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FORMULATION OF A SURROGATE FOR THE SIMULATION OF JET FUEL POOL FIRES

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The simulation of pool fires involving complex hydrocarbon fuels requires the development of a simplified surrogate with a limited number of compounds having known oxidation mechanisms. A series of six-component surrogates was developed for the simulation of JP-8 pool fires, and experiments were carried out with a 30-cm-diameter pool fire to allow comparison of the surrogate fuel behavior to that of the jet fuel. The surrogate was shown to simulate the burning rate, radiant heat flux, and sooting tendency of jet fuel under steady-state pool fire conditions. This study also illustrated the transient nature of batch pool fire experiments and highlighted the difficulties associated with formulating an appropriate surrogate to mimic jet fuel behavior over the lifetime of a batch pool fire. These difficulties were shown to arise from fuel compositional changes, with preferential destruction of lighter components and accumulation of heavier components during the course of the fire.

Keywords: jet fuel (JP-8/Jet-A), pool fire, surrogate fuel

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INTRODUCTION

The rapid advances that have been achieved in the computational fluid dynamic (CFD) simulation of turbulent reacting flows has made it possible to develop CFD codes for pool fire simulation. This, however, raises the challenge of how to represent fuels such as Jet-A/JP-8, used by aviation turbine engines, in computer simulations. JP-8, the current standard U.S. Air Force military aviation turbine fuel (MIL-T83133), is basically Jet-A blended with a military additive package at the concentration of ~0.15 vol% (Dyroff, 1989). The package includes fuel system icing inhibitor, corrosion inhibitor, and a static dissipater additive (Hazlett, 1991; Schulz, 1992b). These additives are not expected to affect the pool fire behavior of jet fuel and they will not be considered. Jet-A/JP-8 contains hundreds of hydrocarbons, and their composition differs geographically and with time. It is impractical to simulate a mixture of such a large number of species, even if the thermodynamics and detailed chemical kinetics for these species were available. Therefore, it is expedient to define surrogate fuels, for which the necessary chemical and physical characteristics are known, for use in CFD simulations. A surrogate should not only be able to capture the physics and chemistry of importance to the practical problem at hand, but also be amenable to inclusion in computer codes. Different surrogates may be formulated for a given fuel depending on the flame properties of interest. For this study, surrogate fuels are formulated for use in the simulation of a pool fire of jet fuel, with particular interest in matching the burning rate and the heat transfer to objects immersed in, or in close proximity to, the fire.

The major categories of hydrocarbons in jet fuels are normal and branched alkanes, cycloalkanes, and aromatics. Several investigators have developed surrogates for jet fuels (Agosta, 2002; Maurice and Lindstedt, 2000; Mawid et al., 2003; Schulz, 1992a; Wood, 1989) but with applications other than pool fires in mind. For our application, each of the components of the surrogate were required to have known chemical kinetics, be representative of the main classes of hydrocarbons present in jet fuels, and be relatively inexpensive. The mixture of components needed should match the volatility of the fuel, flash point, sooting tendency, and heat of combustion, as well as reproduce similar flame characteristics of a Jet-A/JP-8 pool fire, preferably with a small (<10) number of components. This paper provides data on flame characteristics (burning rates, height, puffing frequency, smoke point, and radiative heat flux) from a Jet-A/JP-8 fuel and its surrogate for both steady-state and batch pool fires. A detailed kinetic study of the surrogate and Jet-A/JP-8 has been reported in an earlier paper (Violi et al., 2002).

EXPERIMENTAL

Pool Fire Facility

All test fuels were burned in a steel round pan, 0.3 m in diameter and 0.1 m deep, rigidly placed 0.5 m above the ground. The tests were conducted in an enclosure 5 m × 5 m in cross section, 6 m high, and with an exhaust duct in the center of the ceiling. Dampers were provided in the walls below the level of the pool fire to allow controlled infiltration of combustion air. The bottom of the pan was water-cooled, which helps provide a well-defined boundary condition. For both transient and steady-state experiments, the pool was filled to a depth of 0.100 ± 0.0003 m and ignited with a propane torch. For continuous experiments, the fuel level was maintained constant by feed from a separate constant-head tank, the level of which was monitored by an ultrasonic sensor that was used to control the fuel supply pump. The surface area of the burning pool is four times that of the head tank.

The burning rate for transient tests was determined through measurement of the variation in the fuel level of the head tank. The maximum error is 2% for the flow rates observed in the pool fire. An ultrasonic level sensor (Hyde Park, SM652A-BOB-11FP, Dayton, OH) was used to measure the fuel level variation. A micropump with a magnetic HG drive (Idex Corp., G-184, Vancouver, WA) was used to feed the head tank. A flow sensor (McMillan, Model 101-5, Georgetown, TX) was used to monitor fuel flow rate in steady-state pool fire tests.

Flame heights, shape, and puffing frequency were determined by use of a high-speed videocamera at 2000 frames/s and real-time video. Total heat fluxes and radiative heat fluxes were measured with gas-purged water-cooled radiometers (Vatell 9000-2, Christiansburg, VA). The view angle for the heat flux meters is 120°. The radiometers were placed at locations 20 cm above the top and 40 cm away from the center of the pan. The two heat flux meters were aimed at the flame from diametrically opposed positions.

Fuels and Fuel Characterization

The fuels tested in this paper include Jet-A, Norpar-15, and surrogates composed of various chemical reagents. The jet fuel (Jet-A, density, 805 kg/m^3) was acquired from the local airport. The approximate hydrocarbon class distribution of the tested Jet-A was analyzed by gas chromatography (GC) and GC-mass spectrometry (MS) and is listed in Table 1. Norpar-15 is a narrow-boiling-range mixture of hydrocarbons, acquired from Exxon Chemicals, Inc. The composition of Norpar-15 was analyzed by GC and is listed in Table 1.

GC analyses were performed with a Hewlett Packard (HP) 6890 gas chromatograph equipped with a flame ionization detector and an HP-1 microbore column with a methyl siloxane stationary phase. The GC-MS analyses were performed with a HP 6890 gas chromatograph with a model 6790 mass spectrometer and a model 7693 autosampler. Data were collected and processed using HP Chemstation software.

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Inova 500 spectrometer operated at 499.62 MHz for proton and 125.64 MHz for ^{13}C analysis. Chloroform-d ($CDCl_3$) was the solvent used for all fuel samples. Tetramethylsilane (TMS) was used as the standard reference for 0 ppm in all NMR tests. The concentration of TMS was about 1 vol% for all samples. For proton measurements, the fuel concentration was about 4 vol%. For ^{13}C measurements, the fuel concentration was about 40 vol%. Broadband proton decoupling was gated on during data acquisition and turned off during the subsequent relaxation delay. These conditions, combined with an 80° (5.1-ms) pulse flip

Table 1. Composition of the tested fuels (in mol% except where noted)

	Hex-11		Hex-12		Norpar-15		Jet-A[a]	
	n-C_{8},	3.5	n-C_{8},	3.0	n-C_{14},	34.4	n-paraffin,	$\sim$28
	n-C_{12},	40.0	n-C_{12},	30.0	n-C_{15}	49.0		
	n-C_{16},	5.0	n-C_{16},	12.0	n-C_{16}	13.5		
					n-C_{17+},	3.1	Branched paraffin,	$\sim$29
	Xylenes,	8.5	Xylenes,	15.0			Mono-aromatics,	$\sim$18
	Tetralin,	8.0	Tetralin	13.0			Diaromatics,	$\sim$2
	Decalin,	35.0	Decalin,	27.0			Cycloparaffin,	$\sim$20
							Nondetermined	$\sim$3
Sum		100.0		100.0		100.0		100

[a] The approximate composition of Jet-A in this table is in wt%.

angle, are expected to yield quantitative ^{13}C NMR data free from distortions and Overhauser effects. For the details of spectra interpretation and the calculation of aromatic content, please refer to ASTM standard D 5292 (2001).

Some properties of the tested fuels were measured with standard ASTM test methods (2001): the boiling point distribution was measured according to ASTM standard D86; the smoke point (SP) was measured according to ASTM standard D1322; and the heat of combustion, Q_p, was calculated according to ASTM standard D3338. The flash point (FP) temperature was calculated from the following correlation (Liu, 1991):

$$T_{FP} = 0.654\ T_{10\%} - 0.537\ (T_{10\%} - T_{IBP}) - 60.7 \tag{1}$$

where the temperature at the initial boiling point, T_{IBP}, and the temperature after ten percent of the fuel has been recovered, $T_{10\%}$, are input parameters, and all temperatures are in degrees Celsius.

The SPs for the surrogate mixtures were also predicted from a correlation between threshold soot index (TSI) and SPs of the components of the surrogate fuel. The sooting index decreases as the SP increases. Following the method described by Calcote and others (Calcote and Manos, 1983; Olson et al., 1985), the correlation to estimate TSI from the SP is as follows:

$$\mathrm{TSI} = 4.41\ (\mathrm{MW/SP}) - 4.55 \tag{2}$$

where MW is the molecular weight of the fuel in g/mol and SP is the smoke point of the fuel in mm. The soot index of a mixture ($\mathrm{TSI_{mix}}$) can also be estimated from the soot index (TSI_i) and composition (mole fractions X_i) of the ith component in the mixture with a simple additivity rule (Gill and Olson, 1984):

$$\mathrm{TSI_{mix}} = \sum_i X_i \mathrm{TSI}_i \tag{3}$$

Surrogate Formulation

Based on the criteria of surrogate development described earlier, two surrogates, Hex-11 and Hex-12, each composed of six compounds, were formulated to match volatility (the boiling point distribution) and sooting tendency (SP) of the Jet-A/JP-8 fuel. The compositions of each surrogate are listed in Table 1. Other properties of the jet fuel utilized in this study and the calculated properties of the two surrogates are listed in Table 2. The two surrogates were found to be similar to Jet-A in terms of volatility, which can be reflected by the FP and average boiling point. The SP of the surrogate Hex-12 is close to that of Jet-A, whereas the SP of Hex-11 was off by ~5 mm. The hydrogen contents of the two surrogates are 13.87 and 13.47 wt%, respectively. The estimated latent heats of the surrogate fuels are ~10% higher than the value estimated for Jet-A using the methods described previously, but the surrogate values are close to the value of 280 kJ/kg (at average boiling point) reported for JP-8 by Nicolette and co-workers (1995).

The boiling point curves of two surrogates and Jet-A are shown in Figure 1. The surrogate of Schulz (1992a) and its parent fuel, a JP-8 sample from Wright Patterson Air Force Base, Ohio, are also plotted in the figure as a reference. In general, both surrogate mixtures match the boiling point curve of the Jet-A used in this study. The slope of the middle portion of the curves for the surrogates is slightly lower than that of Jet-A, which may be accounted for by the large amounts of decalin and *n*-dodecane in the surrogate formulations. The agreement in the middle portion of the boiling curve can be improved by increasing the amount of heavy components in the surrogate (e.g., *n*-hexadecane), at the expense of increasing the boiling point for the late stages of the boiling curve. The effect can be seen from the difference in the boiling behaviors of Hex-11 and Hex-12.

Table 2. Some properties of the Jet-A and surrogate fuels

Properties	Jet-A	Hex-11	Hex-12
Smoke point (mm)	24.5	28.7	23.1
TSI	26.7	17.6	22.1
MW (g/mol)	173.5[a]	151.5	152.2
VABP[b] (°C)	220.2	211.1	215.7
Flash point (°C)	40.9	40.3	41.3
Latent heat[c] (kJ/kg)	254.6	280.4	281.8
Combustion heat (MJ/kg)	44.9	44.5	44.6

[a] MW of Jet-A is estimated with API empirical equation.

[b] VABP means volumetric average boiling point; it is the mean of 10, 30, 50, 70, 90% recovery temperature determined in ASTM D86.

[c] Latent heat is estimated at VABP.

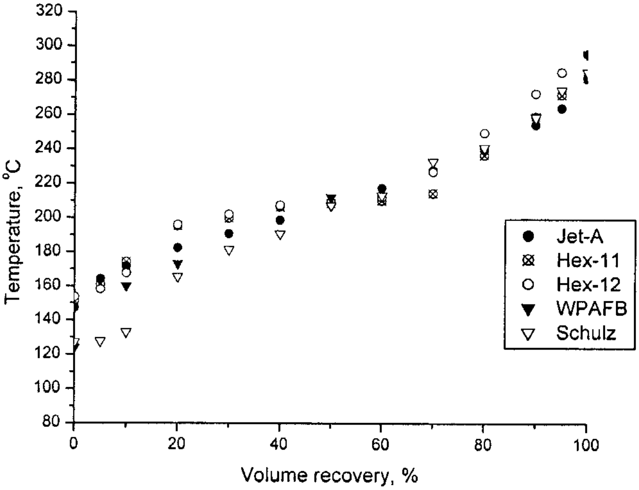

Figure 1. ASTM D86 distillation curve for various jet fuels and surrogates. Jet-A is the jet fuel obtained from the Salt Lake City International Airport as described in the experimental section; Hex-11 and Hex-12 are surrogates formulated to simulate the Jet-A as described in the experimental section; WPAFB is a military jet fuel (JP-8) supplied by Wright-Patterson Air Force Base (for the description, see Schulz, 1992a); Schulz is the surrogate formulated based on WPAFB (c.f. Schulz, 1992a).

RESULTS AND DISCUSSION

The primary purpose of this study was to investigate the effectiveness in matching burning rate and heat fluxes in a Jet-A pool fire with surrogate fuels developed using the methods described earlier. Experiments were performed in the pool fire facility utilizing the actual jet fuel, the proposed surrogate fuels, and other fuels of interest, and comparisons were made of the properties of interest such as burning rate, heat flux, fuel composition, and soot concentration. It was observed that, in some of the previous classic studies of hydrocarbon pool fires (Blinov and Khudiakov, 1961; Burgess et al., 1961; Grumer et al., 1961; also see reference in earlier review by Hottel, 1959), the mode of the pool fire combustion, for example, batch (transient) or continual fuel replacement (steady state), was not always stated. Our tests indicate that the combustion mode, transient or steady state, plays a significant role in the variation of the aforementioned properties of interest.

Steady-State Experiments

In the steady-state experiments, the fuel flow rate is controlled automatically to maintain a constant fuel level in the pan. The flow rate is measured continually during the test by the data acquisition system and it is equal to the steady-state burning rate. Given the pool surface area and the fuel density, the volumetric burning rate (m_v, ml/min) is then converted into a surface regression rate (in m/min) and mass burning rate (in kg/m^{2}s). The liquid-fuel density was assumed to be constant throughout the test. Both the level sensor signal (in mA) and the flow rate signal (in mL/min) from the mass flow controller were collected at a frequency of 1 Hz. In all steady-state experiments, the fuel depth in the pan was maintained at 0.100 m, with a variation of less than 0.0003 m.

Instantaneous volumetric burning rates for the steady-state experiments were calculated and averaged over a time interval of 60 s. The results for an experiment that utilized Jet-A are plotted in Figure 2 as a function of time. For this experiment, 24 min are required after ignition to reach the steady-state burning rate of $\sim 2.07 \times 10^{-3}$ m/min (0.0278 kg/m^{2}s). As suggested by Babrauskas (1986), for liquid pools of diameters greater than 0.2 m, the mass burning rate (m'', kg/m^{2}s) can be predicted with the following equation:

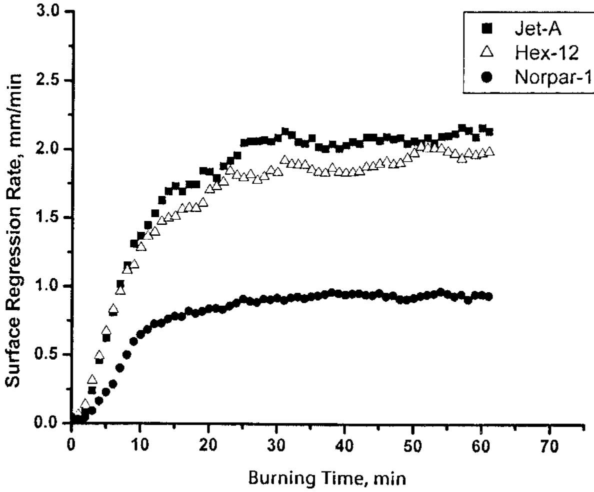

Figure 2. Continuous-feed, constant-level 30-cm pool fire surface regression rate profile.

$$m'' = m''_{\infty} \cdot [1 - \exp(-k \cdot \beta \cdot d)] \tag{4}$$

Because there are no reported constants for Jet-A/JP-8 open pool fires, values of m''_{∞} and $k\beta$ for kerosene were chosen because of the similarity between kerosene and Jet-A/JP-8. The values of 0.039 $\mathrm{kg/m^2s}$ and 3.5 $\mathrm{m^{-1}}$, respectively, are taken from the literature (Babrauskas, 1995). The mass burning rate calculated from Eq. (4) is 0.0258 $\mathrm{kg/m^2s}$ (1.91×10^{-3} m/min), which is close to the experimental value for Jet-A reported in this work. The estimated rate is also in agreement with the value (1.9×10^{-3} m/min) reported for a 30-cm kerosene pool fire by Blinov and Khudiakov (Hottel, 1959).

Similar tests with the surrogate Hex-12 and with Norpar-15 were performed for comparison with the Jet-A results. The minute-averaged Hex-12 and Norpar-15 regression rates are also plotted as a function of time in Figure 2. The steady-state regression rates for Hex-12 and Norpar-15 are 1.90 and 0.96×10^{-3} m/min, respectively. The time required for Hex-12 to reach steady state is also approximately 24 min. This result is also consistent with the latent of heat values for these fuels.

Generalized flame characteristics of interest in a pool fire include flame height and a characteristic puffing frequency. Average flame heights of 1.0 and 1.1 m were identified for the Jet-A and Hex-12, respectively, using the high-speed videocamera and still photographs with a relative background measure. These values are in good agreement with the values reported in the review by Hottel (1959).

The puffing frequency of the pool fires was determined using high-speed video (ranging between 500 and 1000 frames per second). The puffing frequency in hertz has been described by the following correlation:

$$f = \frac{1.5}{\sqrt{d}} \tag{5}$$

where d is the pool diameter in meters; thus, the Jet-A and surrogate fuels should yield the same frequency. The experimental observations for puffing frequency for the Jet-A and surrogate fuels were 2.8 ± 0.2 Hz and 2.4 ± 0.2 Hz, respectively, and the correlation predicts a value of 2.7 Hz.

A key measure of a good surrogate is its ability to yield radiation intensities that match those from a Jet-A flame. Radiation from flames formed by steady-state burning of Hex-12 and Jet-A were made to provide a comparison. Real-time heat flux measurements are shown in Figure 3*a* and the minute-averaged heat flux variations are shown in

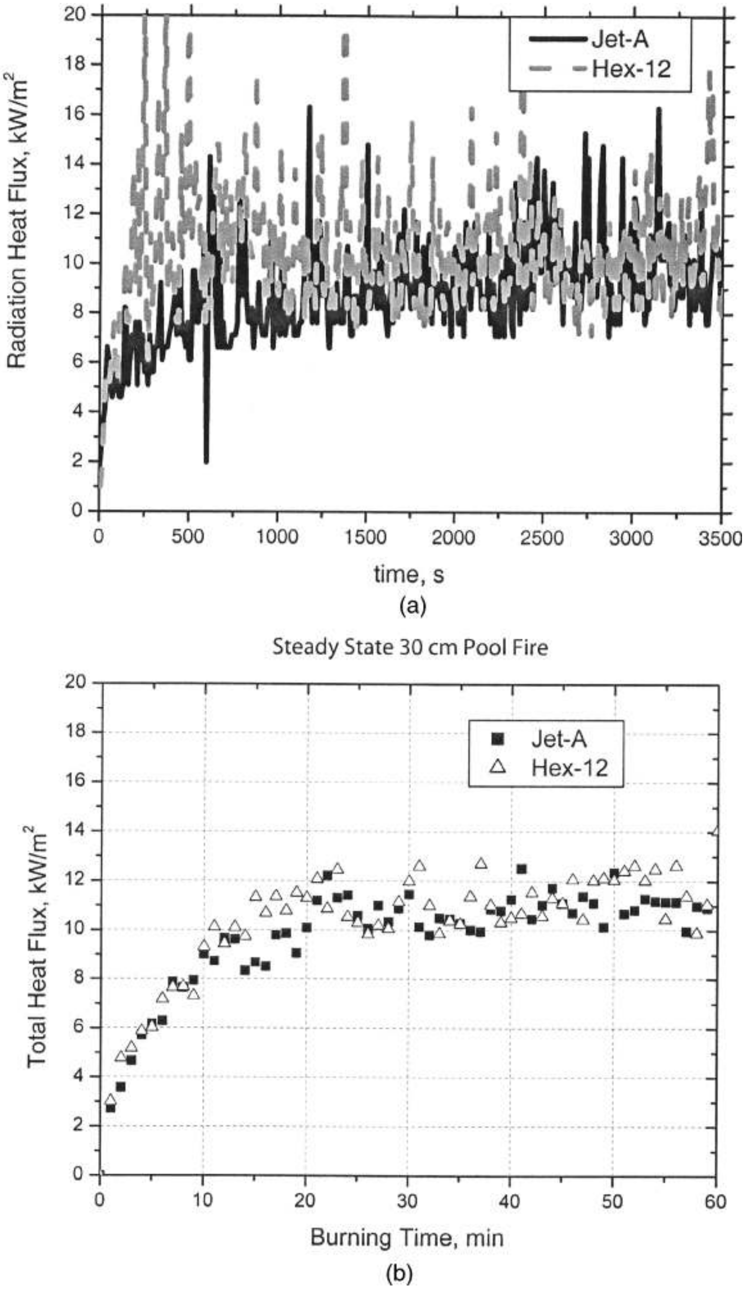

Figure 3. Radiation heat flux measurements of 30-cm continuous-feed, constant-level experiments: (*a*) real-time measurement, (*b*) minute-averaged measurement.

Figure 3*b*. These measurements were taken at a height of 0.20 m above the fuel surface and at a distance of 0.30 m from the edge of the flame (0.40 m from the center of the pan). About 20 min after ignition, the radiation heat flux reaches an approximately constant value of $10.9\,\mathrm{kW/m^2}$ for Jet-A and $11.4\,\mathrm{kW/m^2}$ for the surrogate in the steady-state pool fires. The averaged radiative heat flux for Norpar-15 was found to be about $5.8\,\mathrm{kW/m^2}$, and this lower value is consistent with the burning rate of Norpar-15, which is about half that of Jet-A.

In theory, under steady-state conditions the composition of fuel in the pan does not change over time and the composition of the liquid surface is in equilibrium with the fuel vapor, where the vapor has a composition equal to that of the feed. The concentrations of light components in the liquid surface layer should therefore be lower than the concentrations of the same species in the vapor phase. Fuel samples were taken over time and from different locations in the burning pan once the overall pool fire reached steady state (approximately 25 min based on the mass burning rate). GC spectra show that Jet-A samples do not change over time in composition and a sample from the fuel surface layer varies slightly between the feed and samples from the bulk of the pan.

More quantitative steady-state results can be obtained with the surrogate Hex-11, and these are listed in Table 3. Examination of the concentration of n-C_8 and n-C_{16} shows that the composition of surface layer is enriched slightly in heavy components as expected and the composition of the bulk of the fuel in the pan is essentially identical to that of the feed.

Soot is important in determining radiation from the pool fire flame. One measure of the sooting propensity of a fuel is the SP, which is strongly dependent on fuel composition. Based on the compositional

Table 3. Summary of Hex-11 steady-state pool fire sample analysis[a]

Sample	n-C_8	Xylenes	Decalin	Tetralin	n-C_{12}	n-C_{16}	Misc.	Smoke point (mm)
Fresh feed	2.21	5.69	31.40	7.34	45.49	7.53	0.35	28.7
Top of pan	1.77	4.72	30.36	7.23	46.28	9.39	0.26	29.2
Middle of pan	2.27	5.77	31.54	7.22	45.54	7.43	0.23	28.5
Bottom of pan	2.26	5.79	31.44	7.33	45.56	7.47	0.15	28.5

[a] Species concentrations are in wt%; except for the fresh feed sample, all other samples are taken after the fire reaches steady state.

variation described earlier, it is expected that, in a steady-state pool fire, the SP of fuel samples drawn from different heights in the pan will not change appreciably. The SPs of fuels removed from the pan during a steady-state burning experiment were found to be essentially equal to those of the parent fuels for all tests. Experimental measurements with the surrogate fuel Hex-11 under steady conditions were consistent with this observation, as shown in Table 3.

Transient Experiments

In a typical pool fire, a fixed quantity of fuel is ignited and burned to completion. Due to the complex mixture of hydrocarbons present in liquid hydrocarbon fuels such as the jet fuel studied in this work, transient behavior is observed for many of the key physical and chemical parameters of importance. Lighter hydrocarbons are expected to vaporize and burn preferentially such that, during the later stages of the fire, the fuel should be enriched in residual heavy hydrocarbons. The following discussion quantifies the transient nature of some of these key properties during batch pool fires and contrasts the results with tests carried out using a steady-state feed system for both Jet-A and a surrogate fuel.

A transient experiment is conducted by filling the pan with fresh fuel, then turning off the feed system and allowing the fuel to burn to completion. The pan is prefilled to a depth of 0.100 ± 0.0003 m; after ignition the fuel surface level drops as the fuel is consumed. The variation of the Jet-A level as a function of time during transient tests is shown in Figure 4.

A cursory view of Figure 4 would indicate that the change in fuel level, and therefore the burning rate, is linear with the exception of short periods at the beginning and the end of a burn. A least-squares linear fit generates an average burning rate of 0.827×10^{-3} m/min with R^2 of 0.98. If the data collected during the induction period (immediately after ignition) and the extinction period are excluded, then the apparent surface regression rate can be easily deduced from the slope of fuel level change, and the value obtained is 0.81×10^{-3} m/min. The same method can be applied to the variation in level of the surrogate Hex-12 to yield an average burning rate of 0.82×10^{-3} m/min with R^2 of 0.99.

However, using our real-time fuel level measurements as a basis, the surface regression rate (mm/min) of transient pool fire tests can be computed accurately from the derivative of Figure 4, or the change in fuel level per minute using a central difference formula on the data. The

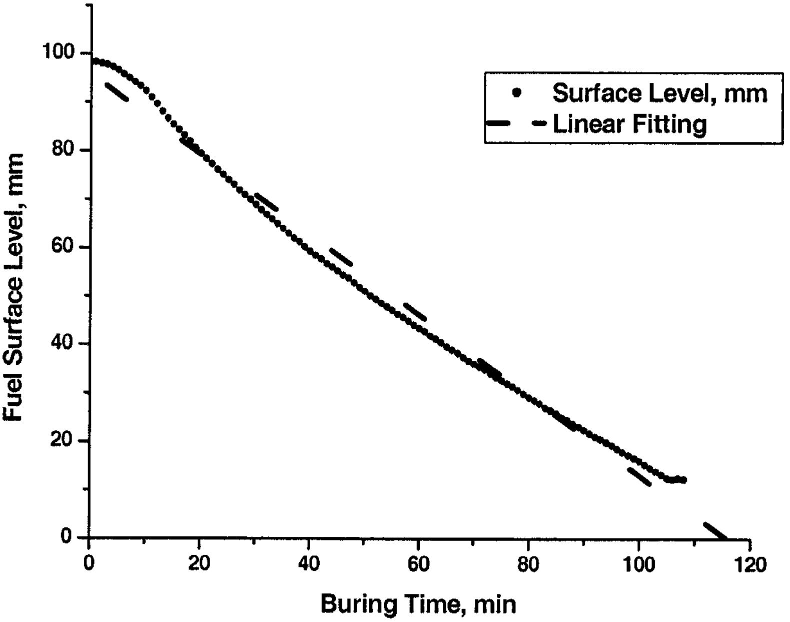

Figure 4. Measurement of fuel level change for a 30-cm transient Jet-A pool fire.

surface regression rate of Jet-A in transient tests computed from this approach is shown in Figure 5. The figure shows that the surface regression rate is not a constant value but has an initial sharp peak followed by a gradual decline. The rate first increases rapidly for times up to approximately 10 min, and it reaches a peak value at approximately 11 min. The rate starts to fall off rapidly over the range 12–35 min and decreases more slowly from 40 to 80 min until the end of burning. The peak value in the transient experiment, 1.84×10^{-3} m/min, was found to be close to the burning rate obtained when using a constant feed rate to maintain the fuel level (steady state). The Jet-A burning rate profile in a transient flame is successfully simulated with the surrogate fuel Hex-12 as shown in Figure 5. The peak burning rate at 1.64×10^{-3} m/min is a bit lower than that of jet fuel; the overall average burning rate for Hex-12 was 0.77×10^{-3} m/min, again slightly lower than the average of 0.82×10^{-3} m/min for the jet fuel.

Iwata et al. (2001) studied 14 different crude oils and kerosene in a 90-mm pool fire (fuel depth 18 mm). It is believed that all of the tests were transient. They also found that the burning rate soon after ignition

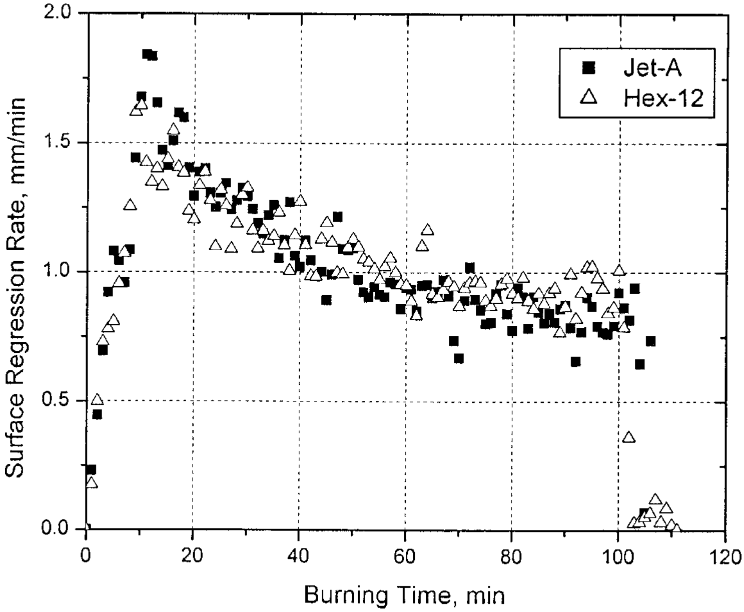

Figure 5. Transient 30-cm pool fire surface regression rate profile.

was higher than at later stages of the experiment. They offered two explanations for the higher burning rate. First, in the initial stages, there is no heat loss to the edges of the fuel pan and the entire amount of heat transferred back from the flame can contribute to fuel vaporization. Second, light components initially burned much faster, and, thus, the burning rate decreased after these species were depleted during the initial spike. They indicated that a steady state in these transient pool fires was reached quickly after ignition even though crude oil is a complex mixture.

Blinov and Khudiakov (1961) reported a variation in burning rate for transient pool fires as well. They observed that the rate could either increase with time (e.g., toluene-rich ethanol/toluene mixtures) or decrease (e.g., ethanol/propanol mixtures). They also attributed the initial rise in rate to both the early heating transient and the composition change.

Grumer and Burgess (Burgess et al., 1961; Grumer et al., 1961), from their observations with binary mixtures, suggested that the burning rates of blended fuels are initially close to those of the light components and decrease to the values of the heavier components with increases in burnout.

A recent study (Chatris et al., 2001) of large gasoline and diesel pool fires ($d = 1.5-4.0\,\mathrm{m}$) also produced an initial increase in mass burning rate. Their gasoline burning rate curve illustrated an initial rise and late decay, with a relatively constant burning rate during the intermediate portion of the burn. The diesel curve, on the other hand, was quite different. It took three times longer to reach the peak burning rate than with gasoline, and then it fell off rapidly with a relatively short period of constant burning rate.

The issue of whether the high initial burning rate is due to intense thermal feedback or compositional variations was addressed by utilizing a narrow mixture of consecutive and homologous hydrocarbons. Nopar-15 is nearly entirely (>99.8%) composed mainly of normal alkanes with 14–16 carbons, as shown in Table 1; thus, it has a rather narrow boiling range and is more likely to exhibit a relatively constant burning rate under transient burning conditions if compositional variations affect the rate. The surface regression rates for a transient Norpar-15 pool fire experiment are plotted as a function of time in Figure 6.

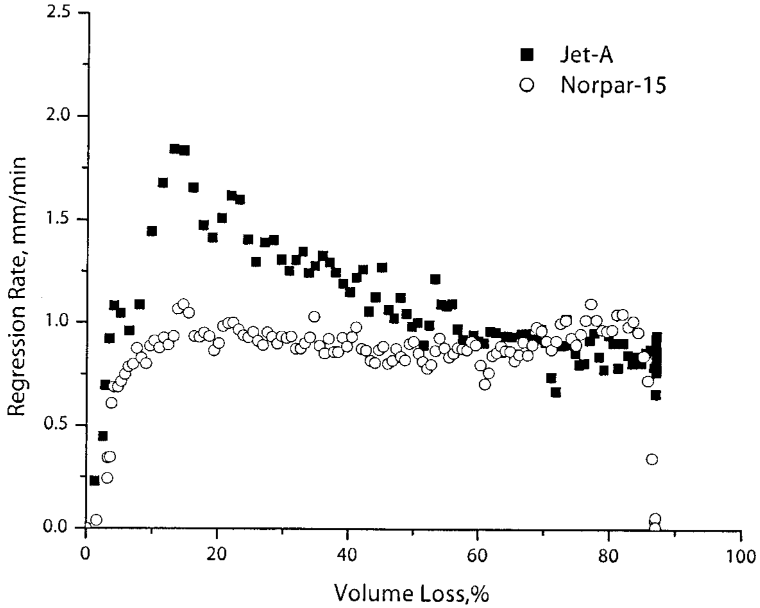

Figure 6. Comparison of burning rate profiles for Jet-A and Norpar-15 in transient 30-cm pool fires.

After an initial transient, the surface regression rate for this narrow boiling range mixture is relatively constant, which supports the view that the initial high boiling rate for Jet-A (and its surrogates) is due to compositional change rather than thermal feedback effects. Further confirmation is provided by the agreement of the mean regression rate for Norpar-15 in the transient (see Figure 6) and steady-state (see Figure 2) experiments.

The initial peak occurring in the burning rate profile of the transient test would also disappear if data are taken at infrequent intervals. Figure 7 illustrates the effect on the burning rate curves of averaging the data over various time intervals.

Thermocouples are often used in pool fire tests to monitor fuel level variation over time and results from these tests usually conclude that the burning rates of blended fuels are constant. In these tests, the thermocouples are placed at different depths in the liquid fuel, and the point at which the liquid surface passes the thermocouple is evident by a sudden increase in temperature when the thermocouple is exposed to the

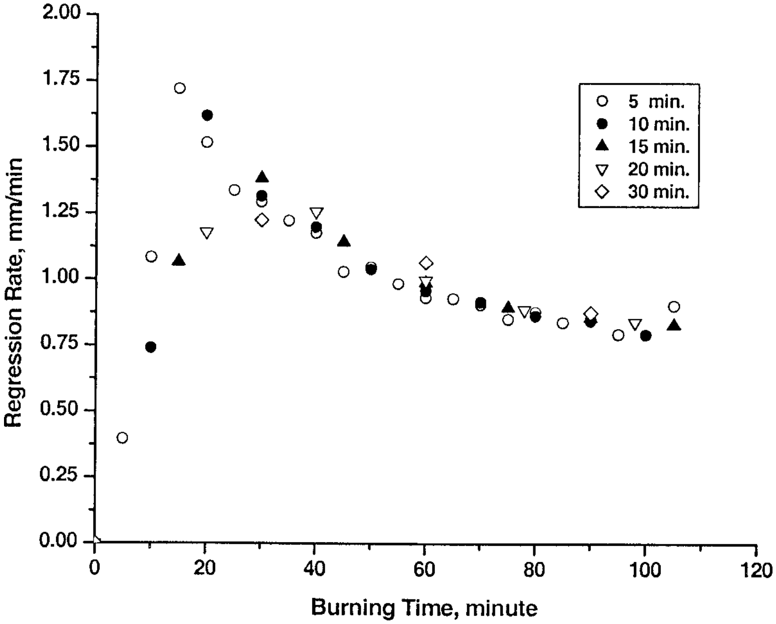

Figure 7. Computed surface regression rates with variable time interval on Jet-A transient 30-cm pool fire.

flame. In general, only a small number of thermocouples are used in such tests. Based on the results illustrated in Figure 7, it would seem plausible that a test with a limited number of data points might yield an apparently constant burning rate for blended fuels such as Jet-A.

There is direct evidence of compositional change over time from GC analysis of Jet-A samples taken from the fuel pan. Figure 8 shows the GC spectra of a fuel sample taken from unburned fuel, and fuel samples taken after approximately 40 and 90 vol% fuel consumption in a pool fire. It is apparent from the spectra that there is a preferential burning of lighter hydrocarbons, which elute at shorter retention times. Light components (e.g., C_8 and smaller), are consumed much faster than the heavier components (e.g., C_{14} and larger). The weight ratio of n-C_{12} to n-C_{17} in the unburned fuel is 7.7, whereas, at 90 vol% fuel consumption, it decreases to 1.0.

The variation in composition with depth from the surface is more quantitatively assessed using the surrogate fuel Hex-11. As shown in Table 4, within 20 min after ignition, the concentration of n-octane drops ~38% from an initial value of 2.21 wt% to 1.38 wt%. At this point, the total volume loss is only 22 vol%. After 80 min (approaching the end of

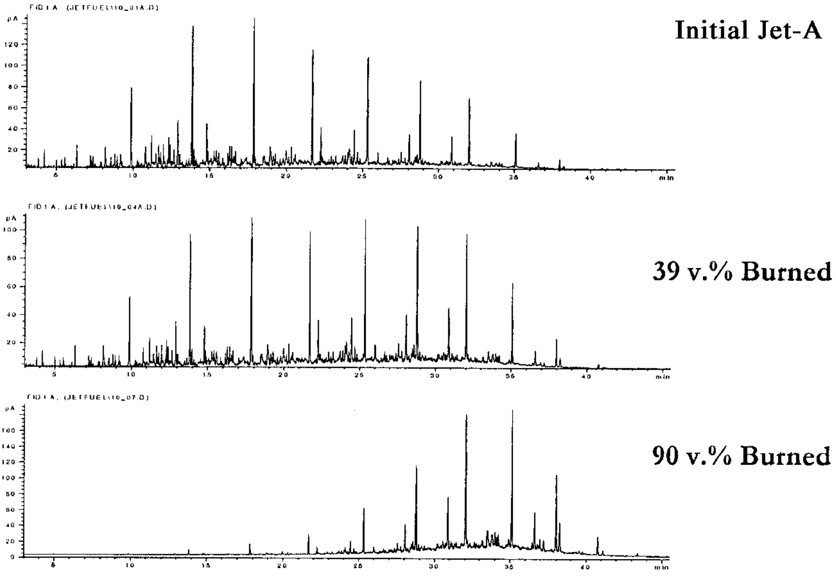

Figure 8. GC spectra of Jet-A at different stages of burn-off.

Table 4. Summary of Hex-11 transient pool fire sample analysis[a]

Sampling time (min)	Vol% loss	n-C_8	Xylenes	Decalin	Tetralin	n-C_{12}	n-C_{16}
0	0	2.21	5.69	31.40	7.34	45.49	7.53
20	22.1	1.38	3.50	29.37	6.93	47.81	10.84
80	89.7	0.26	0.86	17.87	4.86	43.21	32.61

[a] Species concentrations are in wt%.

the batch fire experiment), the concentration of *n*-cetane increased by over a factor of 4 from its initial value to a value of 32.6% due to depletion of lighter species.

The observed behavior is what one would expect from simple distillation of the fuel. Batch distillation calculations of the surrogate Hex-11 indicated that the *n*-octane concentration should decrease by 57%, after 22 vol% is distilled. After 90% of the volume is distilled (comparable to the results after 80 min), the *n*-cetane composition should increase by a factor of 6 to 45.7%. It is clear from the calculations that light components evolve more slowly in pool fires than in simple distillation, even though they do have the same trend.

The flame in the pool fire is observed above a vapor dome that forms immediately above the surface of the liquid. Heat from the flame drives vaporization of the liquid fuel into the vapor dome, and lighter compounds have a higher vapor pressure at a given liquid temperature. The preferential burning of lighter compounds in our pool fire experiments was most evident in sampling liquid near the surface of the fuel. Samples that were taken at greater depths (0.025 and 0.05 m) did not exhibit a rapid enrichment in heavier compounds. Thus, as the surface region was depleted in lighter compounds, it is likely that liquid diffusion of light compounds would replenish the surface. This phenomenon would explain the interesting appearance of the GC spectra in Figure 8 for the surface liquid sample after 39% of the fuel is burned. Although the heavy compounds clearly became enriched, the lighter compounds did not seem to be decreasing as quickly as might be anticipated. The results shown in Figure 8, however, are for samples taken from the surface of the liquid pool and would thus be subject to replenishment from below the surface. On the other hand, in the batch distillation simulation, the liquid is assumed to be well mixed and thus the composition and temperature are uniform. In the transient burning of a pool of significant depth, a large vertical concentration gradient exists due to limited mixing of the liquid in the pan during the burning process. To further illustrate this effect, Jet-A samples were taken after 80 vol% burn-off from both the liquid surface and the pan bottom, and these samples were compared with Jet-A samples taken from an 80 vol% boil-off (or distillation) experiment, as shown in Figure 9. For the distillation experiment, the GC spectra show that the light components with retention times of less than 18 min (lighter than n-C_{11}) are depleted. By contrast, these lighter species still exist in pool fire samples, especially in the bottom of fuel pan, the composition of which is close to that of the parent fuel (cf. Figure 9 with top of Figure 8).

The radiant heat flux from the flame to the surroundings during transient burning was consistent with the change in burning rate as well. Radiation heat flux measurements from both Jet-A and surrogate Hex-12 pool fires, taken in previously described locations, approached an asymptote of about 12 kW/m^2 at 12 min when the transient burning rate reached its peak. After that, the heat flux declined as the burning rate decreased. For Norpar-15, the temporal profile of heat flux in a transient

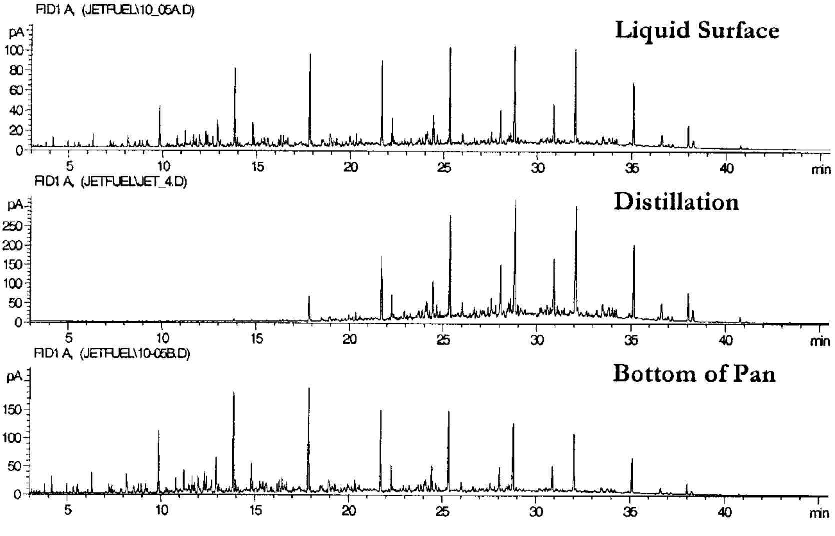

Figure 9. GC spectra of Jet-A samples at 80 vol% lost. Samples were taken from the liquid surface in pool fire (top), distillation experiment (middle), and the bottom of the fuel pan in pool fire (bottom).

fire was quite close to that of the steady-state test, except during the extinction period (which was not present in the steady-state test).

The aforementioned composition changes are expected to lead to a continuous change in SP as well. Based on a batch distillation simulation of the Hex-12 surrogate, SPs were calculated at different stages of volume loss and the results are plotted in Figure 10. In addition, SPs were measured on samples taken at different percentages of fuel volume consumption. SPs for surrogate Hex-12 show an increase with increasing volume loss for samples from pool fire tests and for samples from ASTM D86 distillation tests. Because the soot-promoting species of xylenes, tetralin, and decalin are more volatile than *n*-dodecane and *n*-cetane, the SP increases steadily with fuel consumption (volume loss). By the end of a burn, the fuel is nearly pure *n*-cetane and reaches its highest SP as predicted from the TSI value. It was noted that the SPs of most samples from the pool fire are lower than the SPs from boiling tests with the same volume losses. This behavior is in agreement with the fact that light components are depleted more slowly from a pool fire than during distillation, as previously discussed.

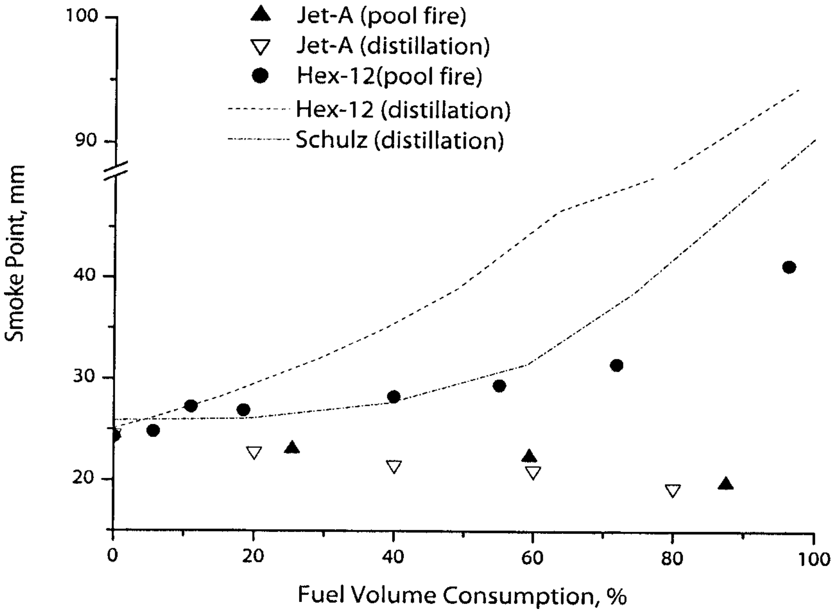

Figure 10. Smoke point variation for jet fuel and surrogates.

For the surrogate of Schulz (1992a), which consists of a 12-hydrocarbon mixture, including *n*-butylbenzene and 1-methylnaphthalene, the SP is relatively constant up to about 50% volume consumption but then increases sharply to the end, which is consistent with the calculations for the Hex-12 surrogate. The difference in SP curves for these two surrogate formulations results from the component selection. The Schulz formula, with twice as many species, has several aromatics, from volatile xylene to less volatile *n*-butylbenzene and 1-methylnaphthalene. This distribution of aromatics results in a relatively constant aromatic content in the liquid phase for a longer portion of the experiment but still leads to a large increase in SP point at high percentages of fuel volume consumption due to aromatic depletion.

SPs for actual Jet-A samples, however, which were analyzed from both transient pool fire tests and ASTM D86 boiling tests, demonstrate an opposite trend. The SP of Jet-A decreases slowly with increasing burn-off or boil-off as shown in Figure 10. The decrease in jet fuel SP is believed to be related to the wide spectrum of aromatics in actual jet fuel, as suggested in the detailed hydrocarbon analysis for Jet-A (Edwards, 2001). The existence of high-MW, high-boiling-point, and high-sooting-index naphthalenes and benzocycloalkanes in the actual fuel helps maintain the SP relatively constant with, in contrast to the surrogate fuels, a slight decreasing trend in the SP at a high percentage of fuel volume consumption.

It seems clear that the increase in SP with surrogate fuels is due to loss of aromatic content in the distillation process. This postulate is supported by fuel aromaticity analysis with proton and ^{13}C NMR, as summarized in Table 5. The Jet-A fuel samples, analyzed by GC as shown in Figure 8, were also tested with NMR. It was found that the total aromatic content of these jet fuel samples does not decrease with the fuel volume consumption, even though the distribution of

Table 5. Aromaticity analysis with NMR for transient Jet-A pool fires[a]

Vol. loss (%)	Aromatic C (%)	Aromatic H (%)
0	10.6	3.3
39	11.4	3.3
90	12.2	3.2

[a] Aromatic C (%) is the ratio of aromatic carbon atoms to total carbon atoms; aromatic H (%) is the ratio of aromatic hydrogen atoms to total hydrogen atoms.

hydrocarbons has changed significantly, as shown in the earlier GC spectra. Instead, ^{13}C NMR results suggest that the relative concentration of aromatics in the fuel gets higher as the pool burns. The investigation of the aliphatic portion of the NMR spectra provides information that complements the GC data. As the pool burns, the length of carbon chains in remaining alkanes gets longer. The increase in aromatic concentration might be attributed to the accumulation of naphthalene- and indan-class compounds with proper shift assignment in the NMR spectra.

Applicability of Surrogates to Batch Pool Fires

The difference in the sooting propensity curves for jet fuel and jet fuel surrogates indicates that it is difficult to use a single surrogate formulation to simulate an entire batch pool fire scenario. Although the burning rate can be matched quite well, the soot production and, thus, the radiation heat flux can vary to some extent between the surrogate fuel and the parent jet fuel during the course of a transient pool fire. A steady-state experiment with a surrogate, however, can match not only the burning rate but also the average radiative heat flux as well as the soot production. Real pool fires, however, are seldom steady state and, thus, it is important to understand the transient nature of the batch pool fire.

Thus, it is recommended that the most effective way to simulate a batch pool fire is by the use of a series of surrogate fuel formulations in steady-state experiments to simulate different time regimes for the batch experiment. In this manner, different aspects of the batch experiment can be studied effectively using a well-characterized surrogate, where the critical physical and chemical properties can be matched with the parent jet fuel for a short period of time. To formulate the intermediate surrogate mixtures, the variations in jet fuel composition must be determined at a number of intervals over the lifetime of the batch pool fire, to identify changes in major classes of species. The use of a series of different surrogate formulations as an approach lends itself well to the validation of complex computational models used for the simulation of pool fires, because at present the cost of computation limits the span of actual burning time that can be simulated. If it is desired to conduct a transient experiment, it is recommended that several aromatic compounds with different volatilities be used to match the soot index variation with time, in addition to the constraints discussed earlier.

CONCLUSIONS

Surrogate fuels were formulated for the jet fuel Jet-A based on fuel volatility and sooting index using a mixture of six components from the principal classes of hydrocarbons found in jet fuels. The proposed surrogate has physicochemical properties similar to those of the parent fuels. Pool fire experiments indicate that the surrogate does an adequate job of reproducing the burning rate, emissive power, flame height, and puffing frequency of a steady-state pool fire. Variations in the SP and composition of the fuel over time in transient tests highlight the difficulties that can be anticipated in simulating batch pool fire scenarios. Transient pool fire tests with currently proposed surrogates can match the burning rate but will not be able to simulate the sooting propensity over the life of the fire due to compositional changes in the liquid fuel. If it is found necessary to model the transient behavior, it is recommended that a batch pool fire be simulated using multiple steady-state pool fire experiments with differing surrogate formulations that reflect the varying compostion of the jet fuel or using a larger number of compounds to match the transient variation in sooting index.

NOMENCLATURE

A	area (m^2)
d	pool diameter (m)
f	flame puffing frequency (Hz)
h	total liquid depth in the pool (m)
k	extinction-absorption coefficient of the flame (1/m)
m_v	volumetric burning rate (ml/min)
m''	mass burning rate (kg/m^2s)
m''_∞	mass burning rate of an infinite-diameter pool (kg/m^2s)
β	mean beam-length corrector
ΔH_v	latent heat of vaporization (MJ/kg)

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