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Chemical structure of a methane counterflow diffusion flame perturbed with the addition of either JP-8 or a jet fuel surrogate

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Abstract

The chemical structure of a methane counterflow diffusion flame doped with small amounts of either JP-8 or a jet fuel surrogate was analyzed by gas sampling via quartz microprobes and subsequent GC/MS analysis. This jet-fuel initial oxidation is consistent with the anticipated chemical kinetic behavior, based on thermal decomposition of large alkanes to smaller and smaller fragments and the survival of ring-stabilized aromatics at higher temperatures. The surrogate captures the general trend but incorrectly mimics the behavior of some species such as benzene and ethylene. Furthermore, the comparison in the behavior of large alkanes is only qualitative, because of difficulties in separating the components of JP-8 as a result of isomerism.

Keywords: Diffusion flames; Counterflow; Surrogate; Jet fuel; JP-8

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1. Introduction

With world events imposing enhanced flexibility in the sources of jet fuels, it is becoming increasingly important to improve scientific knowledge of the combustion properties of different fuel blends. Jet fuels based upon JP-8, JP-8+100, Jet-A, and Jet A-1 will continue to play a central role from both a logistical and an economic viewpoint for the next few decades. The study of the combustion processes in real aero-combustor environments is in principle essential to improve engines efficiency and reduce pollutant formation. However, both the numerical and experimental studies of these processes are challenging not only because of the enormous computational resources needed and the hostility of the combustion environment to quantitative diagnostic techniques, but also because real-world fuels may contain hundreds of chemical species, making their complete chemical kinetic characterization and modeling a daunting, if not totally impractical, prospect. Furthermore, the

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fuel composition can vary significantly with changes in the source of the parent crude and in refinery processing conditions.

A practical approach to the simulation of real fuels is to identify surrogate fuel mixtures, having only a handful of components, whose combustion behaviors capture essential features of those of the real fuels. To date, candidate surrogates have been identified for JP-8, for Fischer-Tropsch JP-8, for Jet-A and for kerosene, and combustion properties of these surrogates have been compared successfully with those of the original fuels in some narrowly defined tests. But, much more comprehensive testing and surrogate validation is needed. In general, one would need a comprehensive effort aimed at: (a) characterizing the best surrogates; (b) determining their relevant chemical-kinetic and transport properties; (c) measuring their behaviors over the ranges of pressures and temperatures of practical interest; (d) establishing their mixing rules for relating mixture properties to those of the individual components; and (e) developing reduced-chemistry descriptions that can be used in design codes for chemical-propulsion and energy-conversion systems. A comprehensive review on the state-of-the-art was presented in [1]. More recently, a joint contribution from the University of Milan and UC San Diego studied the autoignition and the extinction behavior of a 3-component surrogate [2]. Also noteworthy is recent work in a jet stirred reactor in which jet fuel combustion is experimentally studied at pressures as high as 40 atm and compared to the simulation of a kinetic model that relies on a three-component surrogate with reasonable success [3].

Examining the fuel behavior can be performed in a variety of settings, including premixed flames, non-premixed ones, flow or stirred reactors and shock tubes. The latter tend to have better controlled conditions for a rigorous characterization of the fuel chemical kinetic behavior. But the ultimate test remains a flame environment, as in practical applications, since it provides the necessary coupling between chemical kinetics and transport. In this context, the present work, focusing on laminar non-premixed flames, is a natural evolution of a previous contribution from our group [4]. Since the challenge is on the chemical kinetic front, whose modeling will require the use of hundreds of species and thousands of chemical reactions even in a lumped kinetic approach, the fluid mechanics must be kept simple. As a result counterflow flames are considered, since they provide the simplest, one-dimensional environment for subsequent detailed modeling. Since, especially in the context of aero- and aero-derivative turbines, non-premixed scenarios are the preferred choice because of the safety complications associated with the use of the lean premixed alternative, counterflow *diffusion* flames are considered.

One could focus on overall combustion behaviors, such as ignition, extinction, flame propagation speed. However, detailed probing is necessary beyond an overall, qualitative characterization to guide the selection of the surrogate composition and eventually capture also the sooting behavior of these fuels, which is an issue in most aero-turbines, especially at take-off. Sampling in the presence of soot poses additional experimental challenges in connection with the occlusion of the microprobes that are typically used to minimize intrusiveness. As a result, we focused on the detailed chemical characterization of a *non-sooting* counterflow diffusion flame. The objective is twofold: first, to provide a JP-8 flame database for other investigators to use in parallel research efforts in this area; second, to verify if the surrogate formulation that was found successful in capturing overall flame behavior such as extinction strain rates and temperature profiles, indicating a good match of the jet fuel heat release, is also successful in capturing the flame structure in a relatively more stringent test as compared to [4].

2. Experimental setup

The experimental setup consists of a counterflow burner. Carefully designed convergent sections allow for a top-hat velocity profile at each burner mouth [4]. A nitrogen shroud shields the flame from room draft and ensures burning only in the controlled atmosphere that is determined by the composition of the feed streams. Figure 1 shows a schematic of our experimental set-up.

Obtaining complete vaporization of the fuel is one of the critical issues when dealing with mixtures of heavy hydrocarbons, since fractional distillation may occur. Previous work used an ultrasonic atomiser to nebulize the fuel in very small droplets [4]. This system is upgraded by using an electrospray [5], which provides greater flexibility in flow rates without compromising the stability of the flame. To ensure complete fuel evaporation and prevent condensation downstream of the electrospray unit, PID controllers keep the fuel line at 500 K, which is well above the dew point of the liquid-fuel/CH_4/N_2 mixture.

Samples of gas are extracted from the flame through a small silica probe. This probe, that was developed for a completely different application, has an outer diameter of 300 μm and inner diameter of 100 μm and is tapered to a tip diameter of 30 μm (New Objectives, NJ, USA), which should yield good spatial resolution in the flame scan and minimize flame perturbation. Evidence in preliminary experiments showed that, probably because of condensation effects in the unheated probe, the species with largest molecular weights may be underestimated. These problems were compounded by a general lack of reproducibility

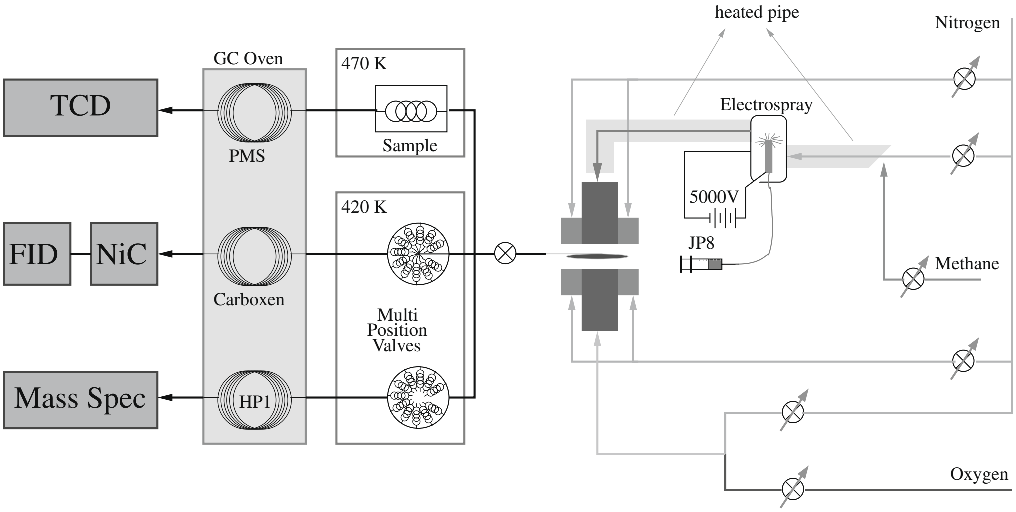

Fig. 1. Schematic of the experimental setup.

of the measurements on the fuel side. To bypass these difficulties, the concentration of fuel in the liquid phase is drastically reduced by replacing part of it with a gaseous fuel, methane. The objective is to use a methane flame as a well-controlled and well characterized chemical reactor that is perturbed by the addition of small amounts, on the order of 4200 ppm on a molar basis, of various liquid fuels, along the lines of [6]. This approach should simplify the interpretation of results in the comparison of JP-8 with surrogate mixtures and individual component liquid fuels.

To control the flame temperature and prevent soot formation, the flames are highly diluted with nitrogen. Inflow conditions and other critical variables are summarized in Table 1. The burner outlet inner diameter is 12 mm and the burner separation is kept at 12.5 mm, resulting in a density-corrected [2] overall strain rate of 78 s^{-1}. To test the surrogate behavior, the JP-8 was replaced by the same six-component surrogate as in [4], keeping all flow rates identical. This surrogate blend accurately simulates the volatility and the smoke point of a practical JP-8 fuel [7].

Temperature measurements are performed by a home-made, silica-coated, S-type thermocouple with an approximately cylindrical junction measuring 0.051 mm in diameter. The radiative correction at the peak temperature is estimated at 120 K. The chemical analysis is performed by a gas chromatograph (Agilent 6890A) equipped with thermal conductivity (TCD), flame ionization (FID) and mass spectrometry detectors (MSD) (Agilent 5973N). The instrument is capable of quantifying complex hydrocarbon mixtures and major species. The GC/MSD uses two columns, a Supelco Carboxen and an Agilent HP-1, connected to the FID and MSD, respectively. In addition, the TCD measures non-hydrocarbon stable gases separated by means of a third column (Alltech, Packed Molecular Sieve). Because of its much wider linear range, this detector is better suited than the MSD for the analysis of gases present as large fractions of the gas sample and/or in greatly varying amounts. A homemade Nickel-based catalytic converter (Methanizer) allows for the FID quantification of CO and CO_2 upon their conversion into methane in the presence of hydrogen. The system can separate and quantify N_2, O_2, CO, CO_2, light gaseous hydrocarbons and higher hydrocarbons up to C_{14}, and even higher.

The GC data are post-processed by identifying the species by both the column retention time and the molecule specific spectrum. GC/MS analysis produces a wealth of information but has one main drawback: it takes a very long time to perform a flame scan. A concentration measurement at any point in the flame typically requires: 5 min to load the sample loop, 2 min for the analysis of O_2 and N_2 by the TCD, 25 min for the analysis of light (C1 and C2) species by the FID and as long as 2 h for the analysis of large molecular-weight compounds via MS. Clearly, a full scan of a flame with a minimum of 10–12 points would entail a tedious procedure lasting in excess of 30 h. Preserving a steady flame over such a time would be challenging, especially in the case of JP-8 that requires precise metering of liquid flow rates. Using a syringe pump, as is typically done at the small flow rates of interest, would entail repeated flame shut-offs with reloading of syringes. If one factors in thermal transients of the burner and other inevitable contingencies, such as, for example, sampling probe distortions through flame start up and shut down over a 30-h time period,

Table 1
Inflow conditions and critical variables of the counterflow flames

		JP-8-CH_4 flame	Surrogate-CH_4 flame
Fuel side	Mole fractions		
	N_2	0.927	0.930
	CH_4	0.065	0.065
	JP-8 (assumed as $C_{11}H_{21}$)	4229 ppm	
	Cyclohexane, methyl-		857 ppm
	Iso-octane		428 ppm
	m-Xylene		642 ppm
	Tetralin		214 ppm
	Dodecane		1285 ppm
	Tetradecane		857 ppm
	Mass flux (kg/s/m^2)	0.317	
	Temperature (K)	375	
Oxidizer side	Mole fractions		
	N_2	0.270	
	O_2	0.730	
	Mass flux (Kg/s/m^2)	0.395	
	Temperature (K)	320	
	Density-corrected strain rate (s^{-1})	102	
	Stoichimetric mixture fraction, Z_f	0.77	

it should come as no surprise that initial measurements were plagued by reproducibility problems, as reflected by data profiles that lacked the required "smoothness".

To address this difficulty, an automated sampling system was developed, along the lines of e.g. [8], to allow for sampling/storing using two multiposition valves, two pneumatic-actuated injection valves and a battery of sampling loops, as shown in Fig. 1. One of the pneumatic valves is responsible for the TCD analysis (top left in the figure) that is executed in real time, since it requires only two minutes per data point. The other valve, on the other hand, controls the FID and the MS. Since these two instruments require a much longer time to complete a measurement, the samples are stored in two sets of 16 sample loops using other two multi-position valves and analyzed overnight by a computer-automated sequence. Extra care was put in avoiding condensation, adsorption or pyrolysis in the stored loops. Repeated analyses of pure dodecane showed that a loop temperature of 420 K can assure the stability of the sample during the time needed for the entire scan. Thanks to this improvement, a full flame scan requires at most 3 h of operator work during which the flame has to run continuously. This dramatic gain in the implementation of the experiment opens the doors to the systematic study of flame structures with relative ease.

The overall accuracy of the instrument has been assessed both by analyzing gas mixtures of known composition and by repeated sampling at the same position in the flame. The peak areas of the chromatograms show good repeatability within ±4% confirming the adequacy of the above described sampling system. Another source of uncertainty is the calibration: for small molecules, calibrated gas mixtures (SCOTTGAS®) are used; for the heavier species, liquid solutions of acetone and carefully measured aliquots of each component are prepared and injected in the GC/MS. The final error estimate is 7% for light species and 12% to 15% for the heavier ones.

3. Results and discussion

A lot of care must be put in the selection of the quantitation ions. When dealing with complex fuel blends as the present one, the chromatograms tend to be noisy because of the presence of many isomers and the fact that the quantitation of compounds featuring isomerism (namely alkenes and alkylbenzenes) is often complicated by the likely overlap of isomer peaks characterized by similar spectra. Figure 2 shows a typical JP-8 MS chromatogram, as measured from a gaseous sample extracted near the burner mouth, that is, before any significant chemistry has taken place. The arrows denote compounds that were identified and quantitated, as specified in the figure legend. The dominant peaks are associated with C9–C16 alkanes, whereas only a few of the smaller peaks, associated with the aromatics, are marked. There is a plethora of small, unidentified peaks and a pedestal on which the peaks are superimposed. The final number of species we were able to identify correcly and measure is 30; another 20 were correctly identified but their quantitation lacks the necessary accuracy. Nevertheless, these data are sufficient to provide a general picture of the chemical structure of a methane diffusion flame doped with JP-8. Further refinements will be pursued in the future with the help of sensitivity studies in the computational modeling with semi-

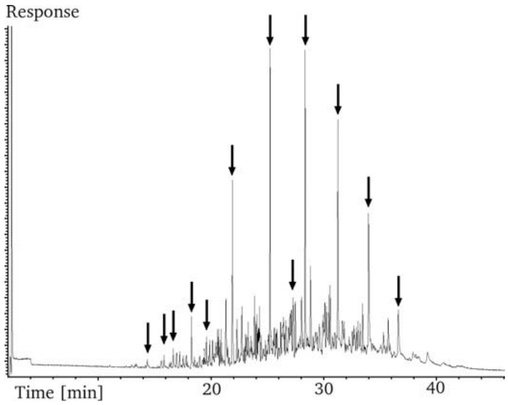

Fig. 2. Typical JP-8 MS chromatogram, as measured from a gaseous sample extracted near the burner mouth. The arrows denote compounds that were identified and quantitated. From left to right: toluene, octane, *m*-xylene, nonane, 123trimethylbenzene, decane, undecane, tetralin, dodecane, tetradecane, pentadecane, and hexadecane, respectively.

detailed chemical kinetics, to identify other minor species that play a significant role from a chemical kinetic standpoint. Figure 3 shows the equivalent chromatogram for the flame doped with the JP-8 surrogate. The spectrum is much simpler than in the preceding figure and the only distinct peaks are the six ones in correspondence with the surrogate components.

Figures 4–8 show the measured molar fraction for a subset of the species identified by the instrument, namely, major species, alkanes, C2-hydrocarbons and the aromatics, as a function of the distance from the fuel outlet for both the JP-8-doped methane flame (solid lines and mostly full symbols) and the surrogate-doped analogue (dashed and mostly open symbols). The figures show only a portion of the entire burner gap between reactant outlets (12.5 mm), since no interesting additional chemistry occurs further on the oxidizer side. For each figure, the discussion will focus first on the JP-8-doped flame and will be followed by brief remarks on major differences in the profiles of the surrogate-doped analogue. Figure 4 shows the major species and the radiation-corrected temperature profiles for the two flames. There is virtually no difference between the two flames, which is partly a consequence of the fact that 91% of heat release is due to CH_4 that is present in both flames, partly a result of the JP-8 and surrogate perturbing the CH_4 baseline flame similarly, as a result of their very similar heat release rates [4].

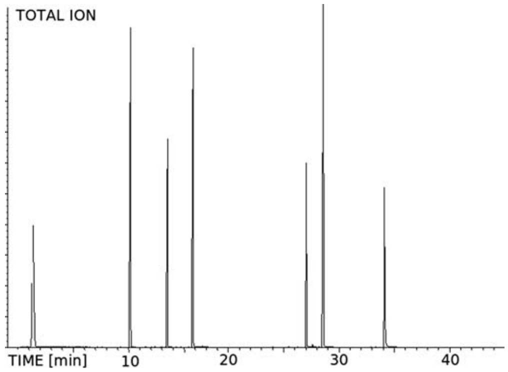

Fig. 3. JP-8 surrogate chromatogram presenting six distinct peaks in correspondence with the components of the surrogate: from left to right, methylcyclohexane, isooctane, *o*-xylene, tetralin, dodecane, and tetradecane.

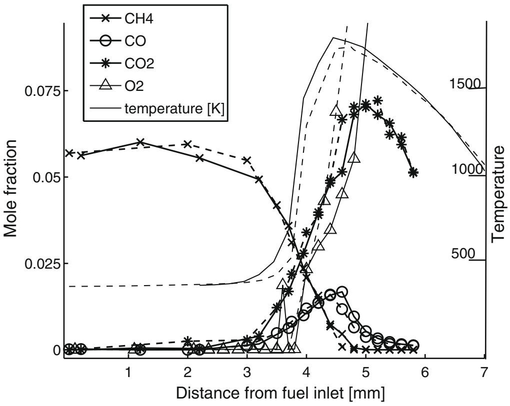

Fig. 4. Comparison of major species and temperature profiles (JP-8-doped flame, solid lines; surrogate-doped flame, dashed lines).

Figure 5 shows the degradation of the larger, C7–C14 alkanes. By comparing the ordinate scales in the two figures we immediately notice that the sum of mole fraction values of the identified alkanes in the JP-8 doped flame is much smaller than in the surrogate flame. As a result, the comparison can be only qualitative. Yet, if the identified alkanes are regarded as tracers for a broader group of large alkanes, some useful information can be drawn. As mentioned earlier, the reason for the modest presence of alkanes in the JP-8 flame has to do with the complexity of the chromatogram in Fig. 2. The jet fuel contains a large number of compounds (namely, alkenes and aromatics) presenting different isomers. Thus, the spectroscopic analysis presents a large "grassy" background and is very difficult to analyze. We only considered the contribution from the major peaks (marked by arrows in Fig. 2) that represent alkanes and some small aromatics, as indicators of similar molecules. The presence of the pedestal prevents us from performing an accurate integration. A carbon count analysis shows that only about 30% of the total carbon in the JP-8 is correctly identified and reported in Fig. 5. Conversely, the chromatogram of the

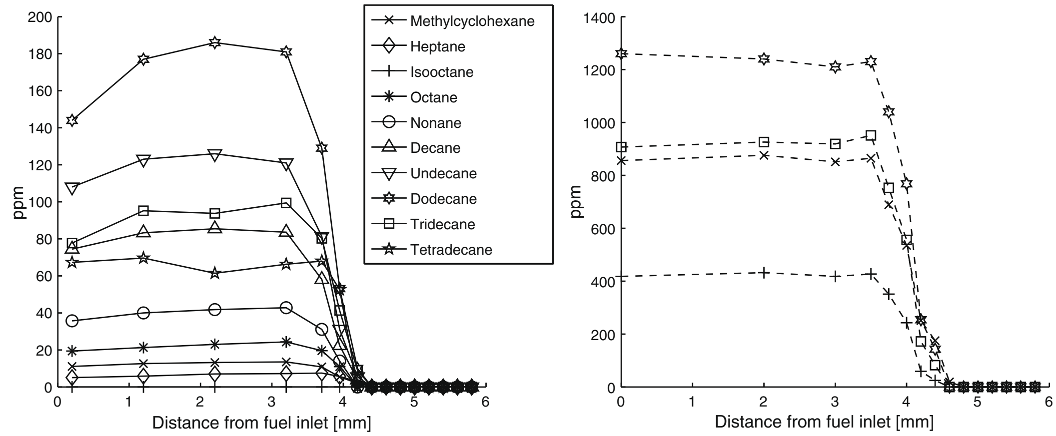

Fig. 5. Mole fractions of C7–C14 alkanes (JP-8-doped flame: left, solid lines; surrogate-doped flame: right, dashed lines).

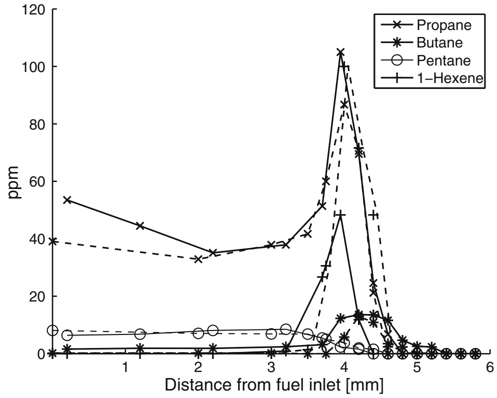

Fig. 6. Mole fractions of C3–C6 alkanes (JP-8-doped flame, solid lines; surrogate-doped flame, dashed lines).

surrogate flame consisted always of distinct peaks that could be properly integrated.

The overall pyrolysis process exhibits a pattern consistent with the disappearance of the larger and more labile hydrocarbons first, as the high-temperature region is approached. In other words, tetradecane, tridecane, dodecane, undecane, decane, and nonane vanish in a one-millimeter thick region centered at $z \approx 4.0$ mm, that is well before the region of peak heat release and highest temperature, as marked by the CO and CO_2 profiles. The data presented here are consistent with a typical hydrocarbon chemical kinetic pathway with large molecules decomposing thermally. The observed pattern is a consequence of the addition of JP-8 to the original flame and is reflective of kinetics relevant to this fuel, since the oxidation of CH_4 *per se* yields no large alkane. By comparing the two flames it appears that the pyrolysis-induced disappearance of alkane compounds is slightly shifted in the surrogate flame towards the oxidizer side. The data for the C7–C10 hydrocarbons in the JP-8-doped flame show a non-monotonic behavior, with a small "hump" in the relatively colder region at $z \approx 4.0$ mm, whose nature requires further investigation. A possible path in the oxidation of paraffins is H-abstraction from atomic oxygen [9]. Consistent with this path, small quantities of 1-octene, 1-decene, and 1-undecene were found immediately after the concentration drop of their parent alkanes. However, following the decomposition of olefines down to ethylene is extremely difficult since multiple isomers can exist, especially in the case of large molecules.

Figure 6 shows the C3–C6 alkanes with peaks of propane and butane at $z \approx 4.0$-4.1 mm. A comparison of the location of these peaks with that of the disappearance of the larger alkanes in the previous figure, starting at $z \approx 3.8$ mm and finishing at $z \approx 4.1$ mm, suggests that these smaller alkanes are the result of the thermal decomposition of the larger ones. The modest presence of these compounds at the boundary is due to impurities in the bottled methane. The surrogate mimics well the behavior of the JP-8 with respect to both peak location and magnitude of these small alkanes. Also shown in Fig. 5 are the profiles of 1-hexene, which can be attributed to the beta-scission of longer alkanes. In this case the peaks value at about 100 ppm for the surrogate-doped flame is roughly twice as large as for the JP-8-doped flame.

Figure 7 shows the FID data pertaining C2 molecules. The maximum concentration of ethane and ethylene is just after the peak of propane and butane in Fig. 6, towards the oxidizer side, since these molecules appear in the last step of the larger alkanes pyrolysis process. The peak of acetylene is shifted to the right by almost 0.4 mm, showing that this molecule is possibly generated in this flame mostly by decomposition of aromatic rings and only to a lesser extent from the alkenes. Turning to the surrogate-doped flame, we notice

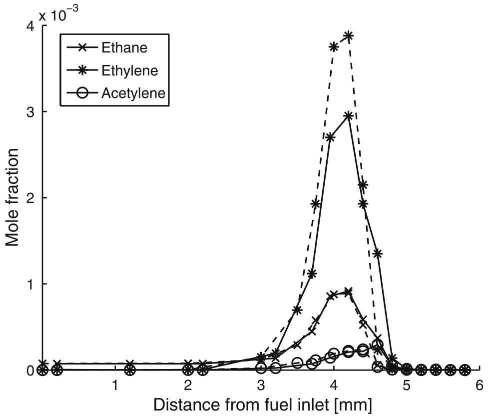

Fig. 7. Mole fractions of C2 hydrocarbons (JP-8-doped flame, solid lines; surrogate-doped flame, dashed lines).

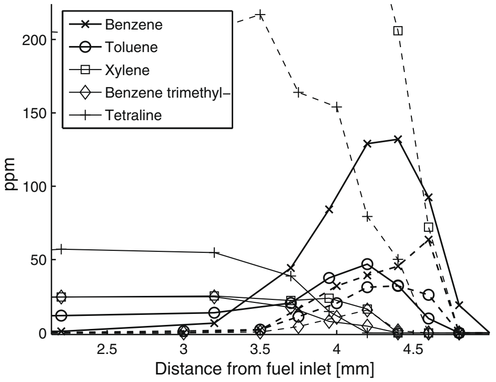

Fig. 8. Mole fractions of aromatics (JP-8-doped flame, solid lines; surrogate-doped flame, dashed lines).

very good agreement in the location and width of the peaks. There is however a difference of about 23% in the concentration of ethylene. As for 1-hexene, non-saturated hydrocarbons seem to be overly represented in the surrogate flame. This difference is even more significant if one thinks that the methane baseline is also contributing to the formation of C_2H_4. Generally, the interpretation of the profiles of the C2-hydrocarbons is, however, somewhat clouded by the contribution to these species from the oxidation of CH_4, which is the primary fuel in the feed stream. The influence of C2-chemistry in methane oxidation through methyl radical recombination is well established, whereas the concentration of even larger molecules, beyond the first generation of radical recombination, is negligible [10]. The flame in the absence of jet fuel or surrogate additives was selfsustained but was too weak to probe, since the introduction of any physical probe and associated heat losses would lead to its extinction.

We shall now investigate how aromatics evolve in these flames. Figure 8 shows how tetralin, toluene, xylene, and trimethylbenzene are converted into benzene through methyl group abstraction in the early stages of the flame, with benzene surviving the longest in the high temperature region because of its ring stabilized structure. Heavier aromatics (e.g. styrene and naphthalene) that may contribute to the formation of particulate were found in small quantities and are currently under investigation. O-Xylene, that is present in the surrogate was not detected in the JP-8/CH_4 flame. Tetralin was detected but its chromatographic peak could not be resolved since it overlaps with that of tetramethyl-benzene. The presence of xylene and tetralin in the surrogate is meant to represent the multitude of single and multi-ring aromatics that are present in JP-8. So, it is not surprising that there is no agreement at all between the two flames away from the reaction zone. More important is the evolution of the aromatics *within* the flame. The aromatic profiles exhibit the most significant difference between the JP-8 flame and the surrogate counterpart, the surrogate being incapable of mimicking the production of benzene in the JP-8 flame. Not only the benzene peak is less than half as in the surrogate flame but the shape of the peak is different and shifted towards the oxidizer side. Such a disagreement, if confirmed under conditions of incipient sooting, unlike the present ones, suggests that this surrogate, that successfully captured some overall features of JP-8 flames such as the extinction strain rate and the temperature profile [4], may fail with respect to sooting behavior, in view of the fact that the aromatics play a very important role in the formation of soot nuclei. Significantly even in the case of the JP-8-doped flame, whose chromatograms are difficult to analyze, the error associated with the identification of these small aromatics (benzene and toluene) is very small, since they do not feature isomerism.

4. Conclusions

The chemical analysis of a JP-8-doped methane counterflow diffusion flame was successfully completed by gas sampling via quartz microprobes and subsequent GC/MS analysis. The addition of the prevaporized liquid fuel results in the fragmentation of heavier alkanes to smaller ones, the onset of C2-hydrocarbons and the appearance of peak aromatic concentrations that are capable of withstanding the highest temperatures as the location of the peak temperature is approached. This sequence is more or less in line with the anticipated kinetic behavior based on thermal decomposition of large alkanes to smaller and smaller fragments and the survival of ring-stabilized aromatics at higher temperatures.

Replacement of the JP-8 with a six-component surrogate that had been successful in capturing the flame extinction behavior and its temperature profile reveal that some species within the flame, namely ethylene and benzene, are not matched correctly.

An important novelty in the experimental implementation of the study is the automation of the GC/MS analysis by using a system of multiposition valves and storage loops, so that the analysis can proceed off-line, without requiring either operator supervision or continuous flame burning. As a result, a complete flame scan requires operating the burner for only three hours, which will enable a systematic study of surrogate candidates.

Acknowledgments

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