

A SHOCK TUBE INVESTIGATION OF SOOT FORMATION FROM TOLUENE/METHANOL MIXTURES. Alexiou, A. and Williams, A., Department of Fuel and Energy, Leeds University, Leeds, LS2 9JT, UK, and Abdalla, A.Y., Helwan University, Cairo, Egypt.

ABSTRACT

Soot formation in toluene and toluene/methanol/argon mixtures was studied behind reflected shock waves using a laser beam attenuation technique. The experiments were undertaken over the temperature range 1484 - 2232K, pressure range 1.69 - 2.77 bar and total carbon atom concentrations for the toluene alone in the range 2.7×10^{17} - 1.1×10^{18} atoms/cm³ (0.5 to 1.5 mol %) and for toluene/methanol mixtures in the range 23 - 66 mol % methanol.

The results indicate that the soot yield decreases with an increase in methanol concentration but the effect is not marked until the addition is greater than 50% methanol. The rates of soot formation from toluene and toluene/methanol mixtures have been determined and exhibit an Arrhenius dependence which was expressed by a correlation equation. The induction periods for soot formation were measured and were found to increase with methanol addition although the maximum soot yields were found to decrease.

INTRODUCTION

Methanol is of considerable practical significance as an alternative fuel or as a blend with petroleum for internal combustion engines. Earlier studies have shown that methanol produces much less soot than typical hydrocarbon fuels but the addition of aromatics greatly increases soot formation (1,2). In contrast, in diesel engines, blends of diesel fuel oil with methanol produce substantially smaller amounts of soot. Surprisingly there has been little previous work on the gas phase combustion of these mixtures and only the benzene-methanol system has been studied by shock-tube techniques (1). In diffusion flames the decreasing fuel type is given by Glassman (3): aromatics > acetylene > olefins > paraffins > alcohols. Since there is usually agreement in the behaviour in diffusion flames and in shock tubes concerning soot tendency, we undertook a shock tube study to evaluate the soot suppression effect. We confined our work to toluene and toluene/methanol mixtures and we present in this paper data on the soot suppression effect of methanol added to toluene mixtures, rather than the alternative approach of adding aromatic fuels to enhance the radiation from methanol flames.

EXPERIMENTAL

The experiments were performed in reflected shock waves and details of the shock tube facility have been previously published (4). The test gas mixtures were prepared manometrically, ANALAR toluene and methanol were further purified by repeated freezing and evacuation. The experimental conditions are summarised in Table 1.

A laser technique was employed and the absorption of the beam at 632.8 nm was used to measure the concentration of soot. Only toluene concentrations up to 1.5 mol % could be studied because of the high levels of absorption. The soot yields were calculated according to Graham's model (5).

$$Y = \frac{C_{\text{soot}}}{C_{\text{total}}} = \left[N \rho \lambda / 72 \cdot \pi \cdot E_{(m)} \cdot \lambda \cdot C_{\text{total}} \right] 2n \left[I_{(o)} / I_{(t)} \right] \quad (1)$$

where C_{soot} = concentration of the particulate carbon per unit volume, C_{total} = the total concentration of carbon atoms per unit volume, N = Avogadro's number, ρ = density of soot, λ = wavelength of the measurement, I = intensity of radiation which is function of time, t , $E_{(m)}^-$ = imaginary part of the function $(m^2-1)/(m^2+2)$, m = the complex refractive index.

Since the soot yield is a function of the refractive index an accurate value is necessary. Many workers, including our previous work, have used the value of Lee and Tien (6) which at this wavelength would give a value of $E_{(m)}^- = 0.174$. In the present work we used the value of $E_{(m)}^- = 0.253$ based on the in flame measurements of Charalampopoulos and Chaung (7). If we had used the Lee and Tien data we would have overestimated the total soot yield as previously observed by Frenklach et al (10); indeed if data by some of the earlier researchers had been used the position would have been worse.

EXPERIMENTAL RESULTS

The results obtained in the toluene pyrolysis experiments are shown in Fig. 1. The amount of soot yield increased monotonically with the amount of toluene pyrolysed. The maximum slope on the oscillogram was measured and defined as the apparent rate of soot formation. The correlation equation of apparent rate of toluene pyrolysis is shown in Fig. 2 for the different concentrations which are given in Table 1. The RH on this figure stands for the fuel concentration term, in this case toluene. The rates exhibited an Arrhenius dependence given by a correlation equation:

$$R_{\text{soot}} \text{ (mol/m}^3\text{s)} = 1.38 \cdot 10^8 [C_7H_8]^{1.32} \exp(-11,900/T) \quad (2)$$

The activation energy which is valid up to 1950 K (1532 - 1950 K) is in agreement with the values quoted by Simmons and Williams (9), namely 99 - 118 kJ/mol depending on the value of the refractive index. The constant and the fuel exponent have changed because of the improved accuracy of the present data. The fuel exponent is now consistent with the value of 1.48 reported by Wang et al (8).

During the course of toluene/methanol pyrolysis mixtures an induction time was observed before any absorption occurred. This induction time was the time between the reflected shock wave and the onset of soot formation. Figure 3 shows the results for the induction times. As it can be seen the induction time increased with the amount of methanol added to the toluene. The following equation for calculating the soot induction time, t_{soot} , based on a 5% rise in signal was obtained.

$$t_{\text{soot}} = 5.448 \cdot 10^{-5} [\text{total fuel}]^{1.92} \exp(-16,644/T) \quad (3)$$

where [total fuel] = $[C_7H_8 + CH_3OH]$. The soot yield decreased monotonically with the increase of the amount of methanol added to toluene as shown in Fig. 4.

The apparent rate of toluene/methanol pyrolysis are measured in the same way as toluene and could be expressed as follows:

$$R_{\text{soot}} \text{ (mol/m}^3\text{s)} = 1.9 \cdot 10^5 [\text{total fuel}]^{-0.412} \exp(-15,300/T) \quad (4)$$

which is valid in a temperature range 1580 - 1950 K.

Fig. 5 shows the correlation equation of the apparent rate of soot formation of toluene methanol mixtures at different concentrations (Table 1).

We attempted to obtain a correlation equation incorporating both $[C_7H_8]$ and $[CH_3OH]$ terms, but we had great difficulty in separating the terms in an equation

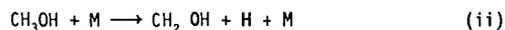
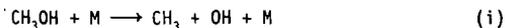
of, for example, the form $R_{\text{soot}} = C_1 [C_7H_8]^a \exp(-E_1/RT) - C_2 [CH_3OH]^b \exp(-E_2/RT)$. Even though the correlation which we obtained is not ideal it can be used to express the rates and by comparing equations (2) and (4) conclusions could be made about the role of added methanol. The experimental determined exponent of the fuel term indicates that an increase of methanol concentration will decrease the apparent rate of soot formation. In addition there are differences in the activation energies and in the pre-exponential factor which are very significant.

DISCUSSION

In the early work by Graham (5) the extent of conversion of initial carbon in the fuel to soot was determined at 2.5 ms. Based on this observation time the soot yield fell rapidly with increasing temperature from 100% at ≈ 1800 K to less than 5% at 2300 K. He developed his well-known scheme which involved condensation reactions at around 1000 to 1800 K and fragmentation reaction above that temperature. Later Frenklach (10) demonstrated that the soot yield is not universal, but is dependent on experimental controllable variables such as observation time, total pressure and laser wave-lengths. He postulated another model for soot formation included polymerisation and fragmentation reactions.

In our work we measure the maximum conversion of the fuel to soot irrespective of the time. As is shown in Fig. 1, the maximum yield occurs at ≈ 1900 K above which fragmentation takes place resulting in a reduction in soot yield. Based on this observation we do agree with Frenklach (10) that the soot yield maximum is not universal and the condensation, fragmentation reactions take place according to experimental conditions.

The unimolecular decomposition of methanol at high temperature is considered to involve two reactions (11).



A computer model for toluene/methanol pyrolysis has been developed in which the initiation reactions (i) and (ii) of methanol together with the low activation energy reactions of H and CH_3 with CH_3OH has been used in order to evaluate the reduction of the soot yield. Preliminary results at about 1900 K not surprisingly demonstrate the importance and the rapid formation of OH and the products H_2O and CO increasingly as methanol is added to toluene. These reactions are also responsible for the increased soot induction period. Therefore it seems that the presence of OH radicals when methanol is added to toluene leads to the behaviour observed experimentally. These results are consistent with the role of OH as an oxidant in carbon-forming flames (12).

More recently, Frenklach (1), in his work on alcohol addition, explained that the reduction is also due to hydrogen atom scavenging. Alcohols undergo the H-abstraction reactions which results in the reduction in the superequilibrium of H atoms. In toluene pyrolysis the overshoot of hydrogen atoms beyond their equilibrium concentration is responsible for the propagation of the ring growth process. Our work is consistent with this since we demonstrate this soot reduction and this effect is not marked until the addition is greater than 50 mol % methanol.

Finally it should be noted that these results are consistent with the behaviour of methanol in fuel blends for gasoline engines. In the case of diesel engines the marked reduction in soot yields cannot arise from gas phase reactions alone and must arise from some physical change such as selective droplet evaporation or disruptive burning.

CONCLUSIONS

The results of the present study show that methanol acts as a suppressing agent for soot formation. However this reduction is only achieved when the presence of methanol exceeds more than 50% in the total fuel mixture to be pyrolysed.

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TABLE 1

	% Mol in Argon	T (K)	P (bar)	Carbon (atoms/cm ³)
1	0.5 C ₇ H ₈	1580 - 2170	1.81 - 2.62	2.54 x 10 ¹⁷ - 3.01 x 10 ¹⁷
2	1.0 C ₇ H ₈	1532 - 2114	1.74 - 2.70	5.83 x 10 ¹⁷ - 6.56 x 10 ¹⁷
3	1.5 C ₇ H ₈	1584 - 2070	1.93 - 2.89	9.38 x 10 ¹⁷ - 1.07 x 10 ¹⁸
4	1.0 C ₇ H ₈ + 0.3 CH ₃ OH	1600 - 2096	1.85 - 2.67	6.19 x 10 ¹⁷ - 6.85 x 10 ¹⁷
5	1.0 C ₇ H ₈ + 0.5 CH ₃ OH	1580 - 2123	1.82 - 2.77	6.33 x 10 ¹⁷ - 7.19 x 10 ¹⁷
6	1.0 C ₇ H ₈ + 1.0 CH ₃ OH	1610 - 2087	1.88 - 2.79	6.65 x 10 ¹⁷ - 7.84 x 10 ¹⁷
7	1.0 C ₇ H ₈ + 2.0 CH ₃ OH	1664 - 2050	2.06 - 2.79	8.17 x 10 ¹⁷ - 8.94 x 10 ¹⁷

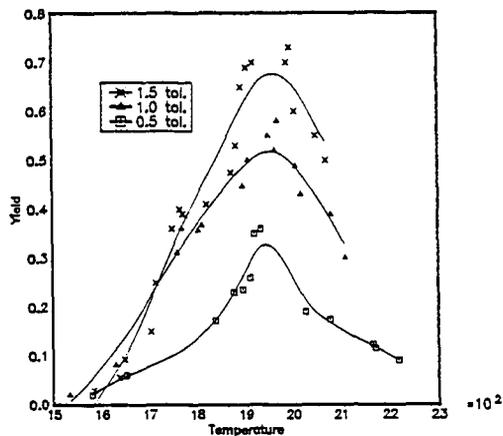


Fig. 1. Comparison of the soot yield at different toluene concentrations.

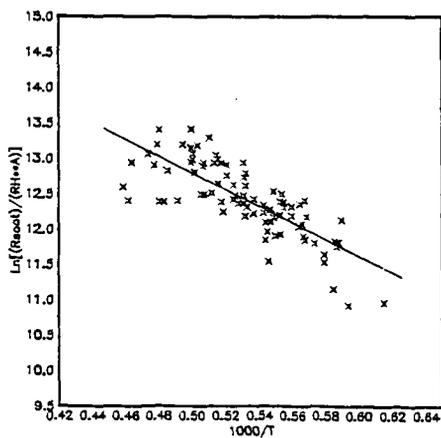


Fig. 2. Correlation equation of apparent rate of soot formation from toluene pyrolysis at different concentrations.

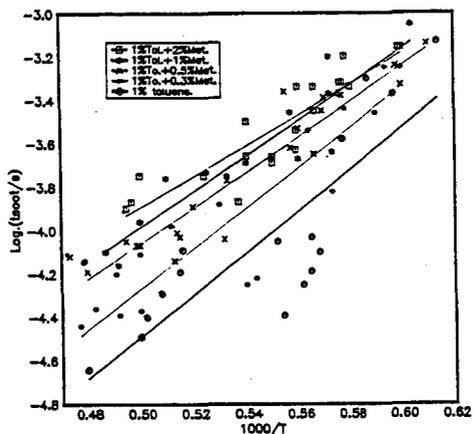


Fig. 3. Induction times for soot appearance at different toluene/methanol concentration.

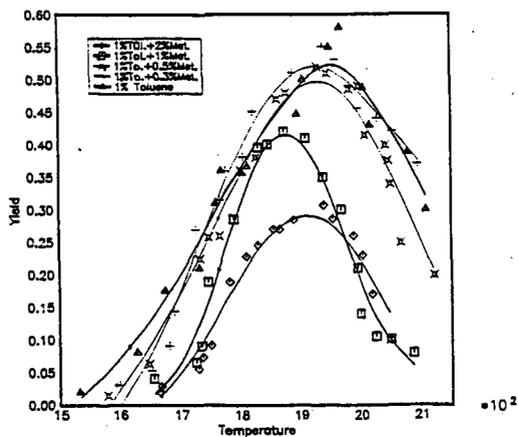


Fig. 4. Comparison of the soot yield at different toluene/methanol concentrations.

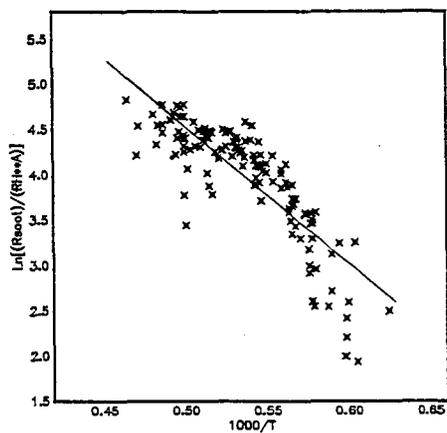


Fig. 5. Correlation equation of apparent rate of soot formation from toluene/methanol pyrolysis at different concentrations.