

energy studies are given in Shepherd et al. (1998) and Lee and Shepherd (1999).

1.1 Outline of This Study

The present study is based on eight fuels prepared by the ARCO Products Company (ARCO). Starting from a production batch of Jet A, flash point 114°F (45.6°C), ARCO created by distillation and mixing seven other fuels with a range of flash points between 84°F (29°C) and 165°F (74°C). ARCO characterized the flash points and performed an analysis of the liquid properties of each fuel.

The chemical analysis of the fuel liquid and vapor was performed by the Center for Environmental Sciences and Engineering, University of Nevada in Reno, NV (UNR). Headspace gas chromatography (GC) was used to determine the partial pressure of fuel vapor components from C_5 to C_{13} at three temperatures (40, 50 and 60°C) and two mass-volume ratios (3 and 400 kg/m^3).

Caltech also carried out flash point measurements on each fuel type, physical vapor pressure measurements on the base fuel, and analyzed the headspace GC results. Spark ignition measurements were carried out on a subset of the fuels. Empirical theories of the flammability limit were used to correlate GC data, flash points and spark ignition limits.

2 Fuels and Characterization

ARCO (DeJovine, 1998) provided Caltech with samples of Jet A that had been processed in order to obtain a range of flash points between 84°F (29°C) and 165°F. ARCO performed standardized tests on the fuel and chromatography (PIANO[1] analysis) to characterize the liquid fuel.

2.1 Fuel Preparation

The fuels were prepared by ARCO from a common feed stock derived from their production of commercial Jet A. Successive amounts of light ends were removed by distillation from the base fuel to create higher flash point mixtures. A small amount of the overhead was added to the base fuel to reduce the flash point to 85°F. The distillation column and procedure used are described in ASTM's standard test method D2892.

The base fuel (Jet A) was distilled and the first 2.5 weight percent of the overhead (OH) was collected (the distillate is designated 2.5 wt% OH). The lower flash point (84-87 °F) fuel was created by mixing 91 wt% of base fuel with 9 wt% of the overhead (2.5 wt% OH). The resulting fuel blend is designated by the distillate name "2.5 wt% OH" in this report. The higher flash point fuels were created by distilling the base fuel and retaining only a fraction of the bottom of the distillation (Btm). These fuels are designated according to the fraction of the initial fuel weight used to create them. A

[1]Paraffins, Iso-paraffins, Aromatics, Napthalenes, Olefins

value of x in the designation "x wt% Btm" means that the initial $100 - x$ wt% distillate was removed from that lot. In increasing order of flash points, the fuels are: one lot of base Jet A enriched with 9 wt% of light hydrocarbons (2.5 wt% OH), one lot of Jet A (base fuel), and six lots of concentrated heavy hydrocarbons from the mixture base jet, ranging from the lowest in molar mass (97.5 wt% Btm) to the highest (85 wt% Btm).

2.2 Liquid Fuel Characterization

ARCO characterized the composition of the liquid fuel using the PIANO method and the same fuels were analyzed by UNR using gas chromatograhic methods and comparison with reference hydrocarbons. In addition, ARCO carried out all the tests called for in the ASTM D1665 specification of Jet A and demonstrated that these fuels either met or only slightly deviated from the requirements in all tests.

2.2.1 ARCO Liquid Analysis

PIANO stands for Paraffins (P), Iso-paraffins (I), Aromatics (A), Naphthenes (N), and Olefins (O). About 1 microliter or less of liquid sample is injected into a 100-meter GC column with about 200:1 split ratio. A flame ionization detector and retention time library is used to identify compounds with a carbon number up to 14. This method is based on ASTM test method D 5134-92 but uses a 100-meter capillary column instead of a 50-meter column. The PIANO method is mainly used for gasoline-type samples, which is why it is limited to compounds with carbon numbers less than 14. Any C15 compounds or heavier are reported as unknown. That is the main reason why 50% of the Jet A samples are reported as unknown, since Jet A is much heavier than gasoline. GC-MS studies at Caltech identified compounds with up to C20 in similar flash point Jet A samples (Shepherd et al., 1997) as did UNR in their study.

2.2.2 UNR Liquid Analysis

The same fuels were analyzed at UNR (Woodrow, 2000) by injecting the neat liquid into a gas chromatograph and using a flame ionization detector to determine retention times for compounds grouped by the number of carbon atoms. The GC was calibrated against a mixed hydrocarbon standard with between 5 and 20 carbon atoms and the data was analyzed as described further below in Section 2.4. This analysis method does not discriminate between different types of molecules (alkanes vs. aromatics, etc.) but does have the advantage that essentially all of the liquid is quantified, unlike the PIANO method that did not identify about 50% of the mass. The results are given in Fig. 3. The average molar mass of the liquid was computed from these measurements to be between 169 g/mol (30°C flash point) and 181 g/mol (73°C flash point). Raoult's law (see Section 4) and pure component vapor pressures were used to estimate vapor compositions and molar masses by Woodrow (2000). These estimates are in reasonable agreement with the direct headspace GC measurements of vapor properties.

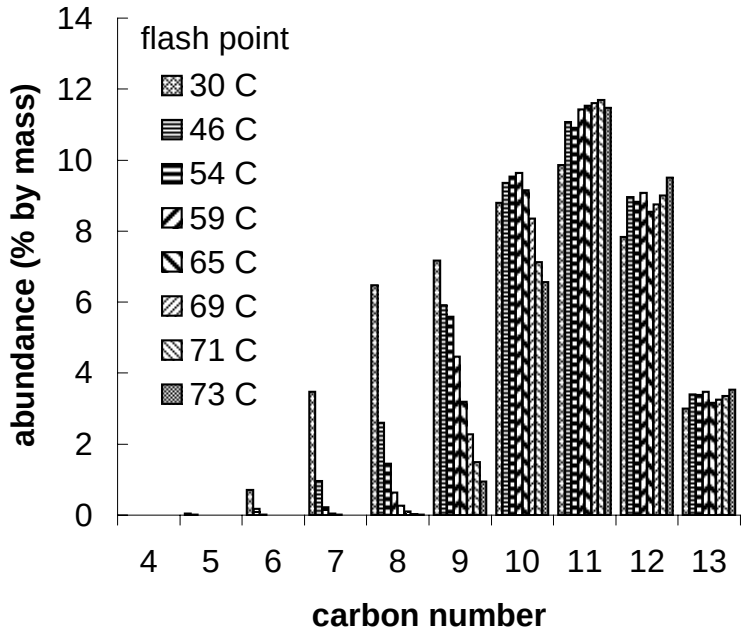

Figure 1: The liquid composition for the eight ARCO fuels measured using the PIANO method by ARCO (DeJovine, 1998). Carbon subsections by mass percentage; about 50% of the mass is not quantified.

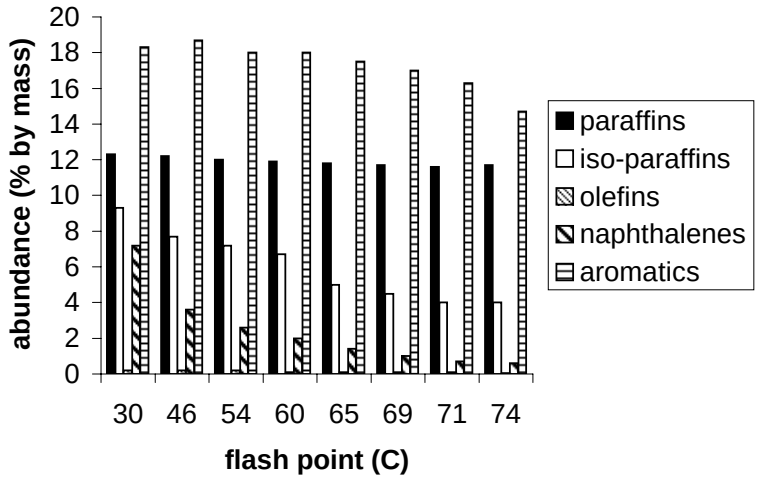

Figure 2: The liquid composition for the eight ARCO fuels measured using the PIANO method by ARCO (DeJovine, 1998). Fractions of various molecular types; about 50% of the mass is not quantified.

2.3 Flash Point

The fuel flash points were measured by ARCO and Caltech with the Tag closed-cup apparatus and the results are given in Table 1 and Fig. 4. The flash point of a fuel is not

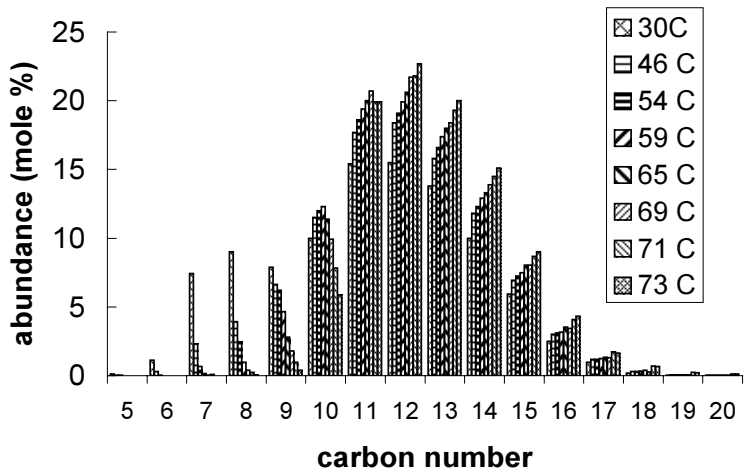

Figure 3: The liquid composition for the eight ARCO fuels measured by UNR (Woodrow, 2000).

a fundamental property but rather the result of a standardized test carried out at one specific fuel loading and atmospheric pressure.

The most commonly-used standard test method used to measure the flash points of the fuels is designated D56 (the tag tester) by the American Society for Testing and Materials (ASTM D56, 1988). The flash point is measured by gradually heating 50 ml of fuel in a container of 130 ml volume. At regular temperature intervals during the heating process, the vapor generated above the liquid in the vessel is put in contact with a small flame for one second. The temperature at which the first ignition occurs is the "flash point". Note that continuous combustion is not established but only a transient burn or "flash". As discussed in the ASTM D56 documentation, the repeatability and reproducibility of this test has been determined experimentally by multiple trials on identical samples. For the temperature range of interest in the present study, the repeatability between successive measurements by the same operator will exceed 1.1°C only in one case out of twenty. The reproducibility between different laboratories is reported to exceed 2.2°C only in one case out of twenty.

In the D56 test, the flash point is measured at a mass-volume ratio of approximately 300 kg/m^3 (slightly less than a half-full container) which can be categorized as a high mass-volume ratio in terms of the flammability of the fuel vapor (Shepherd et al., 1998, Lee and Shepherd, 1999). In this study, flash point and vapor pressure measurements at high mass-volume ratio are used to correlate the flash point with both fuel-air mass ratio and LeChatelier's rule.

Note that there is no accepted methodology for extrapolating a flash point measured by ASTM D56 to other mass loadings and initial pressures. Once we have correlated the flash point with other vapor properties, it may in fact be possible to give a reasonable extension of the flash point notion to other conditions. This is of great interest to aviation safety studies since a variety of fuel tank loadings and altitudes (pressures) are

encountered in the course of a typical transport airplane flight. In the case of the TWA 800 crash, the explosion conditions were a mass-volume ratio of 3 kg/m^3 and an altitude of 14 kft (pressure of 0.585 bar).

Table 1: Fuel flash points.

Fuel sample's descriptive designation	Fuel sample's designation in this report	EDL measured Flash Point °C(°F)	ARCO measured Flash Point °C(°F)
Base Jet A + 2.5 wt% OH	2.5 wt% OH	29.0 (84.2)	30.6 (87)*
Base Jet A	Base Fuel	46.4 (115)	45.6 (114)
Jet Fuel 97.5 wt% Btm	97.5 wt% Btm	54.0 (129)	55.6 (132)
Jet Fuel 95 wt% Btm	95 wt% Btm	59.5 (139)	59.4 (139)
Jet Fuel 92.5 wt% Btm	92.5 wt% Btm	65.0 (149)	64.4 (148)
Jet Fuel 90 wt% Btm	90 wt% Btm	68.9 (156)	70.6 (159)
Jet Fuel 87.5 wt% Btm	87.5 wt% Btm	71.2 (160)	71.1 (160)
Jet Fuel 85 wt% Btm	85 wt% Btm	73.5 (164)	73.9 (165)

*This value was remeasured by ARCO in September 1999

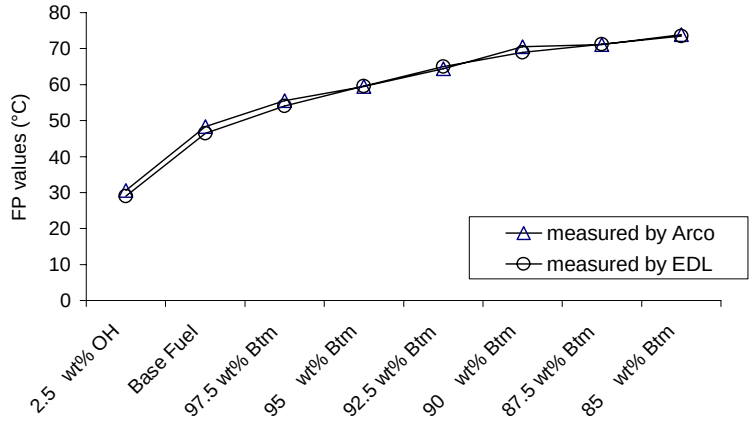

Figure 4: The flash points for the eight ARCO fuels of Table 1 measured at CIT with the Tag closed-cup tester (ASTM D56, 1988) and measured by ARCO (DeJovine, 1998).

2.4 Vapor Gas Chromatography

James E. Woodrow of UNR analyzed the jet fuel vapor and provided the data to Caltech (Woodrow, 2000). A headspace GC method (Woodrow and Seiber, 1997) was used to determine the partial pressures of the individual fuel components and total vapor pressures for the eight fuel samples listed in Table 1. The total vapor pressures were calculated

by assuming a model of jet fuel vapor consisting of just a few n-alkane reference standards, i.e., the jet fuel vapor, a complex mixture of hydrocarbons, was not completely characterized. Measurements were made at 40, 50, and 60°C (104, 122 and 140°F) and at vapor volume-to-liquid ratios (V/L) of 1.2 (half-filled tank; $\sim$ 400 kg/m^3) and of 274 (nearly empty tank; $\sim$ 3 kg/m^3). The method was calibrated using a mixed hydrocarbon standard, which consisted of an equal volume mix of the normal alkanes pentane (C_5H_{12}) through dodecane ($C_{12}H_{26}$) or tridecane ($C_{13}H_{28}$), for some samples. The mixed standard was processed in the same way as the fuel samples. Using the GC retention times of the hydrocarbon standards, the fuel vapor chromatograms were divided into eight subsections (C_5, C_6, C_7, C_8, C_9, C_{10}, C_{11}, C_{12}), sometimes nine (with C_{13}). Each subsection was approximately centered about the retention time of a hydrocarbon standard, using the carbon number for designation. The peak areas in each subsection were summed and treated as single peaks in the vapor density regression equations to calculate subsection vapor densities. The latter were used to calculate subsection partial pressures for the fuel samples. The subsection partial pressures were summed to obtain total vapor pressures for each fuel.

Two sets of data are produced, one for each of the mass-volume ratios (400 kg/m^3 and 3 kg/m^3). In each of the sets, the subsection partial pressure and subsection vapor density are listed at the three temperatures (40, 50 and 60 °C) for each of the components detected in the fuels. The fuels' vapor pressure is then calculated in each case by adding up the subsection partial pressures. The component's subsection mole percent in vapor is calculated as the ratio of the component's partial pressure to the fuel vapor pressure. The part of this data used here consists only of the pressures and the molar mass (Tables 2 and 3).

Table 2: Subsection partial pressure (mbar) of fuel components at three different temperatures. These are headspace gas chromatography results at a V/L ratio equivalent to a half-filled tank (400 kg/m^3). [Source: Woodrow (2000)].

T (°C)	Fuel	C_5H_n	C_6H_n	C_7H_n	C_8H_n	C_9H_n	$C_{10}H_n$	$C_{11}H_n$	$C_{12}H_n$	$C_{13}H_n$	Fuel Vapor Pressure (mbar)	Average Molar Mass (g/mole)
40	2.5wt% OH	1.83	3.24	7.84	4.78	1.56	0.649	0.380	0.148	*	20.4 ± 0.5	103.8
	Base	0.962	0.818	2.20	1.88	1.19	0.745	0.397	0.149	*	8.34 ± 0.11	110.4
	97.5wt% Btm	0.344	0.125	0.568	0.926	1.03	0.799	0.492	0.174	*	4.46 ± 0.06	123.4
	95wt% Btm	0.143	0.048	0.151	0.362	0.682	0.793	0.496	0.164	*	2.84 ± 0.06	132.7
	92.5wt% Btm	0.141	0.002	0.025	0.158	0.400	0.666	0.464	0.165	*	2.02 ± 0.07	137.5
	90wt% Btm	0.100	0.030	0.086	0.136	0.280	0.584	0.501	0.179	*	1.90 ± 0.07	138.0
	87.5wt% Btm	0.107	0.002	0.002	0.024	0.15	0.456	0.500	0.182	*	1.42 ± 0.02	143.5
	85wt% Btm	0.073	**	**	0.010	0.08	0.310	0.485	0.198	*	1.16 ± 0.01	147.4
50	2.5wt% OH	2.50	4.99	11.6	8.51	2.82	1.15	0.666	0.224	*	32.5 ± 0.3	105.1
	Base	1.15	1.16	3.41	3.10	2.01	1.29	0.742	0.223	*	13.1 ± 0.3	112.6
	97.5wt% Btm	0.407	0.142	0.808	1.52	1.71	1.29	0.745	0.264	*	6.89 ± 0.06	124.8
	95wt% Btm	0.161	0.009	0.173	0.559	1.14	1.30	0.764	0.240	*	4.35 ± 0.05	134.6
	92.5wt% Btm	0.147	**	0.036	0.229	0.688	1.26	0.909	0.277	*	3.55 ± 0.15	140.1
	90wt% Btm	0.116	0.040	0.114	0.177	0.435	1.00	0.866	0.262	*	3.01 ± 0.05	140.0
	87.5wt% Btm	0.119	**	**	0.034	0.220	0.728	0.926	0.286	*	2.31 ± 0.11	146.0
	85wt% Btm	0.082	**	**	0.004	0.105	0.516	0.838	0.302	*	1.85 ± 0.03	149.3
60	2.5wt% OH	3.10	6.16	14.7	11.1	4.19	1.77	1.07	0.388	*	42.5 ± 0.9	106.3
	Base	1.46	1.63	4.82	4.46	2.98	1.96	1.13	0.397	*	18.8 ± 0.6	113.8
	97.5wt% Btm	0.512	0.202	1.24	2.32	2.67	2.10	1.33	0.478	0.151	11.0 ± 0.1	127.5
	95wt% Btm	0.163	0.016	0.255	0.825	1.73	2.13	1.39	0.504	0.155	7.17 ± 0.22	138.0
	92.5wt% Btm	0.161	0.003	0.047	0.300	0.955	1.85	1.40	0.503	0.149	5.37 ± 0.13	143.3
	90wt% Btm	0.128	0.053	0.192	0.265	0.657	1.60	1.57	0.651	0.202	5.32 ± 0.17	144.5
	87.5wt% Btm	0.109	0.002	0.002	0.044	0.305	1.12	1.55	0.586	0.187	3.90 ± 0.29	150.7
	85wt% Btm	0.067	0.002	**	0.010	0.136	0.787	1.35	0.527	0.160	3.04 ± 0.22	153.2

* Not measured
** No peak detected

Table 3: Subsection partial pressure (mbar) of fuel component at three different temperatures. These are headspace gas chromatography results at a V/L ratio equivalent to a nearly-empty tank (3 kg/m^3). [Source: Woodrow (2000)].

T (°C)	Fuel	C_5H_n	C_6H_n	C_7H_n	C_8H_n	C_9H_n	$C_{10}H_n$	$C_{11}H_n$	$C_{12}H_n$	$C_{13}H_n$	Fuel Vapor Pressure (mbar)	Average Molar Mass (g/mole)
40	2.5wt% OH	0.309	1.47	5.10	3.56	1.24	0.547	0.341	0.138	*	12.7 ± 0.30	108.6
	Base	0.120	0.398	1.52	1.46	1.01	0.678	0.385	0.150	*	5.72 ± 0.20	117.8
	97.5wt% Btm	0.058	0.069	0.356	0.658	0.775	0.632	0.373	0.162	*	3.08 ± 0.10	128.4
	95wt% Btm	0.031	0.035	0.103	0.266	0.537	0.629	0.426	0.165	*	2.19 ± 0.05	136.3
	92.5wt% Btm	0.020	**	0.016	0.128	0.347	0.558	0.427	0.166	*	1.66 ± 0.05	142.4
	90wt% Btm	0.010	0.013	0.052	0.099	0.211	0.458	0.404	0.151	*	1.40 ± 0.03	142.7
	87.5wt% Btm	0.017	**	0.029	0.042	0.114	0.352	0.400	0.157	*	1.11 ± 0.05	146.6
	85wt% Btm	0.016	**	**	0.035	0.066	0.253	0.401	0.172	*	0.94 ± 0.06	150.0
50	2.5wt% OH	0.331	1.90	7.16	6.02	2.21	0.963	0.582	0.214	*	19.4 ± 0.7	110.4
	Base	0.115	0.461	2.04	2.28	1.64	1.10	0.672	0.228	*	8.54 ± 0.28	119.9
	97.5wt% Btm	0.052	0.060	0.499	1.12	1.37	1.07	0.633	0.233	*	5.04 ± 0.14	129.7
	95wt% Btm	0.014	0.003	0.110	0.412	0.908	1.09	0.684	0.243	*	3.46 ± 0.06	138.3
	92.5wt% Btm	0.008	**	0.022	0.158	0.504	0.964	0.721	0.248	*	2.62 ± 0.04	143.9
	90wt% Btm	0.007	0.015	0.068	0.121	0.317	0.725	0.696	0.230	*	2.18 ± 0.08	144.2
	87.5wt% Btm	0.004	**	**	0.023	0.166	0.560	0.730	0.231	*	1.71 ± 0.11	150.2
	85wt% Btm	0.011	**	**	0.005	0.081	0.428	0.702	0.262	*	1.49 ± 0.01	152.3
60	2.5wt& OH	0.356	2.43	9.36	8.58	3.54	1.63	1.01	0.385	*	27.3 ± 0.8	112.2
	Base	0.126	0.566	2.70	3.22	2.45	1.72	1.04	0.391	*	12.2 ± 0.4	121.5
	97.5wt& Btm	0.044	0.067	0.704	1.66	2.14	1.85	1.23	0.481	0.171	8.35 ± 0.32	133.2
	95wt% Btm	0.009	0.003	0.172	0.616	1.45	1.88	1.31	0.555	0.191	6.19 ± 0.29	141.7
	92.5wt% Btm	0.010	**	0.030	0.236	0.829	1.72	1.42	0.591	0.189	5.02 ± 0.10	147.0
	90wt& Btm	0.007	0.019	0.119	0.200	0.534	1.35	1.35	0.556	0.212	4.35 ± 0.28	147.9
	87.5wt& Btm	0.006	**	**	0.030	0.250	0.986	1.32	0.518	0.176	3.29 ± 0.12	153.2
	85wt% Btm	**	**	**	0.007	0.117	0.714	1.30	0.600	0.197	2.94 ± 0.10	156.3

* Not measured

** No peak detected

3 Data Analysis

The main goal is to relate the experimentally determined flash points with the measured vapor composition. In order to do this, we need to relate the flash point to some average property of the fuel vapor. Empirical models of flammability suggest at least two such properties: 1) the mean fuel-air mass ratio; 2) a weighted sum of the fuel concentrations, which we dub the Le Chatelier ratio. In order to compute these quantities as a function of temperature, we need to represent the limited data from the headspace GC so that we can evaluate partial pressure and molar mass at temperatures other than the measuring points of 40, 50 and 60°C. We do this by fitting the data to physically motivated functional forms that have been sucessfully employed in previous studies. We can check our work for the base fuel because detailed independent measurements of the vapor pressure are available.

3.1 Vapor Pressure

In a previous work (Shepherd et al., 1997), a model based on the Clausius-Clapeyron relationship was used to correlate the vapor pressure with the fuel temperature for Jet A. The Clausius-Clapeyron relationship is an exact thermodynamic identity, but we will use an approximate version. In the case of an ideal gas vapor, negligible liquid specific volume, and constant heat of vaporization, the Clausius-Clapeyron relationship can be integrated to obtain:

$$P_\sigma = C_1 \exp(-C_2/T), \tag{1}$$

where P_σ is the vapor pressure and T is the temperature. We will obtain the coefficients C_1 and C_2 by fitting Eq. 1 to experimental measurements.

The vapor pressure of ARCO base fuel was measured using the procedure described in Shepherd et al. (1997) and calculated based on the GC measurements (Woodrow, 2000). Both results are shown in Fig. 5 together with previous (Shepherd et al., 1997) experimental data for a sample of LAX Jet A (flash point of 48°C) used in some of the CIT tests. Note the excellent agreement between the three sets of data.

Since these measurements were performed at high mass-volume ratios (half-full containers), the composition of the fuel vapor was not influenced by the depletion of low-molecular weight components. A least-squares fit to the logarithm of the vapor pressure as a function of the inverse temperature (Fig. 6) is used to extract the coefficients of Eq. 1 for the base fuel, resulting in the following fit:

$$P_\sigma = 2.256 \times 10^6 \exp(-3899/T), \tag{2}$$

where P_σ is the vapor pressure (mbar) and T is the temperature (K). The same procedure applied to the three vapor pressure measurements of Woodrow (2000) yields:

$$P = 6.465 \times 10^6 \exp(-4243.3/T), \tag{3}$$

where P_σ is the vapor pressure (mbar) and T is the temperature (K). To compare these two results, these two fits were evaluated at temperatures ranging from 0 to 100°C and

plotted together in Fig. 7. We observe that in a restricted range of temperatures (from 20°C to 70°C), the difference between the two functions is less than 10%. We conclude that within this range of temperatures, the simple correlation of Eq. 1 for the vapor pressure is reasonably accurate when fit to vapor pressures from GC data (Woodrow, 2000) taken at only three temperatures (40°C, 50°C, and 60°C). Equation 1 was used to

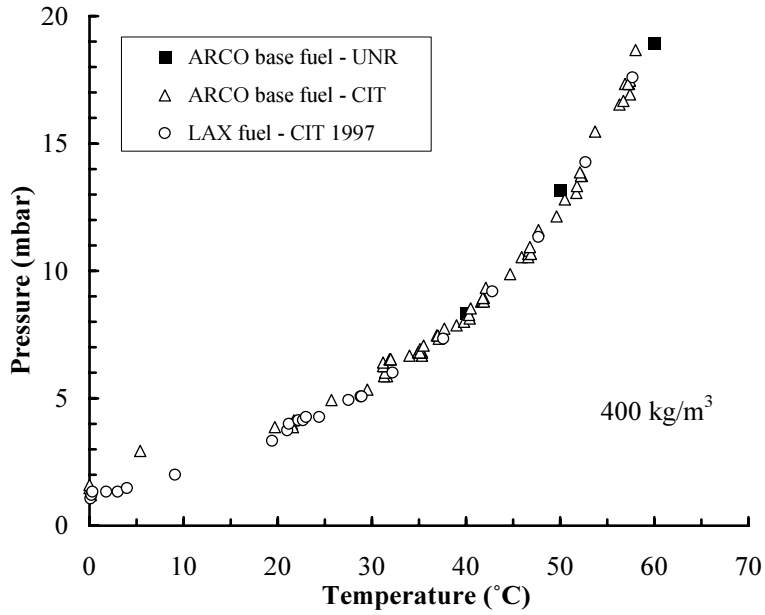

Figure 5: Vapor pressure of three Jet A samples as a function of temperature. The measurements were done at CIT (Shepherd et al., 1997) and UNR (Woodrow, 2000). The mass-volume ratio is about 400 kg/m^3.

fit the vapor pressure dependence on inverse temperature for the seven other ARCO fuel samples listed in Table 1. For each fuel, the coefficients of the fit are determined from vapor pressures calculated from GC measurements (Tables 2 and 3) at three temperatures (40°C, 50°C, and 60°C) and two mass-volume ratios (400 kg/m^3 and 3 kg/m^3). Figure 8 illustrates the quality of the fits that are obtained and the resulting coefficients are shown in Table 4. The dependence of the vapor pressure on temperature for a mass-volume ratio of 400 kg/m^3 is shown in Fig. 9. At a given temperature, the vapor pressure is observed to decrease as the flash point of the fuel increases. We also observe that as the flash point of the fuel increases, the dependence of the vapor pressure on temperature is weaker; i.e., the slopes of the curves decrease. Finally, we observe that as the flash point of the fuel increases, the vapor pressure at the flash point temperature appears to decrease systematically. Figure 10 shows similar behavior for a mass-volume ratio of 3 kg/m^3.

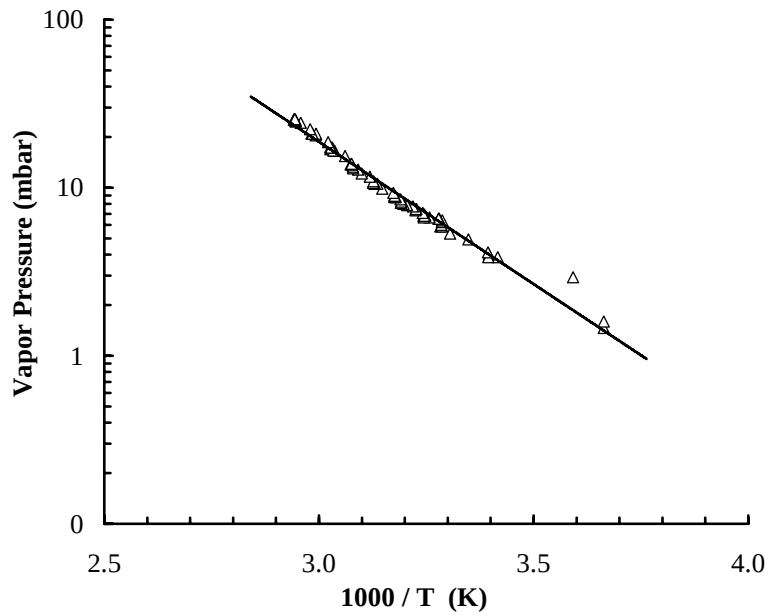

Figure 6: Least squares fit on a log scale used to determine the coefficients of the vapor pressure fit Eq. 1 for ARCO base fuel (mass-volume ratio = 400 kg/m^3). Data from CIT measurements (Shepherd et al., 1997).

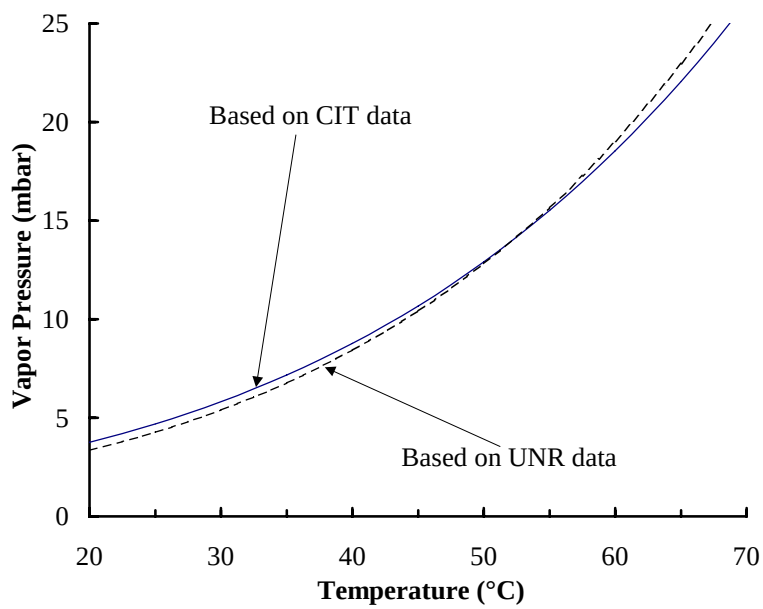

Figure 7: Comparison of the CIT and UNR vapor pressure correlations of ARCO base fuel as a function of temperature. The mass-volume ratio is about 400 kg/m^3.

3.2 Vapor Molar Mass

The average molar mass can be calculated from the GC analysis of a fuel. Although physical and chemical properties related to the multi-component nature of a fuel are lost

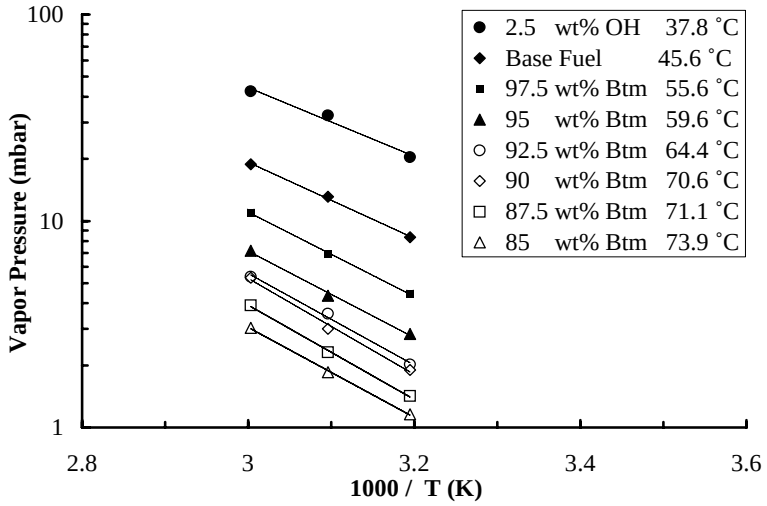

Figure 8: Vapor pressure (mbar) as a function of 1000/temperature (K) for the eight different ARCO fuels. The trendlines are the fits to Eq. 1.

Table 4: Coefficients of the vapor pressure fit for each of the eight ARCO fuels for two cases of mass-volume ratio.

Fuel	Flash Points (°C)	∼400 kg/m^3		∼3 kg/m^3	
		C_1	C_2	C_1	C_2
Base Jet A + 2.5 wt% OH	29.03	4387817	3834	4426151	3991
Base Jet A	46.42	6464809	4243	1738213	3952
Jet Fuel 97.5 wt% Btm	54.03	14733009	4701	49431198	5195
Jet Fuel 95 wt% Btm	59.55	13652001	4821	67772753	5406
Jet Fuel 92.5 wt% Btm	65.05	24697083	5102	154527726	5755
Jet Fuel 90 wt% Btm	68.93	50522245	5358	200896744	5893
Jet Fuel 87.5 wt% Btm	71.20	28055100	5262	73278011	5649
Jet Fuel 85 wt% Btm	73.48	10530113	5018	151961088	5929

when considering the average molar mass, it can be used to calculate many useful global parameters such as the fuel-air mass ratio.

GC analysis was used to calculate the average molar mass of the fuel vapor for the eight ARCO fuels investigated in this report. The molar mass of the fuels was calculated for three temperatures (40°C, 50°C, and 60°C) and two mass-volume ratios (400 kg/m^3 and 3 kg/m^3). The results are shown in Tables 2 and 3. Figure 11 shows the molar mass as a function of temperature for three of the fuels: 85wt% Btm, base fuel, and 2.5wt% OH. Between 40°C and 60°C, the molar mass appears to increase linearly with temperature. However, the dependence of molar mass on temperature is relatively weak. For example, at a mass-volume ratio of 400 kg/m^3, the average molar mass increases

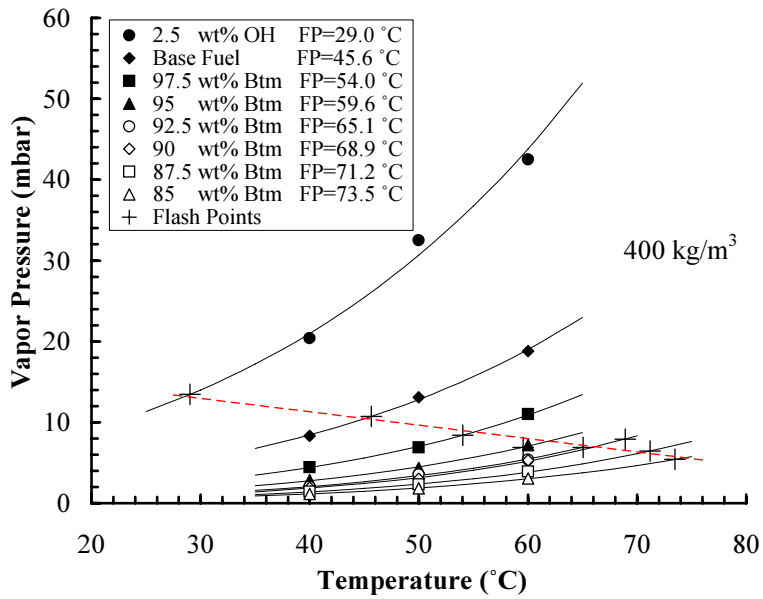

Figure 9: Vapor pressure as a function of temperature. The trend lines are the fits to Eq. 1. The flash points of the fuels are also shown and the corresponding linear fit is indicated by a dashed line. The mass-volume ratio is 400 kg/m^3.

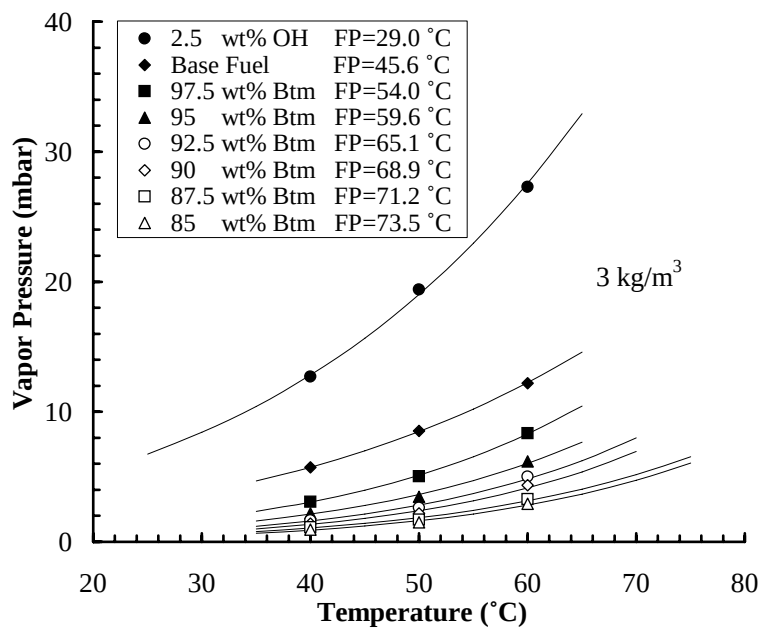

Figure 10: Vapor pressure as a function of temperature. The trend lines are the fits to Eq. 1. The mass-volume ratio is 3 kg/m^3.

from 110.4 to 113.8 g/mole as the temperature increases from 40°C to 60°C. This is due

to the increase in the fraction of fuel components with a higher molecular weight in the vapor as the temperature increases, see Woodrow (2000).

Figure 11 also shows that the molar mass at 3 kg/m^3 is systematically higher than the molar mass at 400 kg/m^3. This is a result of the depletion of low-molecular mass fuel components at low mass-volume ratios (e.g. 3 kg/m^3). From the data of Woodrow (2000), we conclude that the molar mass also depends weakly on the mass-volume ratio. Finally, Fig. 11 shows that for a given mass-volume ratio and temperature, the base fuel (flash point of 46.4°C) has a molar mass about 6% higher than that of 2.5wt% OH (flash point of 29.0°C), and that 85wt% Btm (flash point of 73.5°C) has a molar mass about 34% higher than that of base fuel. Hence, the strongest influence on the molar mass is the type of fuel, i.e., the flash point of the fuel.

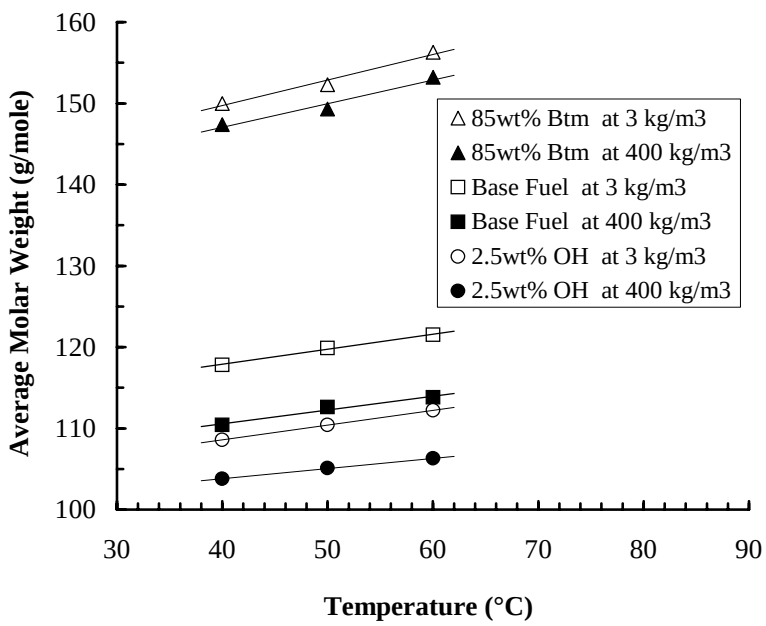

Figure 11: Molar masses at 3 kg/m^3 and 400 kg/m^3 for three fuels: 85wt% Btm (flash point of 73.5°C), base fuel (flash point of 46.4°C), and 2.5wt% OH (flash point of 29.0°C). The linear fit for each case is also shown.

3.3 Fuel Vapor Composition

The UNR report (Woodrow, 2000) contains extensive data on subsection mole percent of the components. This data and the component partial pressure are used to examine the relation between the vapor composition and the flash point of the fuel. The effect of temperature on the vapor composition is also discussed.

The partial pressures of the hydrocarbon fuel components at 400 kg/m^3 are given in Table 2 and are shown graphically in Fig. 12 for a temperature of 60°C. The hydrocarbon components are identified by their carbon number from 5 to 13. For the low flash point

fuels such as 2.5wt% OH (FP=29.0°C), the fuel vapor is dominated by low-molecular weight (lighter) components such as C5 to C8. As the flash point of the fuel increases, the dominant hydrocarbon components in the fuel vapor shift towards high-molecular (heavier) components. This can clearly be seen in Fig. 13 which shows the subsection mole percent of the hydrocarbon components for each fuel. The most abundant hydrocarbon components for each fuel (components having the highest mole percent) shift systematically towards heavier components as the flash point of the fuel increases.

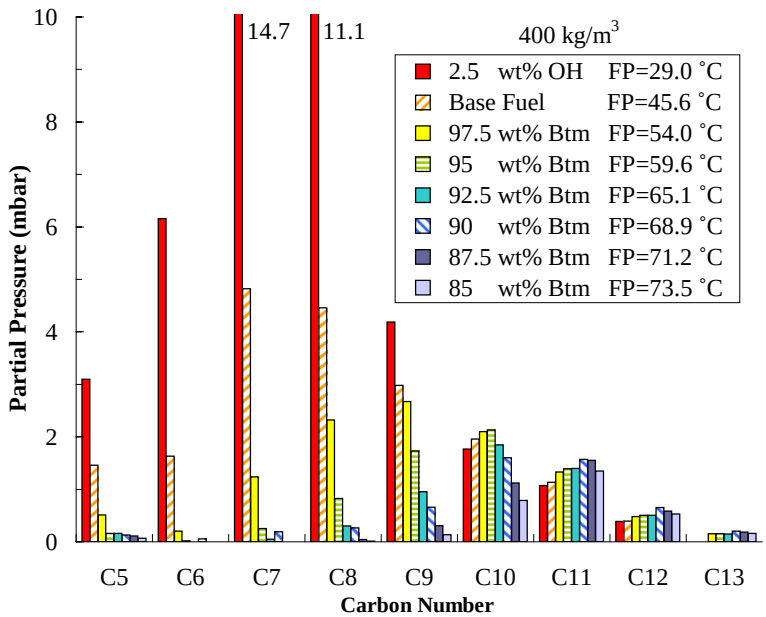

Figure 12: Partial pressures of hydrocarbon components in the fuel vapor at 60°C, 400 kg/m^3, for the eight ARCO fuels classified by flash point. The values of the pressures of C7 and C8 for 2.5wt% OH are indicated to the right of their respective column. The peaks of these two components are not visible because the range of the vertical scale (pressure) was reduced to make the pressures of the other components visible. Data of Woodrow (2000).

To more clearly represent the effect of increasing flash point on the fuel components, the flash point dependence of three components spanning the range of hydrocarbons is investigated. The three components chosen to characterize each fuel are C5 (the lightest component), C9 (the median component) and C12 (the second heaviest component). The behavior of these three components is observed for each fuel, identified by its flash point. The dependence of the partial pressure of the three components on flash point is shown in Fig. 14. As the flash point temperature increases, the partial pressures of C5 and C9 decrease rapidly while the partial pressure of C12 remains relatively unchanged. Hence, the fraction of C5 and C9 in the vapor decreases with increasing flash point.

The subsection mole percent shows that as the flash point increases, the mole percent of C5 decreases (Fig. 15). The mole percent of C9 increases and reaches a peak for

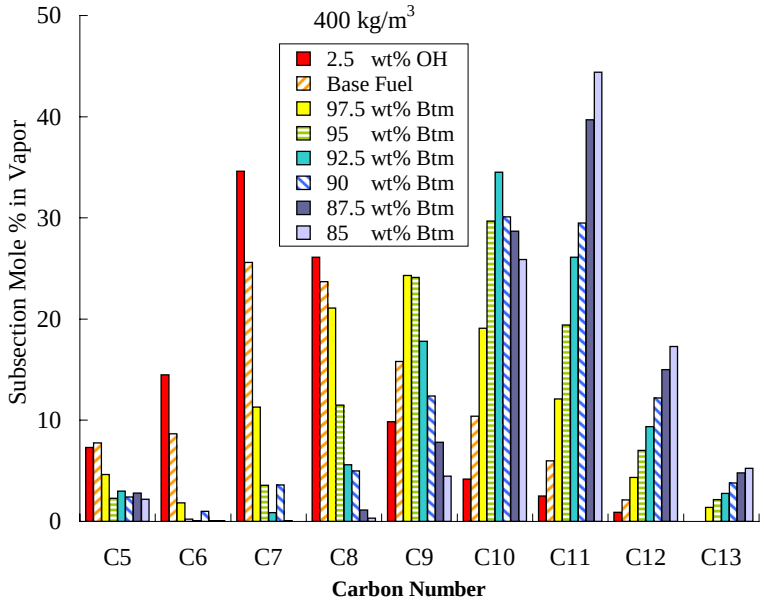

Figure 13: Subsection mole percent of hydrocarbon components in the fuel vapor at 60°C, 400 kg/m^3, for the eight ARCO fuels classified by flash point. Data of Woodrow (2000).

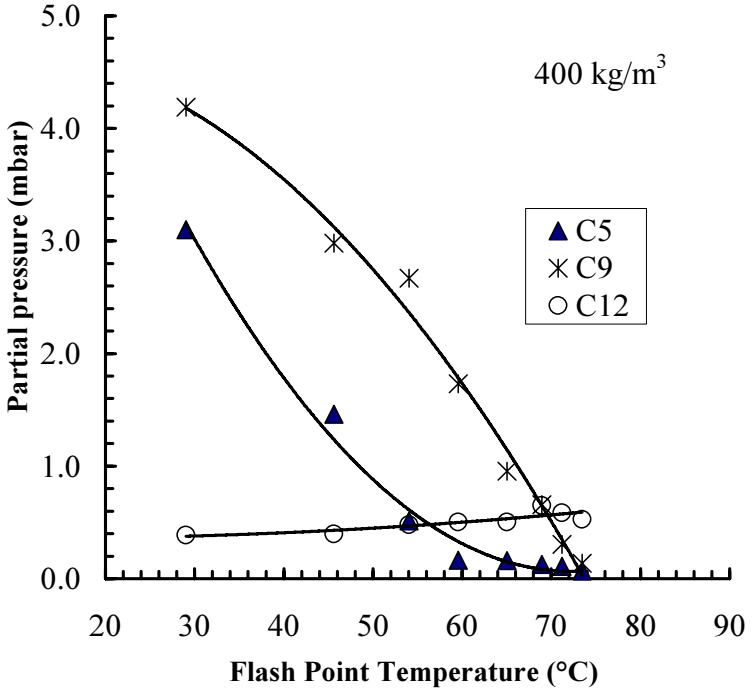

Figure 14: Partial pressure of three hydrocarbon components (C5, C9, and C12) in the fuel vapor at 60°C, 400 kg/m^3, as a function of the flash point. Data of Woodrow (2000).

fuels with a flash point between 50°C and 60°C. The mole percent of C12 increases steadily as the flash point increases. The behavior of the mole percent of the three components highlights the systematic shift in concentration of components from light to heavy hydrocarbons. For low flash point fuels around 30°C, the concentration of C5 and C9 is high. As the flash point of the fuel increases to about 50°C, the concentration of C9 is the highest. For the high flash point fuels around 70°C, the concentration of C12 is the highest.

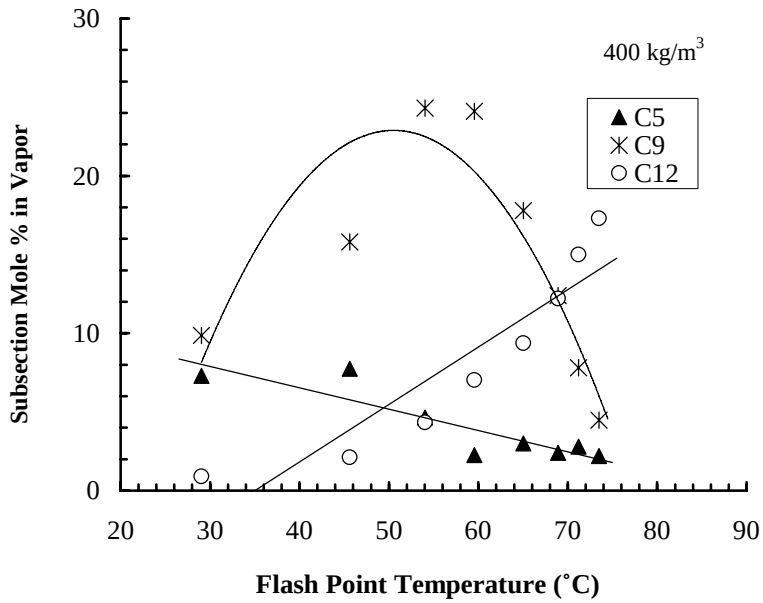

Figure 15: Subsection mole percent of three hydrocarbon components in fuel vapor (C5, C9, and C12) at 60°C, 400 kg/m^3, as a function of the flash point. Data of Woodrow (2000).

4 Flash Point Prediction

The flash point has been successfully correlated with many other flammability properties for pure hydrocarbon fuels (n-alkanes) (Affens, 1966). A partial listing of these properties includes the lower flammability limit (LFL), the carbon number and the vapor pressure. A key concept developed from these studies is that the flash point temperature for a pure substance can be determined by finding the partial pressure of fuel at which the vapor concentration is equal to the LFL as measured with pure vapors. This idea was extended to binary mixtures of hydrocarbon fuels using simple mixing rules and basic thermodynamic relations (Affens and McLaren, 1972). That work serves as the basis for our treatment of Jet A.

We have used two separate prediction methods for determining the flash point of Jet A. First, we have used an empirical model of mixture flammability known as Le Chatelier's rule and considered the fuel vapor to be composed of an idealized mixture of C5 to C12 hydrocarbons as determined by Woodrow (2000). Second, we have used a separate empirical model based on a constant value of the fuel-air mass ratio at the LFL. The fuel-air mass ratio is predicted by using Woodrow (2000) measurements of vapor average molar mass and predicted vapor pressures.

4.1 Flash Point Prediction with Le Chatelier's Flammability Rule

Le Chatelier's flammability rule (Coward and Jones, 1952) is an empirical formula developed to correlate flammability limits for fuel mixtures of two or more components with the flammability limits of the individual components. Flammability limits for many fuels have been measured (Coward and Jones, 1952, Zabetakis, 1965, Kuchta, 1985) and are available for some of the C5 to C12 species that make up Jet A. The flammability limit is usually given in terms of the fuel mole fraction L_i for a mixture of fuel component i with air at sea level and room temperature. For a mixture of N components each with a fraction X_i in the total fuel-air mixture, Le Chatelier's flammability rule can be written

$$LCR = \sum_{i=1}^{N} \frac{X_i}{L_i} = \begin{cases} > 1 & \text{flammable} \\ = 1 & \text{flammability} \quad \text{limit} \\ < 1 & \text{nonflammable} \end{cases} \tag{4}$$

For a liquid fuel at temperature T in equilibrium with its vapor, the component concentration X_i can be determined from the measurements of the component (subsection) vapor partial pressure $P_{\sigma,i}(T)$

$$X_i = \frac{P_{\sigma,i}(T)}{P} \tag{5}$$

where P is the total pressure.

In the case of Jet A, we are considering effective "components" that are not pure substances and also are not at room temperature. We do not consider the actual individual components for two reasons. First, the individual components were not resolved

in the analysis of Woodrow (2000) so we do not have the actual concentration of each molecular species that is present in the vapor. Second, there are over 100 individual species in Jet A and the flammability limits have not been measured for many of these species. For these reasons, we consider components that are actually composites that are representative of a subsection with a particular number of carbon atoms. As shown in Fig. 2, the fuel is a mixture of paraffins, iso-paraffins, olefins, napthalenes, and aromatics. The data indicate that the two major categories are the alkanes and the aromatics. Data on the flammability limits of these two representative components are given in Table 5. The effective values of L_i for each subsection were obtained by applying Le Chatelier's

Table 5: Lower flammability limits (volume %) of representative Jet A components at 25°C, Kuchta (1985).

	C_5H_n	C_6H_n	C_7H_n	C_8H_n	C_9H_n	$C_{10}H_n$	$C_{11}H_n$	$C_{12}H_n$	$C_{13}H_n$
alkanes	1.4	1.2	1.1	0.95	0.85	0.75	$0.7^{(2)}$	0.6	$0.395^{(1)}$
aromatics	$1.455^{(1)}$	1.3	1.2	1.08	0.79	0.805	$0.615^{(1)}$	$0.475^{(1)}$	$0.335^{(1)}$
(1) Extrapolated. (2) Estimated.									

flammability rule to a mixture of 80% alkanes and 20% aromatics for each subsection. If the fraction F of the fuel component is alkane and $1 - F$ is aromatic, then the effective value of L is given by

$$\frac{1}{L} = \frac{F}{L_{alkane}} + \frac{(1-F)}{L_{aromatic}} \tag{6}$$

The temperature correction (Affens and McLaren, 1972) is

$$L(T) = L(25°C)\,(1.02 - 0.000721T) \tag{7}$$

where T is given in °C. The predicted variation is relatively small (less than 3.3% variation in L) for the temperature range (30 to 60°C) that we are considering.

The flash point is determined by computing the Le Chatelier ratio LCR (Eq. 4) as a function of temperature. This computation uses the vapor pressure for each subsection given in Table 2, the relationship between vapor pressure and fuel fraction (Eq. 5), the pure substance flammability limits of Table 5, the temperature correction of Eq. 7 and the mixing rule of Eq. 6. Numerical solution of the equation $LCR(T_{FP}) = 1$ determines the predicted flash point T_{FP}. Since composition data were only available at three temperatures, the results were fit to a Clausius-Clapeyron type exponential dependence on reciprocal temperature to interpolate or in some cases extrapolate, in order to determine the value of T at which the Le Chatelier ratio was unity. Values of the LeChatelier ratio at experimental flash point are listed in Table 6 along with the predicted values of flash point. Plots of the Le Chatelier ratio as a function of temperature are shown in Fig. 16 for all eight fuel samples. A comparison between predicted and measured flash points is shown in Fig. 17.

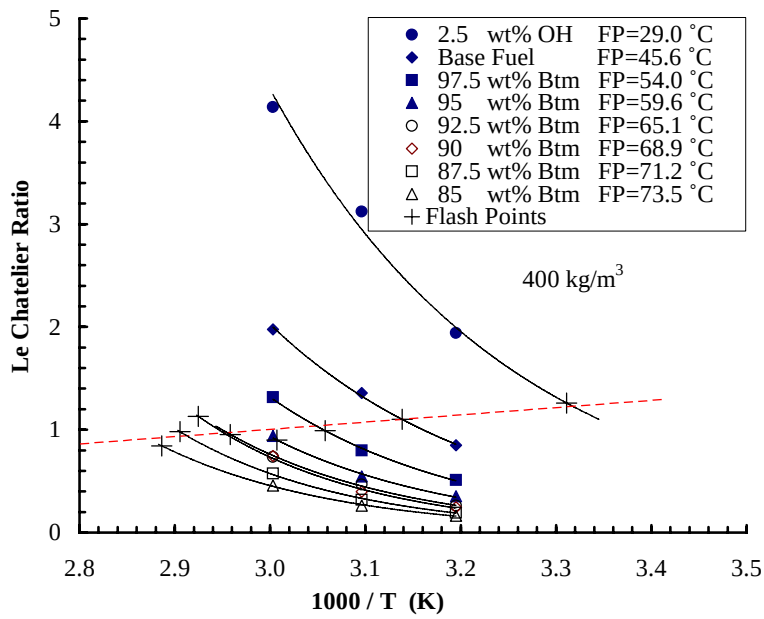

Figure 16: Le Chatelier ratio vs. temperature for all of the ARCO fuel samples. Trend lines are exponential functions of reciprocal temperature. The mass-volume ratio is 400 kg/m^3.

Table 6: Le Chatelier ratio and predicted flash points for all ARCO fuel samples, 400 kg/m^3 mass loading.

Fuel	FP (°C)	40°C	50°C	60°C	LCR	$T_{FP}(LCR = 1.0)$ (°C)
2.5wt% OH	29.0	1.94	3.12	4.14	1.26	23.7
Base Fuel	45.6	0.85	1.36	1.97	1.10	43.4
97.5wt% Btm	54.0	0.51	0.80	1.32	0.99	54.2
95wt% Btm	59.5	0.35	0.55	0.94	0.90	61.8
92.5wt% Btm	65.0	0.26	0.47	0.74	0.95	66.0
90wt% Btm	68.9	0.24	0.40	0.74	1.13	66.4
87.5wt% Btm	71.2	0.19	0.32	0.57	0.98	71.6
85wt% Btm	73.5	0.16	0.26	0.46	0.84	77.3
				Average =	1.02	

4.2 Flash Point Prediction with Fuel-Air Mass Ratio Rule

A second method used to estimate flash point relies on the empirical observation (Kuchta, 1985) that the fuel-air mass ratio f assumes a nearly constant value for a wide range of fuels at the LFL. This is supported by data given in Kuchta (1985) (p. 27), who observes: "For most saturated hydrocarbons, their lower limits on a weight basis are approximately

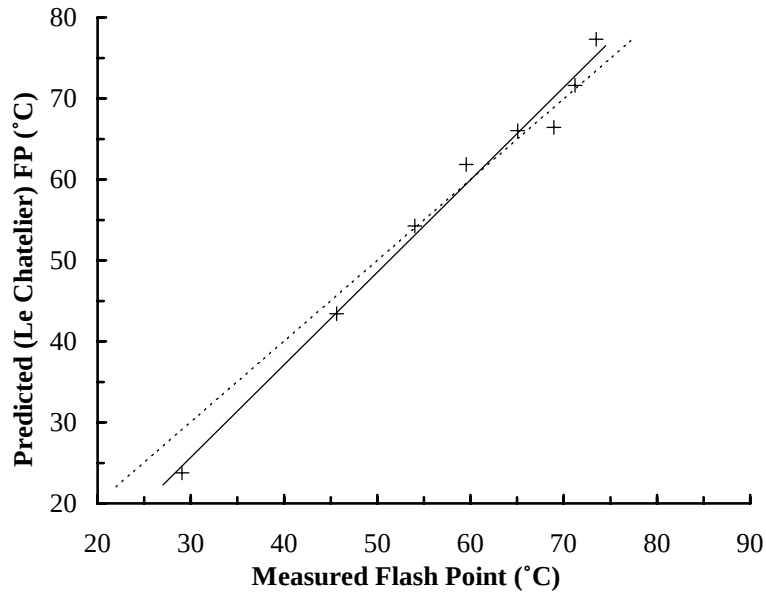

Figure 17: A comparison of the measured flash points and the values predicted using the Le Chatelier ratio technique.

45±5 mg/liter of air at standard conditions (25°C and 1 atm)." This is equivalent to a fuel-air mass ratio f_{LFL} at the lean limit of $0.033 < f_{LFL} < 0.041$. Previously, a single value of $f_{LFL} = 0.035$ was used for Jet A based on the evaluation presented in Table 2 of Shepherd et al. (1997) and Fig. 41 of Shepherd et al. (1998). In the present study, a value of $f_{LFL} = 0.038$ was found to better represent the data.

The fuel-air mass ratio f can be computed from the molar mass W_f and amount (moles) N_f of fuel and that of air, W_{air} and N_{air},

$$f = \frac{N_f W_f}{N_{air} W_{air}}. \tag{8}$$

The partial pressure P_σ of fuel can be used to find the ratio N_f/N_{air}

$$\frac{N_f}{N_f + N_{air}} = \frac{P_\sigma}{P} \tag{9}$$

or equivalently

$$f = \frac{P_\sigma W_f}{P_{air} W_{air}} \tag{10}$$

where $P_{air} = P$ - P_σ. For the cases of interest, the fuel partial pressure is much smaller than the atmospheric pressure and we can approximate $P_{air} \approx P$. Setting the fuel-air ratio equal to a constant value of 0.038 and solving for the temperature yields the predicted flash point. As in the Le Chatelier method, the data are interpolated and extrapolated by fitting the mass ratios to an exponential function of reciprocal temperature. The results are shown in Fig. 18 and given in Table 7. The comparison of observed and predicted

values for the flash point are shown in Fig. 19. The quality of the comparison is similar to the results obtained with the Le Chatelier method.

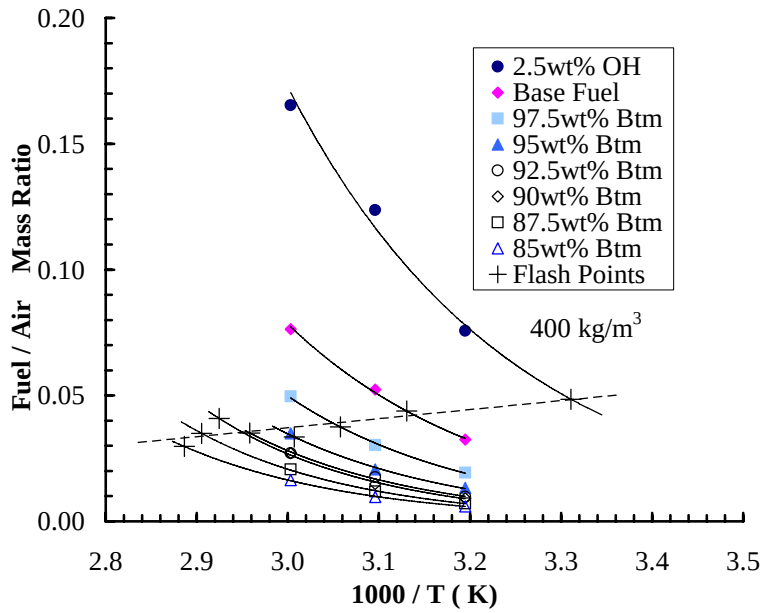

Figure 18: Fuel-air mass ratio in vapor as a function of $1000/T$ (K). The trend lines are exponential functions of reciprocal temperature.

Table 7: Fuel-air mass ratios and predicted flash points. Mass loading of 400 kg/m^3 and pressure of 1 atm.

Fuel	Measured FP (°C)	40°C	50°C	60°C	Projected Mass ratio at FP	Predicted FP MR=0.038 (°C)
2.5wt% OH	29.0	0.0757	0.1236	0.1652	0.0485	23.6
Base Fuel	46.4	0.0325	0.0523	0.0763	0.0438	43.2
97.5wt% Btm	54.0	0.0193	0.0303	0.0496	0.0375	54.3
95wt% Btm	59.5	0.0132	0.0206	0.0349	0.0335	62.3
92.5wt% Btm	65.0	0.0097	0.0175	0.0271	0.0351	66.8
90wt% Btm	68.9	0.0092	0.0148	0.0270	0.0409	67.4
87.5wt% Btm	71.2	0.0071	0.0118	0.0206	0.0349	73.0
85wt% Btm	73.5	0.0060	0.0097	0.0163	0.0297	79.2
				Average =	0.0380	

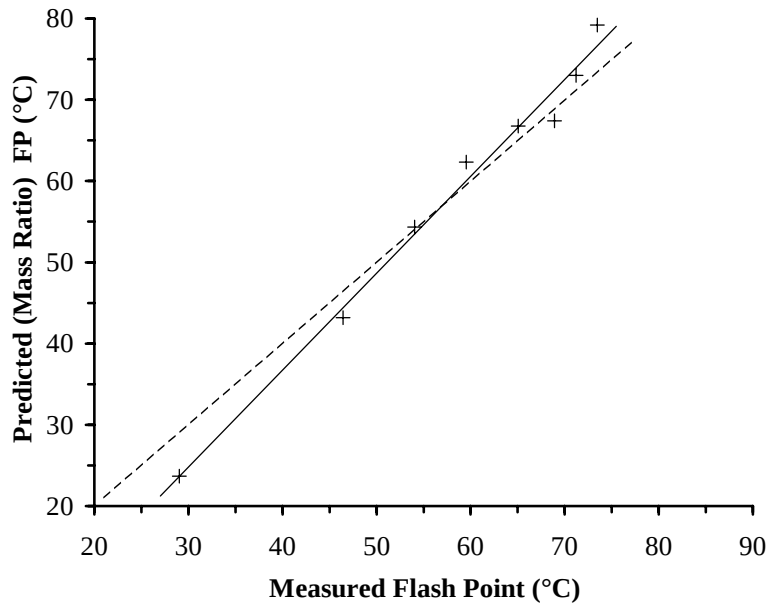

Figure 19: A comparison of the measured flash points and the values predicted using the mass ratio method ($f_{LFL} = 0.038$). Mass loading of 400 kg/m^3.

4.3 Effect of Mass Loading and Altitude on Predicted Flash Point

The ASTM D 56 flash point measurement is only carried out at one value of fuel loading so no direct evaluation of the effect of fuel loading on flash point is possible using this method. However, using the flash point estimation techniques developed above and the GC characterization of the fuel at 3 kg/m^3, a prediction of the shift in flash point can be made. The Le Chatelier ratio and the fuel-air mass ratio are plotted in Figs. 20 and 21 for a mass loading of 3 kg/m^3. Quantitative analysis of this data in comparison to the 400 kg/m^3 results can be used to infer the shift in flash point. The predicted flash points and shifts in flash point are given in Table 8. Note that the flash point is predicted to increase with decreasing mass loading in all cases except for the highest flash point fuel. It is not clear if the sign reversal for the highest flash point is physically reasonable. We suspect that this is an artifact of the rather large amount of extrapolation of the data for this case. On the basis of the measured shift in composition and decrease of vapor pressure with decreasing mass loading, we would expect that that flash point would be higher for lower mass loadings.

The changes predicted by both methods, Le Chatelier and mass ratio, are within about 10% of each other and the differences between 3 and 400 kg/m^3 consistently decrease as the measured flash point increases. It is not clear if this trend is a true physical effect or a consequence of the increasing amount of extrapolation that is required with increasing flash point. The shift in the base fuel flash point is predicted to be an increase of 8°C with a decrease in mass loading from 400 kg/m^3 to 3 kg/m^3.

In order to apply this to the case of the accident aircraft (TWA 800), we must also account for the change in flash point with altitude. As indicated in Eqs. 5 and 10, as the pressure decreases with increasing altitude, a smaller vapor pressure of fuel is needed to achieve a given fuel-air mass ratio. This is the physical basis for the rule-of-thumb that the flash point decreases linearly by 1°F for every 800 ft increase in altitude (Nestor, 1967), which is in reasonable agreement with ignition energy tests as reported by Lee and Shepherd (1999). The mass ratio method can be used to test this relationship by setting $f = 0.038$ in Eq. 10 and using the vapor pressure correlations of Eq. 1 together with a model dependence of pressure P on altitude z given by

$$P(z) = P_\circ \exp(-z/H) \tag{11}$$

where H is the so-called scale height of the atmosphere, 8.435 km. Differentiation of Eq. 10 yields the following estimate of the flash point variation with altitude.

$$\frac{\mathrm{d}T_{FP}}{\mathrm{d}z} = -\frac{T^2}{C_2 H} \tag{12}$$

Evaluating this equation for the base fuel yields a value of 2.84 °C/km, which is equivalent to a decrease of 1°F per every 524 ft, a rate of decrease that is about 30% greater than the rule of thumb given by Nestor. Given the approximate nature of this estimate, the agreement appears reasonable.

By subsituting the pressure of 0.585 atm at the incident altitude of 14 kft into Eqs. 5 and 10, we can predict the flash point at that altitude by using either the Le Chatelier or mass ratio. For the base fuel, the predicted flash point at a fuel-air mass ratio of 3 kg/m^3 and altitude of 14 kft is 38.4°C (mass ratio method) or 38.5°C (le Chatelier method). This is consistent with the ignition energy measurements (Lee and Shepherd, 1999) that showed ignition and flame propagation was possible for a mass loading 3 kg/m^3 at a temperature of 40°C with an ignition energy of 0.3 J.

5 Ignition Energy

A relation between the flash point and the spark energy has recently been investigated in Lee and Shepherd (1999). In that study, it was found that for ARCO fuels at a high mass-volume ratio of 35 kg/m^3 and a pressure of 0.986 bar, the temperature at which the fuel vapor can be ignited by an 0.3 J electrical spark is approximately equal to the flash point energy. It was further found that the minimum temperature for spark ignition of the fuel vapor correlates linearly with the flash point temperature (Fig. 22). Hence under specific conditions, the spark ignition energy appears directly correlated to the flash point.

6 Fuel Weathering

The fuel in the accident airplane center wing tank had been loaded in Athens and had been subjected to large changes in temperature and altitude, collectively refered to as

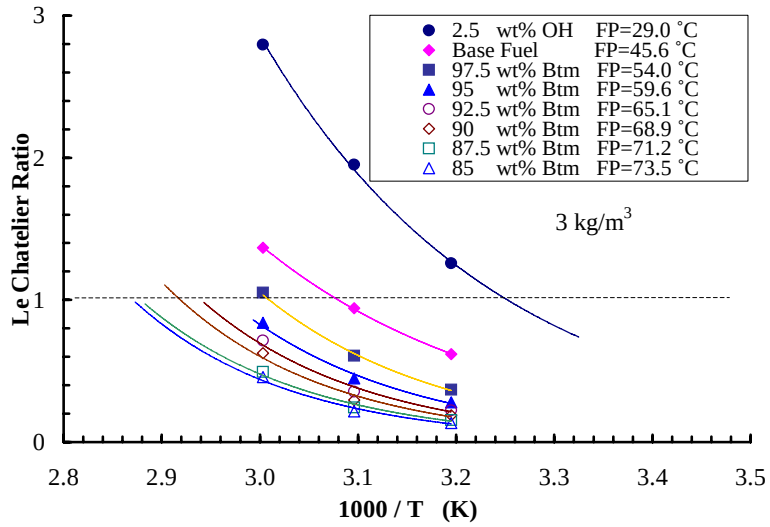

Figure 20: Le Chatelier ratios calculated for a mass-volume ratio of 3 kg/m^3 and a pressure of 1 bar. The trend lines are exponential functions of reciprocal temperature. The horizontal line shown is for a Le Chatelier ratio of unity.

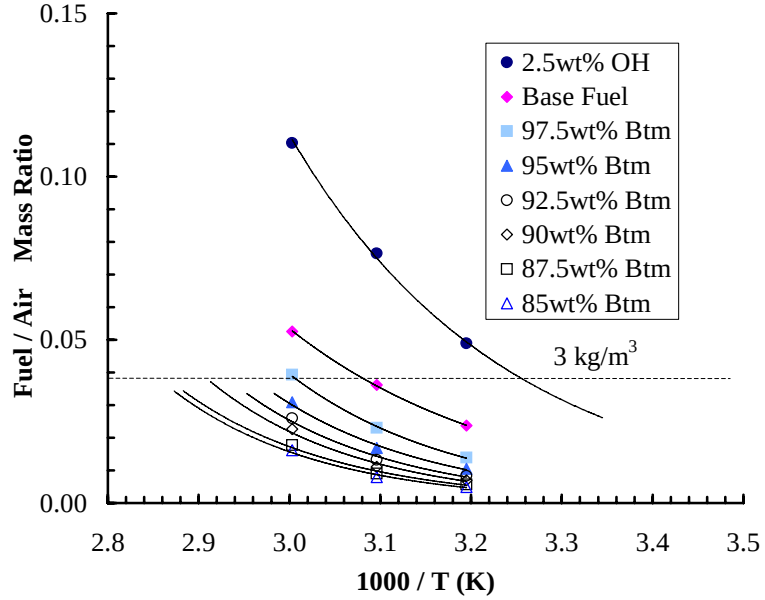

Figure 21: Fuel-air mass ratio computed for mass-volume ratio of 3 kg/m^3 and a pressure of 1 bar. The trend lines are exponential functions of reciprocal temperature. The horizontal line shown is for a limit mass ratio of 0.038.

"weathering", during the flight to JFK. There was speculation that the weathering might have affected the flammability and combustion properties of the fuel. A preliminary discussion of the weathering issue is given on pp. 6–11 and 53–57 of Shepherd et al.

Table 8: Prediction of the effect on flash point (atmospheric pressure) of reducing fuel loading to 3 kg/m^3. $\Delta T_{FP} = T_{FP}$(3 kg/m^3) - T_{FP}(400 kg/m^3), where the value of T_{FP} at 400 kg/m^3 is that predicted by the same technique as used for the 3 kg/m^3 case.

Fuel	Le Chatelier ($LCR = 1$)		mass ratio ($f = 0.038$)	
	T_F (°C)	ΔT_{FP} (°C)	T_F (°C)	ΔT_{FP} (°C)
2.5wt% OH	34.5	10.7	34.1	10.4
Base Fuel	51.7	8.3	51.4	8.3
97.5wt% Btm	59.3	5.0	59.5	5.2
95wt% Btm	64.1	2.2	64.7	2.4
92.5% Btm	67.1	1.1	68.1	1.3
90wt% Btm	69.6	3.1	70.7	3.3
87.5wt% Btm	74.4	2.8	75.9	2.9
85wt% Btm	75.3	-1.9	77.1	-2.1

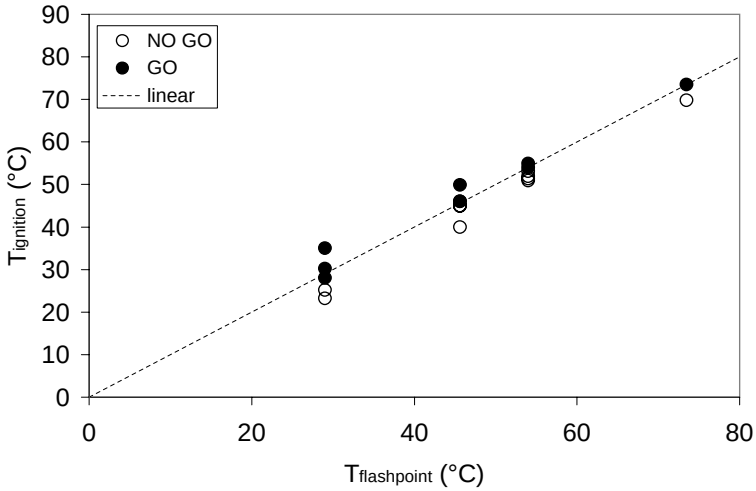

Figure 22: The minimum temperature for ignition of base fuel vapor by a 0.3 J spark at 0.986 bar, 35 kg/m^3 for different flash point fuels (reproduced from Lee and Shepherd (1999)).

(1997). The main effect of weathering is apparently in the loss of lower molecular mass components of the fuel associated with the flow of air-fuel mixture out of the fuel tank vapor space when the airplane is climbing. Subsequently, flight tests were carried out (Bower, 1997) and liquid fuel samples were obtained during these tests. The fuel was subjected to a number of take-off, cruise and landing cycles to simulate the operation of the airplane prior to and during the accident. The fuel samples were analyzed at UNR

using the headspace GC technique and the results were reported in Woodrow and Seiber (1997). A preliminary evaluation of the effect of weathering on vapor pressure and molar mass are give on pp. 50–53 in Shepherd et al. (1998). We observed a systematic decrease in vapor pressure, an increase in molar mass, and a decrease in the concentration of lighter components with increasing number of operational cycles. Despite these changes, fuel weathered for three cycles was still flammable at 50°C and 0.585 bar.

We have carried out flash point tests on these fuel samples to determine how the fuel was affected by the repeated cylces experienced in the flight test program. Three determinations of flash point were made for each sample. The individual determinations and the average are reported in Table 9. The fuel sample numbers are the same as reported by Bower (1997) and Woodrow and Seiber (1997). A cycle refers to a take-off, cruise, and landing sequence that simulates airplane operation for travel between two locations. A systematic increase in flash point with the number of cycles can be observed.

Table 9: Effect of weathering on measured flash point for fuel samples obtained in July 1997 flight tests (Bower, 1997).

Sample No.	Cycles	$T_{FP,1}$ (°C)	$T_{FP,2}$ (°C)	$T_{FP,3}$ (°C)	$T_{FP,avg}$ (°C)
1	0	48.2	46.1	45.7	46.7
2	1	50.6	51.9	50.4	51.0
3	2	50.6	50.7	51.7	51.0
4	2	50.6	52.2	51.7	51.5
5	3	51.6	54.6	53.1	53.1
6	4	53.3	53.1	53.2	53.2
7	5	54.1	55.6	54.1	54.6

The largest increase occurs in the first cycle and there is very little change observed due to the second cycle. On the average, the flash point increased about 1.5°C per cycle of operation. The fuel in the center wing tank of the accident aircraft experienced one cycle and part of another so that an increase in flash point temperature of about 1.5-3°C can be ascribed to the weathering process.

These results are consistent with measured (Woodrow and Seiber, 1997) vapor pressure and composition comparisons shown in Shepherd et al. (1998). It is also clear that the flash point measurement has some uncertainty and care must be taken not to read too much into small differences in flash point. The uncertainty is unavoidable due the crude scales (0.5°C increments) employed on the ASTM thermometers and the use of open loop control on the temperature bath.

Finally, it is important to note that the flash point tests were carried out 2-1/2 years after the fuel samples were obtained. During this time, all samples were kept in 1-liter glass bottles with teflon-gasketed screw tops. The samples were also sealed in plastic bags to check for any leakage; none was observed. The samples were obtained at JFK

and then shipped to Reno for testing. After being stored in Reno for about 6 months they were then shipped to Caltech. Samples 1, 2, 4, 5, and 7 were kept refrigerated (5–7°C) at Caltech and samples 3 and 6 were kept at room temperature. No visible degradation was observed in the samples during this time with the except of a slight change in coloring (yellowing). Samples 3 and 4 were subjected to the same number of cycles and the flashpoints are nearly identical, indicating that the storage temperature did not affect the flashpoint significantly.

Our experience with storing Jet A is consistent with industry experience (Batts and Fathoni, 1991) with long term stability of stored fuel. The military stores aviation kerosene for periods of up to 10 years and periodically tests the fuel for degradation. The most serious problems occur when the fuel is exposed to dissolved metals like copper and there are large amounts of dissolved oxygen or air in the fuel. This can result in oxidation of the fuel and formation of deposits when subjected to high temperature stress tests. The method of storage we used minimized exposure to oxygen and no metals were in contact with the fuel. No sediment or obvious microbial contamination (Gaylarde et al., 1999) was observed. Repeat tests[2] of fuel stored at Reno over a similar period of time showed no measurable changes in headspace GC results. Repeat measurements of flash point on the ARCO fuel (stored for about 1-1/2 years at ambient temperature in painted metal cans) showed no systematic changes over this time. For these reasons, we believe that the storage did not affect the flash point of the flight test samples and that these results are representative of the actual changes that occured due to the weathering.

7 Summary and Conclusions

The relationship of composition and flash point has been studied for Jet A fuel with flash points between 30 and 73°C. We have shown that the flash point can be predicted within ±3°C by using either Le Chatelier's flammability rule or a constant value of fuel-air ratio equal to 0.038.

The effect of mass loading and altitude on flash point have been examined using the fuel-air mass ratio method of predicting flashpoint. We find that a decrease in fuel loading from 400 to 3 kg/m^3 is predicted to increase the flash point of the base fuel (measured flash point of 46°C) by 8°C at fixed pressure (1 atm). Increasing the altitude from sea level to 14 kft (lowering the pressure to 0.585 bar) and simultaneously reducing the mass loading to 3 kg/m^3 is predicted to lower the flash point by about 5°C. The predicted flashpoint under the accident conditions for TWA 800 is between 38 and 40°C.

Based on a limited number of data points, it appears that the minimum temperature for ignition at a spark energy of 0.3 J is equal to the flash point. This suggests that it is possible to shift the ignition energy vs. temperature curves to account for flash point variations.

The effect of weathering is to increase the flash point by about 1.5°C per operational cycle. The effect on the fuel in the center wing tank of TWA Flight 800 would have been

[2]Private communication from J. Woodrow, March 2000.

to increase the flash point slightly (1.5 to 3°C) over the unweathered value.

Acknowledgment

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