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Full Length Article

Modelling analysis of PAH and soot measured in a premixed toluene-doped methane flame

C. Russo[a], A. Ciajolo[a], A. D'Anna[b], M. Sirignano[b,*]

[a] *Istituto di Ricerche sulla Combustione – CNR, Piazzale V. Tecchio 80, 80125 Napoli, Italy*
[b] *Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale – Università degli Studi di Napoli Federico II, P.le Tecchio 80, 80125 Napoli, Italy*

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ABSTRACT

A detailed gas-phase kinetic model coupled with a multi-sectional approach for the particle phase was used for inferring the effect of toluene addition on the sooting structure of a fuel-rich laminar premixed methane flame. Premixed methane flames at different C/O ratios established the reference environments to gain insight on the influence of toluene addition.

Experimental data derived from a detailed analysis of the combustion aerosol sampled along the methane flame and the toluene-doped flame, burning in similar temperature conditions, were compared with the predictions of the model to assess its sensitivity to small changes in the fed mixture composition.

Modeling results predicted reasonably well the gas- and the particle-phase concentrations. Overall, the effect of small amounts of toluene on the sooting yield and structure of the methane flame strongly tending toward the sooting structure typical of aromatic fuels, was observed. Experimental evidences and modeling results suggest that the relative importance of soot inception and surface growth by C_2H_2 and PAH onto existing particles or aggregates is significantly affected by toluene addition.

1. Introduction

Surrogate mixtures composed of aliphatic (linear and branched) and aromatic hydrocarbons are useful to study and foresee the behavior of liquid petroleum-derived fuels as gasoline, diesel oils, and jet fuels [1]. Among aromatic hydrocarbons, toluene is the simplest alkylated aromatic compound representative of aromatic components of gasolines, but also considered as a prototypical fuel for the investigation of the combustion behavior of large aromatic components of diesel and jet fuels [2]. Most of the experimental work on toluene chemistry has regarded pyrolysis in flow reactor and oxidation in a jet stirred reactor (see Yuan et al., 2015 [3] and references therein). Some works on toluene chemistry have been focused on the analysis of the gas phase in flames burning pure toluene at low pressures [4–7] and in flames burning aliphatic hydrocarbons as ethylene [8] and methane [9] doped with toluene. Botero et al. [10] analyzed soot collected from diffusion flames of n-heptane, toluene, their mixture, and gasoline by means of HRTEM measurements. Toluene soot exhibited the longer, less curved and more stacked fringes. This finding was in agreement with literature where it is reported that the combustion of aliphatic fuels generates soot particles with a lower degree of graphitization than those produced by aromatic fuels [11–14]. More recently, the sooting behavior of toluene-doped flames was investigated in a high-pressure diffusion flame [15] and in laminar premixed flames of n-heptane [16] and methane [17]. Russo et al. [17] reported on a considerable impact on soot formation and properties by the addition to a premixed methane flame of only 10% of the total carbon as toluene. Zhang et al. investigated the effect of *n*-propylbenzene addition to n-dodecane on soot formation and aggregate structure in a laminar coflow diffusion flame [18]. They showed that aromatic fuel chemistry strongly affects soot inception.

In the present work, the effect of toluene addition to methane on the sooting structure of fuel-rich laminar premixed flames burning in similar temperature conditions and C/O ratio [17] was investigated by a detailed gas-phase kinetic model coupled with a multi-sectional approach for the particle phase. Experimental and modeling results of the basic methane [11,19,20] and toluene-doped flames [17] were compared with the aim of a deeper understanding of the effect of aromatic addition on particle gas–phase precursors and on the different stages of soot formation and growth. The experimental data of the main combustion mixture components in gas phase are already published, nevertheless they are important for validating the detailed gas-phase kinetic modeling. Concentration profiles of individual PAH are, instead, unpublished data. Overall, the use of Multi-Sectional method and

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* Corresponding author.
E-mail address: mariano.sirignano@unina.it (M. Sirignano).

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Table 1
Operative conditions of the flames.

	CH_4		O_2		Toluene		Max T	Max T location
	SLPM	%	SLPM	%	SLPM	%	K	mm
Methane Flame	4.47	54.5	3.73	45.5			1760 ± 25	2 ± 0.3 mm
Toluene-doped flame	4.47	54.1	3.73	45.1	0.066	0.8	1780 ± 25	2 ± 0.3 mm

reaction analysis performed allows to better understand the role of aromatics in the fuel mixture and explore combustion conditions not accessible by experiments.

2. Experimental methods

A laminar premixed flame was stabilized on a McKenna (Holthuis & Associates) water-cooled burner. The target experimental conditions are presented in Table 1. The methane flame establishes the base environment in this study [11,19,20], toluene is then added to the fed mixture at 0.8% (about 10% of the fuel C). Even though the typical value of aromatics percentage in gasoline is much higher (around 30%), this value of toluene doping was sufficient to affect soot formation without changing the temperature field, so that the toluene doping effect could be studied without interference of such parameter. A more systematic investigation on the effect of different amounts is under study.

The cold gas velocity of the toluene-doped flame was nearly equal to that of the baseline methane flame (5 cm/s) at STP conditions.

Flame temperature was measured using a fast-response silica-coated fine wire Pt/Pt-13% Rh thermocouple and corrected for the radiative losses [17]. The temperature profile was considered quite unperturbed and a reliable reference for adjusting the axial coordinates of intrusive sampling data. Gaseous and condensed phases were sampled from the flames by a stainless steel, water-cooled, isokinetic probe. On-line gas analysis of C1–C6 hydrocarbon species was carried out using an HP5890A gas chromatograph equipped with a 7515 Chrompack Al2O3 = KCl 50m_0.92-mm (i.d.) capillary column and a flame ionization detector (GC-FID). On an HP5700A gas chromatograph equipped with an 8700 Alltech coaxial column and a thermal conductivity detector (GC-TCD) the analysis of CO_2, CO, H_2, and N_2 was performed [17]. Condensed phases collected in an ice-cooled trap and on a teflon filter placed along the sampling line were extracted with dichloromethane (DCM) to separate the soluble condensed species, named DCM-extract, from soot. Twenty-four polycyclic aromatic hydrocarbons (PAH) [17] with molecular masses up to 300 u were detected and quantified by gas chromatography/mass spectrometry (GC-MS) of the DCM-extract by an HP5890 gas chromatograph coupled with an HP5975 mass spectrometer equipped with an HP-5MS crosslinked 5% PhMe siloxane 30 m × 0.25 mm × 0.25 µm. More information on the temperature, gas-phase concentration measurements, condensed phases sampling and treatments can be found elsewhere [17,19].

3. Kinetic model

3.1. Gas-Phase chemistry and PAH formation

The mechanism of oxidation and pyrolysis of small aliphatic hydrocarbons was built onto the GRI-Mech 3.0 for C1 and C2 species and the Miller and Melius mechanism for C3 and C4 species [21]. It has been used to model several flame conditions at atmospheric pressure showing reasonable ability to predict the structures of aliphatic and aromatic hydrocarbon flames [22].

In rich combustion, acetylene and methane are the most abundant intermediate species. Benzene formation was considered to derive from the addition of n-C4 radicals to C_2H_2 and the self-combination of propargyl radicals (C3-route) – the most effective one. The formation of benzene from toluene decomposition, i.e., benzyl radical and its oxidation to form also cyclopentadienyl radicals, becomes important when toluene is present in the fuel mixture. The sequential addition of C_2H_2 to phenyl radical (hydrogen abstraction acetylene addition – HACA – mechanism [23,24]) and the combination of resonantly-stabilized radicals, i.e. the combination of two cyclopentadienyl radicals and the combination of benzyl and propargyl radicals [25], were the pathways considered for the growth of aromatic cycles up to pyrene. Recently, HAMA (hydrogen abstraction methyl addition) mechanism [26] has been proposed. The mechanism is not considered here, although it could play a role for the formation of PAH. The resonantly-stabilized radical routes for aromatic growth were particularly active during the oxidation of toluene. The four-ring PAH as pyrene (molecular weight MW = 200 u), was considered as the largest aromatic compound in gas phase. All species with molecular weight MW > 200 u were treated as particles and thus divided into classes, or lumped species. The gas-phase kinetic mechanism consists of 460 reactions involving 120 species. Details of the reaction rates used are reported in Refs. [27,28].

3.2. Advanced multi-sectional approach

The Multi-Sectional model, previously set up [22,27–29], was here used without making any modification or change in reaction rates. More details on the model, including the list of the reaction rates, are reported in such previous works [22,27–29] whereas a brief description of the main assumptions are reported in the following.

Compounds with molecular weight larger than pyrene are very difficult to model due to the large number of species and isomers. Our approach to follow the formation of high-molecular weight species is to divide molecules larger than pyrene in intervals of molecular masses, i.e., lumped species, to evaluate a collision frequency and to assign an activation energy for each chemical reaction involving these species, i.e., molecular decomposition and growth, H-atom abstraction, oxidation. The molecular mass distribution was defined by a range of sections, each containing a nominal hydrocarbon species in order of increasing atomic mass. Carbon number ranged from 24 to 2 × 1E10 and atomic H/C ratio for each carbon number ranges from 0 to 1. Thirty-one sections were used in a geometric series of carbon number with a ratio of two between sections; five sections were used for H/C variation; radical and neutral molecules were separately grouped.

Reactions among molecules and radicals belonging to the high-molecular weight classes lead to the formation of clusters of molecules. The model introduced another discretization, which accounted for the level of agglomeration of the compounds. Three entities were defined: molecules (T1), clusters of molecules (T2) and agglomerates of clusters (T3).

Overall, 465 lumped species for the stable form and 465 for radicals were modelled. The equivalent size range of 1–800 nm was obtained with this discretization considering a density varying from 1 g/cm^3 for the smallest species with the highest hydrogen content to 1.8 g/cm^3 for species above 10 nm with the lowest hydrogen content.

The discretization operated for the lumped species furnished a rough estimation of their molecular structure. For a given C atom number, molecules with high H/C ratios must be aromatic units connected by σ-bonds (e.g. biphenyl-like compounds) forming oligomers of