

Detailed Chemical Kinetic Modelling of Aromatic Diesel Fuel Components

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The ability to predict the inter-conversion of poly-aromatic hydrocarbons (PAHs) of different toxicities and emissions of fine carbon-based particles from Diesel engines are of increasing relevance given their harmful effects. The matter is complicated by the complexity of Diesel fuels and model fuel blends have to be used in numerical simulations of practical engines. The use of aromatic fuel component(-s) in such blends provides a route towards the modulation of the propensity of a fuel to produce such emissions – provided the chemistry is sufficiently well understood. The current work extends past efforts related to the oxidation of 1-methyl naphthalene, which has been identified as a potential key component of surrogate Diesel fuels. Specifically, 1-methyl naphthalene may be used to modulate sooting tendencies and the methyl groups on aromatic rings (e.g. xylenes and tri-methyl benzenes) have also been identified as important in the context of fuel reactivity.

Background

Past work on the oxidation of single-ring aromatics include the studies by Emdee et al. [1], Lindstedt and Maurice [2] and Klotz et al. [3]. Studies of two-ringed structures are less prevalent. However, Shaddix [4] investigated the oxidation of naphthalene and 1-methyl naphthalene under turbulent flow reactor (TFR) conditions and Pitsch [5] proposed a kinetic mechanism for the oxidation latter species. Lindstedt et al. [6] considered a wide range of PAH formation paths and Dagaut and co-workers [7,8] studied the oxidation of m-xylene and 1-methyl naphthalene under jet-stirred reactor (JSR) conditions. The chemistry of soot/PAH growth and oxidation tends to be slow compared to flow time-scales and detailed studies of turbulent flames are less prevalent. Lindstedt and Louloudi [9] reported a study of the formation and oxidation of soot in turbulent diffusion flames using a transported PDF method combined with the method of moments and with a soot surface oxidation analogy based on naphthalene. The explicit functional form of the latter was obtained using the systematic reduction technique of Peters (e.g. Peters and Rogg [10]). The chemistry of naphthalene and indene were subsequently explored by Lindstedt et al. [11] in an effort to further evaluate the ability of a fixed sectional method [12] to compute soot particle size distributions in the size range from < 1 nm to 100 nm. Critical reaction steps in the oxidation process were identified and subjected to detailed investigations via quantum mechanical methods using Gaussian-03 [13] with rate constants determined from the potential energy surfaces using variable transition state theory and Rice-Ramsperger-Kassel-Marcus/master equation approaches. The critical reaction paths included $C_9H_7 + HO_2/O_2$ channels and the linkage of C_5 and C_6 rings as part of the oxidation process [11]. The current work further assesses the progress made in the understanding of the associated reaction paths for two-ringed aromatics. In particular, attention is given to 1-methyl naphthalene which has

been identified as a means of modulating the sooting propensity of surrogate Diesel fuels. The applied detailed chemical reaction mechanism was initially created from reaction classes derived from studies of the oxidation and pyrolysis of toluene, benzene and cyclo-pentadiene. Accurate thermodynamic data is particularly important given the large number of isomerisation reaction present in detailed reaction sequences for PAH formation/oxidation. As part of the present work, earlier estimates, often obtained on the basis of variants of Benson's additivity method, were replaced by data derived from quantum mechanical methods using Gaussian-03 (at the G3MP2B3 level) in combination with density functional theory (DFT) analysis for internal rotations. The validation of the derived mechanism was achieved by comparison with experimental data from jet stirred and turbulent flow reactors.

Results and Discussion

The 1-methyl naphthalene chemistry was initially tested under JSR conditions using data from Mati et al. [8] for the conditions shown in Table 1. The data is suitable for clarifying the decomposition channels of the fuel and provides extensive information on stable species.

Φ	P (atm)	T (K)	O ₂	C ₁₁ H ₁₀
0.5	1.0	1097-1290	0.0270	0.001
1.0	1.0	1094-1400	0.0135	0.001
1.5	1.0	1147-1440	0.0090	0.001

Table 1: Experimental and modelling conditions for the oxidation of 1-methyl naphthalene in a jet-stirred reactor [8]. The species concentrations correspond to mole fractions.

Shaddix [4] performed gas-phase sampling to study the oxidation of 1-methyl naphthalene in a TFR and obtained time-dependent concentration

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Towards Clean Diesel Engines, TCDE 2009

profiles for major species under the conditions shown in Table 2. In the current study, computations were performed corresponding to all the experimental conditions. The focal point of the current discussion is the ability of the developed mechanism to reproduce the oxidation behaviour under fuel rich conditions, due to the importance to the formation of particulates. However, the obtained agreement was similar for fuel lean cases.

Φ	P (atm)	T (K)	O ₂	C ₁₁ H ₁₀
1.0	1.0	1169	0.01485	0.0011
1.5	1.0	1166	0.00990	0.0011

Table 2: Experimental and modelling conditions for the oxidation of 1-methyl naphthalene in a turbulent flow reactor [4]. The species concentrations correspond to mole fractions.

In contrast to other studies, the developed mechanism does not feature any global reaction steps and generally reasonable agreement was obtained between computations and the experimental data obtained by Mati et al. [8] as exemplified for fuel rich oxidation shown in Fig. 1.

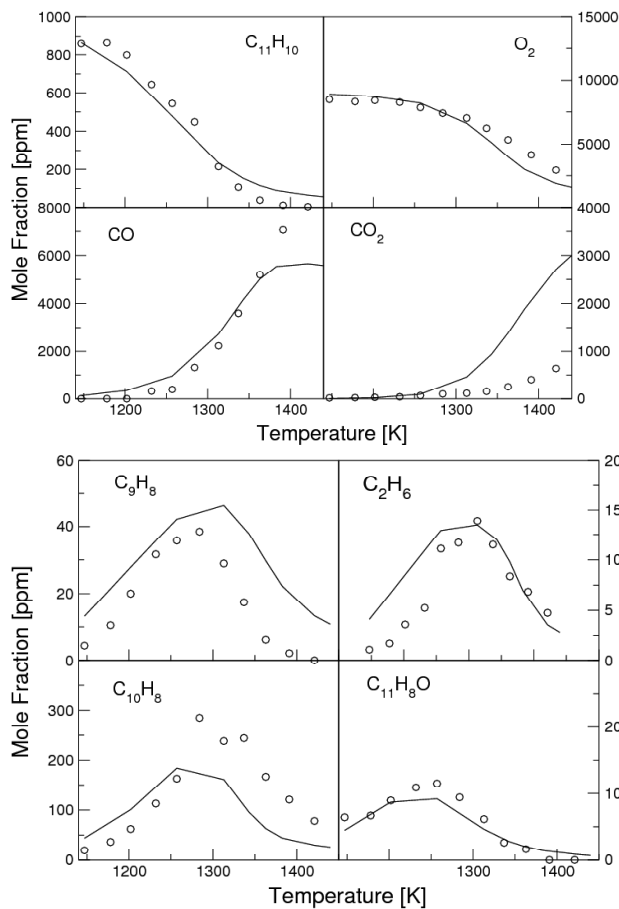
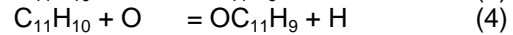
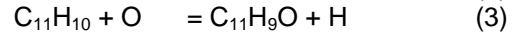
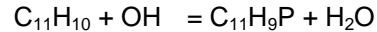
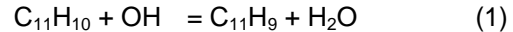
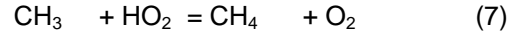
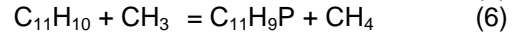
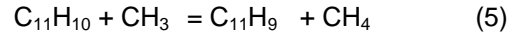


Fig. 1: Major and intermediate species for 1-methyl naphthalene oxidation in jet-stirred reactor. $\Phi = 1.5$, $P = 1$ atm and $T = 1147 - 1440$ K. Circles are experimental data [8] and the solid lines the current simulations.

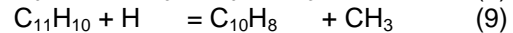
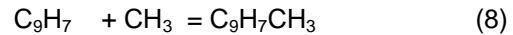
A rate analysis was performed at a temperature of 1202 K to highlight key reaction pathways. The 1-methyl naphthalene oxidation is overall controlled by reactions (1) to (4). Reaction (1) is the major consumption channel and contributes up to 25%. Reaction (4) is responsible for 23% of consumption and reactions (2) and (3) contribute a further 16% and 12% respectively. The 1-methyl naphthyl radical, formed by the benzylic H removal (1), is partly recycled back to C₁₁H₁₀ via H recombination. The pathway leading to the 1-naphthyl methoxy radical (C₁₁H₉O) is responsible for ~70% of the naphthalene production.



Methane is produced by reactions (5) and (6) which contribute 67% and 22% respectively. The rate of reaction (5) is increased by 21% and reaction (6) by 7% compared to the fuel lean case. Reaction (7) is responsible for less than 2% of CH₄ production.



The CH₃ radical pool is predominantly formed via reactions (8) and (9). Reaction (8) is responsible for 80% of the methyl radical production and reaction (9) contributes 15%. The consumption of the methyl radical is strongly influenced by reactions (5) and (6), which contribute 30% and 11% respectively. The methyl radical recombination leading to ethane (C₂H₆) formation contributes up to 26%, compared to the lean case where it is responsible for the 32% of the total CH₃ consumption. It may be noted that ethane levels are reproduced with reasonable accuracy as shown in Fig. 1.



The 1-methyl-4-naphoxy radical (OC₁₁H₉) leads almost exclusively to the 1-methyl indenyl radical (C₉H₆CH₃), which in turn leads to benzofulvene and 1-methyl indene (C₉H₇CH₃) via H addition. The former subsequently leads to naphthalene via isomerisation reactions. The pathway is responsible for 5% of the total naphthalene production and suggests that the linkage between C₅ and C₆ ring structures [6] also prevails to some extent at lower temperatures. The overall distribution between single and two ring aromatics is reasonably well reproduced as shown in Figs. 1 and 2.

Conclusions

The current work has shown that the breakdown products resulting from the oxidation of 1-methyl naphthalene can be modeled with reasonable accuracy. The actual distribution of the primary two-ring and secondary single-ring aromatics is important as it can be expected that the product distribution will influence the distribution of subsequent PAHs formed during the fuel oxidation process. Irrespective of such considerations, the ability to represent the chemical kinetics of a key surrogate fuel component represents an important step towards the creation of increasingly accurate surrogate Diesel fuel blends for the use in practical engine simulations following the application of simplification techniques.

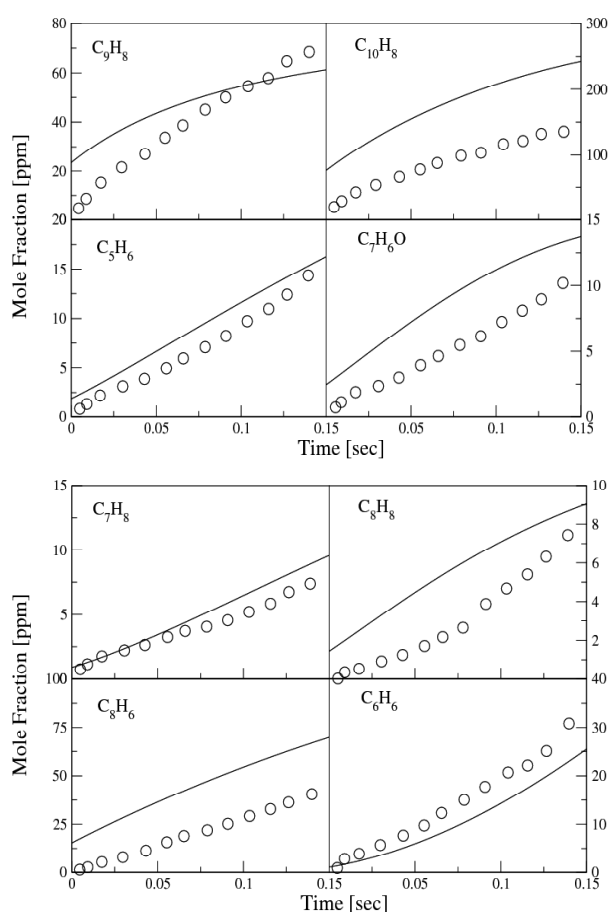


Fig. 2: Examples of concentration profiles of species during 1-methyl naphthalene oxidation in a flow reactor ($\Phi = 1.0$, $P = 1 \text{ atm}$, $T = 1169 \text{ K}$). Circles are experimental data [4] and solid lines the current simulations.

Acknowledgement

The authors are grateful for the financial support of EOARD under award FA8655-06-1-3052 and BP Global Fuels Ltd.

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