

## COMPARISON OF AROMATICS FORMATION IN DECANE AND KEROSENE FLAMES

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Keywords : Flame Structure, Aromatics, Modelling

### INTRODUCTION

Most studies on aromatics formation in flames have been concentrated on small fuel molecules<sup>1-6</sup>. On the other hand, practical combustion systems such as automotive or airplane engines burn hydrocarbon fuels containing seven to fourteen carbon atoms. Moreover, the few kinetic studies on the combustion of liquid fuels have been oriented towards knock phenomenon and have been conducted in a temperature range (lower than 1000K) where peroxides formation dominates<sup>7,8</sup>. Aromatics and soot are formed at higher temperature, and to improve knowledge on formation of these pollutants in practical systems, there is a need for experimental and modelling studies on flames of large fuel molecule.

A few years ago, we started both experimental and modelling studies on rich premixed kerosene flames. Since kerosene is a complex mixture with alkanes as major components, the structure of a near sooting decane flame (equivalence ratio 1.9) was studied first and we developed a kinetic model which predicted the mole fraction profiles of species involved in the formation of benzene with a good accuracy<sup>9</sup>.

In this work we present the result of temperature and mole fraction measurements in sooting kerosene and decane flames. Results show that for all species except benzene there is a close similarity between the two flames so that the kinetic mechanism derived for decane is also valid for modelling kerosene combustion with only one change concerning benzene formation. A specific study was carried out to identify an additional source for aromatics formation in kerosene flames.

### EXPERIMENTAL

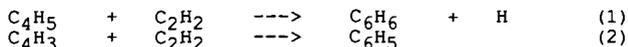
The premixed sooting kerosene flame (8.0% kerosene, 56.4% oxygen, 35.6% argon) was stabilized on a flat flame burner at low pressure (6 kPa). If kerosene was decane, this corresponds to an equivalence ratio of 2.2. Gas velocity at burner exit was 24 cm/s. A decane-O<sub>2</sub>-Ar flame with the same initial composition was stabilized and analyzed in identical conditions. Temperature and mole fraction profiles were measured along the symmetry axis. Molecular beam mass spectrometry technique was used for species analysis and Pt-Pt 10% Rh thermocouples for temperature measurements (wires diameter 50  $\mu$ m). Coating with BeO/Y<sub>2</sub>O<sub>3</sub> prevented catalytic effects, and heat losses due to radiation were compensated by electrical heating. Identification of species and calibration of the mass spectrometer have been described elsewhere<sup>10,11</sup>.

A Gilson pump manufactured for Liquid Chromatography was used to control the flow rate of kerosene. The fuel was first atomized by dragging through a small orifice by a high pressure argon jet and then

vaporized in a heated chamber. Adjustment of atomizer and vaporizer temperature was rather critical. Temperature had to be maintained between 170°C and 200°C to prevent fuel condensation or polymerization, respectively.

## RESULTS

In a previous study on the modelling of acetylene flames, the formation of the first aromatic rings was described by acetylene addition to C<sub>4</sub> species :



Kinetic parameters for these reactions were taken from Westmoreland<sup>12</sup>. The mechanism for rich decane flames was built upon addition to the acetylene mechanism of a few reactions for decane consumption<sup>9</sup>. The ability of the mechanism to predict aromatic formation depends strongly on the accuracy of the modelling of C<sub>4</sub> species and their precursors : C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>. Maximum mole fraction measured for the major molecular and active species, and for the species involved in aromatics formation, in the kerosene and decane flames have been compared in Table I.

Slight differences are observed for some species. They were not considered as significant but rather due to a lower accuracy of the measurements in the kerosene flame where very low electron energies were used to prevent fragmentations of the fuel components. However the maximum mole fraction for benzene in the kerosene flame exceeds by one order of magnitude the maximum measured in the decane flame.

This point deserved attention and a specific comparative study on the formation of benzene and two others aromatic species : phenyl acetylene and vinyl benzene in decane and kerosene flames was undertaken. To check the possibility of a change in the mechanism for aromatics formation described above, acetylene was measured as well.

### Aromatics formation in kerosene and decane flames

Detailed analysis of the structure of one flame is time-consuming and this study was limited to signal measurements. On the other hand, they were repeated for many flames with equivalence ratio in the range 1.0 - 2.5. Change in fuel composition have been done keeping constant both the overall and the argon flowrates. Gas velocity at the burner exit was 27.5 cm/s (at 298K and 6.0 kPa).

Figure 1 shows that the maximum mole fraction of acetylene in decane flames is slightly greater than in kerosene flames. In both flames, a linear increase is observed for equivalence ratios above 1.6.

Benzene measurements have been performed with an electron energy adjusted to 13 eV. For kerosene flames a second determination has been done with an electron energy of 11 eV to check the occurrence of fragmentations in the ionization source of the mass spectrometer. A similar result (linear variation of the maximum signal with the equivalence ratio) is obtained in both cases, so that we can conclude that measurements of the benzene signal are free from fragmentation

effects (Figure 2). Extrapolation of the signal gives a null value for an equivalence ratio equal to 0.8.

Measurements in the decane flame confirm that benzene is formed in lower concentration than in kerosene flames. The ratio is about 10 for an equivalence ratio of 2.0. A second difference with kerosene flames is observed for the variation of the maximum signal with the equivalence ratio, the exponent in a law  $[C_6H_6] = f(\phi)$  being greater than 1.

The curves plotted in figure 2 show that benzene formation results from two different mechanism in decane and kerosene flames. In the former, benzene is formed by reactions (1) and (2) so that the signal is proportional to acetylene and either  $C_4H_3$  or  $C_4H_5$ . Since in turn,  $C_4$  species are formed from acetylene, benzene dependence with  $[C_2H_2]^2$  must be observed. The dashed line in figure 2 corresponds to the variation with  $\phi$  of the expression  $k[C_2H_2]^2$  with the constant  $k$  adjusted so that the value calculated for  $\phi = 2.4$  coincide with the signal measured for benzene. These two curves remains very close over the whole range of equivalence ratios. ( $[C_2H_2]$  represents the maximum signal measured for acetylene).

In kerosene flames, the linear variation of the benzene signal with  $(\phi - \phi_c)$  shows that the aromatics components of the fuel contribute directly to benzene formation. The procedure adopted to change the equivalence ratio of the flames (constant values of overall an argon flowrates) leads to the following relationship between decane flowrate and  $\phi$  :

$$F_d = (F_o - F_{Ar}) \frac{2(\phi - \phi_c)}{2(\phi - \phi_c) + 31}$$

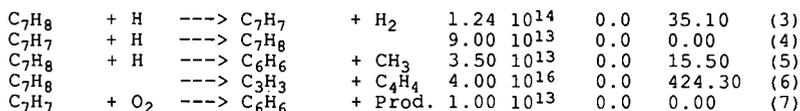
( $F_d$ ,  $F_o$ ,  $F_{Ar}$  represents respectively decane, overall and argon flowrates).

Since  $2(\phi - \phi_c)$  is small compare to 31, this expression predicts a linear variation for  $F_d$  with  $(\phi - \phi_c)$

Phenyl acetylene and vinyl benzene signals correspond as well to different sources for aromatics. In decane flames, these two species are not observed for equivalence ratios lower than 1.5, while a marked increase in the signal is observed for richer flames (Figure 3). Since these species are formed by addition of acetylene to benzene or phenyl radical we have plotted the variation of the expression  $k[C_6H_6][C_2H_2]$  versus  $\phi$ . Here again, the value of the constant  $k$  was arbitrarily adjusted in order to match either the phenyl acetylene or the vinyl benzene signal at  $\phi = 2.4$ . The same comparison in kerosene flames leads to values derived from  $[C_6H_6]$  and  $[C_2H_2]$  lower than the experimental signal when  $\phi$  is close to 1.0 (Figure 4). Expressions based on the product of the reactants signals give only an upper limit for the formation of a given species since consumption is not taken into account. Therefore, from the relative positions of the experimental points and the dashed curve, we can conclude that phenyl acetylene and vinyl benzene measured in stoichiometric or slightly rich kerosene flames result from the aromatic components of the fuel.

#### Benzene formation in kerosene flames

This comparative study clearly shows that consumption reactions of at least one aromatic species must be added to the decane mechanism to predict the structure of rich kerosene flames. Tri-methylbenzene is the main aromatic species in the kerosene that was used in this work. However, to simplify both the mechanism and the search for kinetic data, the aromatic part of kerosene was considered as toluene and the following reactions were considered to describe its consumption :



Kinetic data for these reactions have been taken from Rao and Skinner<sup>13</sup>.

#### Modelling of kerosene flames

These five reactions have been added to the mechanism validated previously for decane combustion<sup>9</sup>. Simulation of the kerosene flame has been performed with a fuel composition of 10% toluene and 90% decane. Warnatz's computation code was used with the experimental temperature profile as input data, so that the energy equation was neglected. Temperature profiles were measured by moving the burner in the vertical direction. The thermocouple was kept at a fixed position, close to the quartz cone tip, in order to take into account flame perturbation by the cone. The measurements have been repeated for various distance (d) between the thermocouple bead and the cone tip (Figure 5). In the burned gases only a cooling effect is observed, while in the main reaction zone, flame attachment shifts the profiles towards larger distance from the burner surface. No one profile is representative of the gas sampling conditions in the whole flame : profiles with very small d correspond to the temperature evolution for sampling close to the burner surface, while profiles with large d give a better description of the temperature history for a gas sample taken far from the burner. In this work, the profile measured with d = 3 mm was chosen as the best compromise between these extreme situations.

The SANDIA thermodynamic data base<sup>14</sup> has been used for species involved in  $H_2$ ,  $C_1$  and  $C_2$  submechanisms and Burcat's data<sup>15</sup> for decane and toluene combustion reactions.

Simulated mole fraction profiles are compared to the experimental ones for the reactants, the main products, and species involved in the formation of aromatics from the alkane part of the fuel (Fig. 6-9). In figure 10, prediction of the mole fraction profile is compared to experimental results for a decane and a kerosene flame. This figure shows that in the latter, benzene results mainly from the aromatic part of the fuel. This contribution can be modelled with a good accuracy by addition to the mechanism of a few reactions for the consumption of one aromatic.

#### CONCLUSION

This work was concerned with the formation of aromatics in kerosene flames. In previous studies we checked the possibility to substitute decane to kerosene to perform modelling in simpler conditions. Results showed that structure of decane and kerosene flames are similar except

for benzene that is formed in larger amount in kerosene flames. A specific study based on the systematic measurement of acetylene, benzene, phenyl acetylene and vinyl benzene in decane and kerosene flames was carried out. Variation of the maximum signal with the equivalence ratio leads to the conclusion that the aromatic part of kerosene is the main source of aromatics, while it is the addition of acetylene to C4 radicals in the decane flame. This difference was taken into account by addition of a few reactions for the consumption of toluene to the decane combustion mechanism used so far. This change leads to predictions in good agreement with the experimental mole fraction profiles in decane and kerosene flames.

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	Decane-O <sub>2</sub> -Ar flame	Kerosene-O <sub>2</sub> -Ar flame
CO	3.4 10 <sup>-1</sup>	2.9 10 <sup>-1</sup>
H <sub>2</sub> O	3.0 10 <sup>-1</sup>	2.4 10 <sup>-1</sup>
H <sub>2</sub>	2.3 10 <sup>-1</sup>	3.0 10 <sup>-1</sup>
CO <sub>2</sub>	6.0 10 <sup>-2</sup>	7.0 10 <sup>-2</sup>
H	8.9 10 <sup>-3</sup>	1.2 10 <sup>-3</sup>
OH	2.7 10 <sup>-4</sup>	3.7 10 <sup>-4</sup>
C <sub>2</sub> H <sub>4</sub>	5.3 10 <sup>-2</sup>	1.7 10 <sup>-2</sup>
C <sub>2</sub> H <sub>2</sub>	6.1 10 <sup>-2</sup>	3.9 10 <sup>-2</sup>
C <sub>4</sub> H <sub>2</sub>	1.4 10 <sup>-3</sup>	1.8 10 <sup>-3</sup>
C <sub>4</sub> H <sub>4</sub>	5.9 10 <sup>-4</sup>	1.1 10 <sup>-3</sup>
C <sub>4</sub> H <sub>5</sub>	3.3 10 <sup>-5</sup>	1.0 10 <sup>-4</sup>
C <sub>6</sub> H <sub>6</sub>	1.2 10 <sup>-4</sup>	2.2 10 <sup>-3</sup>

Table I

Comparison of the maximum mole fraction in decane and kerosene flames (equivalence ratio : 2.2, pressure : 6 kPa).

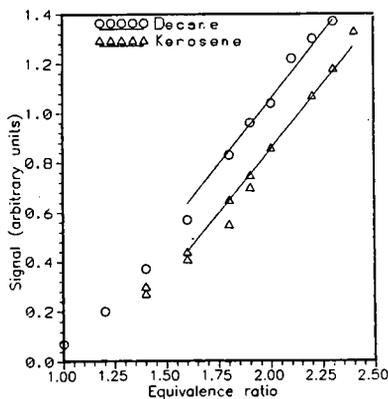


Figure 1  
Evolution with  
the equivalence ratio  
of the maximum signal of C<sub>2</sub>H<sub>2</sub>

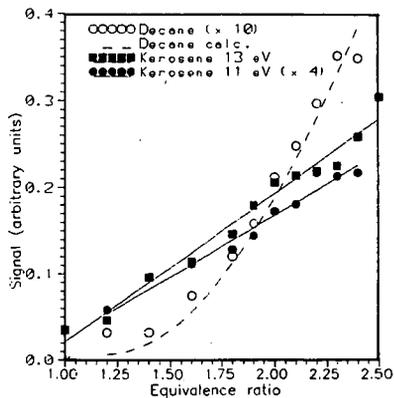


Figure 2  
Evolution with  
the equivalence ratio  
of the maximum signal of C<sub>6</sub>H<sub>6</sub>

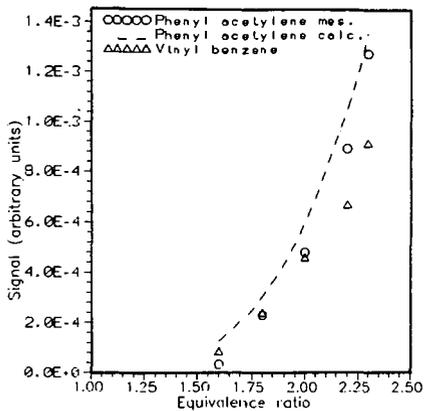


Figure 3  
Decane flames

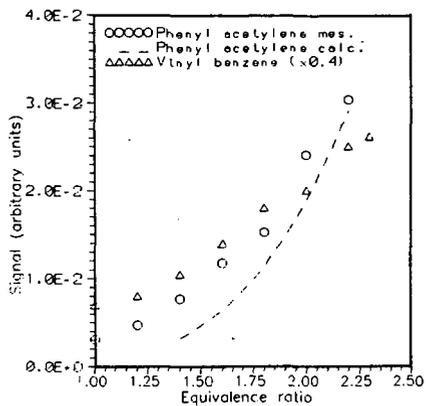


Figure 4  
Kerosene flames

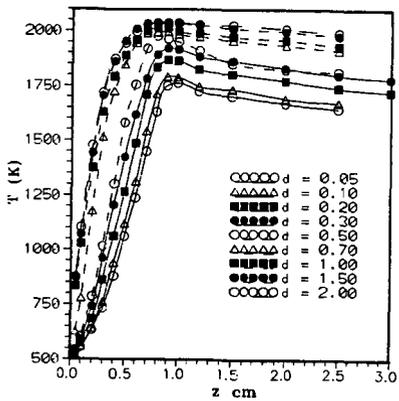


Figure 5  
Temperature profiles  
in a  $\varnothing = 2.2$  Kerosene- $O_2$ -Ar flame

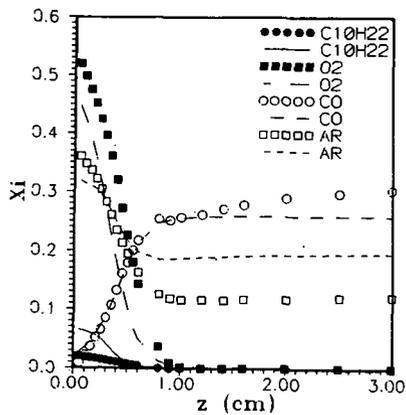


Figure 6  
Comparison of experimental (points)  
and simulated (curves)  
mole fraction profiles  
 $\varnothing = 2.2$  Kerosene- $O_2$ -Ar flame

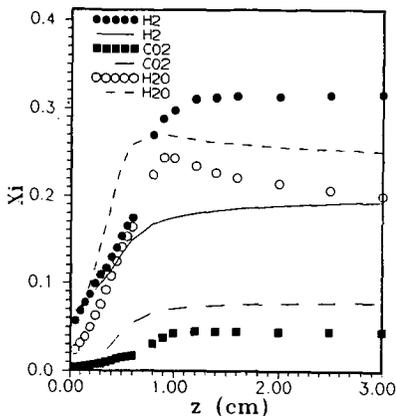


Figure 7  
Comparison of experimental (points)  
and simulated (curves)  
mole fraction profiles  
 $\phi = 2.2$  Kerosene-O<sub>2</sub>-Ar flame

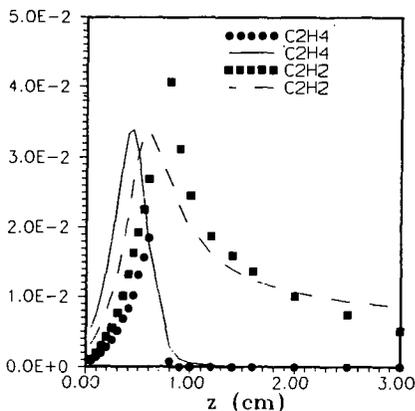


Figure 8  
Comparison of experimental (points)  
and simulated (curves)  
mole fraction profiles  
 $\phi = 2.2$  Kerosene-O<sub>2</sub>-Ar flame

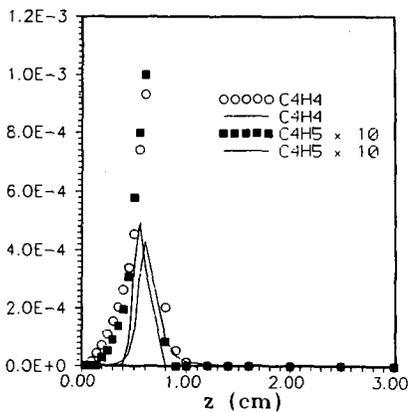


Figure 9  
Comparison of experimental (points)  
and simulated (curves)  
mole fraction profiles  
 $\phi = 2.2$  Kerosene-O<sub>2</sub>-Ar flame

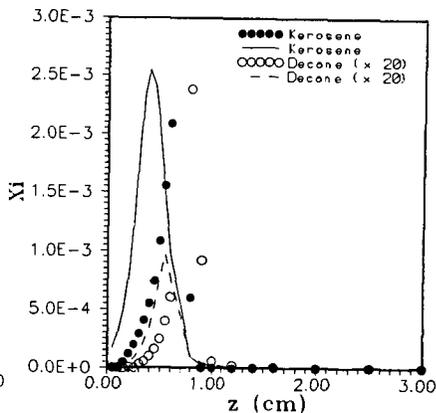


Figure 10  
Comparison of experimental (points)  
and simulated (curves)  
mole fraction profiles  
 $\phi = 2.2$  Decane and Kerosene flames