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A wide range kinetic modeling study of PAH formation from liquid transportation fuels combustion

Mamady Keita[a,b,*], André Nicolle[a], Abderrahman El Bakali[b]

[a] IFP Energies nouvelles, 1 et 4 avenue de Bois-Préau, 92852 Rueil-Malmaison, France; Institut Carnot IFPEN Transports Energie, France
[b] Laboratoire PC2A, UMR CNRS 8522, 59655 Villeneuve d'Ascq, France

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ABSTRACT

A new detailed chemical kinetic mechanism was herein developed to describe accurately the combustion of liquid transportation fuels (gasoline, jet-A1 and diesel fuel) as well as laboratory fuels (single components) over an extended range of equivalence ratios, temperatures, pressures and dilution levels. This mechanism is able to simultaneously reproduce PAH mole fraction profiles, ignition delay times and flame speeds for a variety of fuels. Three surrogate mixtures of n-decane, iso-octane and n-propylbenzene in different amounts were formulated to represent the above-mentioned commercial fuels based on their derived cetane numbers and threshold sooting indexes. Based on this mechanism, the impacts of fuel composition (ethylene vs. jet-A1 fuel) and reaction progress (height above the burner) on the respective importance of benzene and naphthalene formation pathways were characterized. In addition to HACA mechanism, naphthalene was found to be formed mainly from phenyl+vinylacetylene and benzyl+propargyl pathways for jet A-1 flames. A path involving dibenzofuran oxidation was also found to play a key role in naphthalene production in jet-A1 flame, highlighting the significant contribution of oxygenated compounds to PAH production.

1. Introduction

Aromatic hydrocarbons are considered as major precursors of soot [1] and their impact on health [2,3] and environment [4] has been clearly established. It is therefore important to predict aromatics production accurately to design and control cleaner and sustainable transportation technologies. However, fuel composition and combustion conditions impact considerably aromatic production pathways. In fact, benzene formation from n-alkanes and acetylene combustion was shown to involve mostly propargyl radical recombination or reaction with allyl radical [5,6], whereas additional C_4 paths ($nC_4H_3+C_2H_2$ and $nC_4H_5+C_2H_2$) may also come into play in the combustion of buta-1,3-diene [5], n-butane [7], ethylene [8–10] or iso-octane [10,11]. Several other benzene production pathways like cycloalkanes sequential dehydrogenation [5,12], toluene decomposition [10] or cyclopentadienyl combination with methyl radical [6] have also been evidenced. Although the production of naphthalene from benzene may proceed through the popular HACA mechanism [13–16] consisting in sequential H abstractions and acetylene additions, several alternate pathways have been put forward such as those involving methyl, vinyl, propargyl, vinylacetylene, cyclopentadienyl or phenyl addition and subsequent cyclization [13,17–19]. Besides, cyclopentadienyl radicals recombination [13], as well as benzyl radical reaction with propargyl [17] or acetylene [20] may be favored under specific conditions (doped methane flames, toluene pyrolysis). Slavinskaya et al. [9] included the phenyl+vinylacetylene pathway to improve the description of naphthalene production in rich ethylene flames. Recently, biomass combustion studies [21,22] suggested a possible contribution of dibenzofuran oxidation to naphthalene formation.

While most of the kinetic modeling studies of naphthalene production focused on single component fuels combustion, few works addressed the important issue of aromatics production during liquid transportation fuels combustion. To the best of our knowledge, no systematic comparative modeling study of the relative importance of naphthalene production pathways for laboratory fuels (e.g ethylene) and commercial liquid transportation fuels (e.g jet-A1 fuel) has not been published yet. As far as we know, examining the impact of fuel structural properties on aromatics production paths is meaningful and useful since ethylene is an important intermediate in transportation fuels combustion and may be present in recirculated exhaust gas [23], thereby impacting PAH production paths. Sarofim and coworkers [5] focused on comparing benzene production paths from ethylene and jet A1

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[*] Corresponding author at: IFP Energies nouvelles, 1 et 4 avenue de Bois-Préau, 92852 Rueil-Malmaison, France. Fax. +33147525751.
E-mail addresses: keita.mamad@gmail.com, mamady.keita@ifpen.fr (M. Keita).

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Table 1
Surrogate fuels formulation to represent real fuels.

	Diesel surrogate (%vol.)	Jet-A1 surrogate (%vol.)	Gasoline surrogate (%vol.)			
n-decane	61.6	**53.2**	5.0			
Iso-octane	0.3	**21.6**	75.0			
n-propyl-benzene	38.1	**25.2**	20.0			
	Diesel	Diesel surrogate	Jet-A1	Jet-A1 surrogate	Gasoline	Gasoline surrogate
CN	49.0	53.7	**46.0**	**48.3**	17.0	15.9
TSI	28.0	26.9	**21.4**	**20.0**	16.0	17.3
	[39]		[40]		[39]	

fuel. However, they did not study naphthalene production paths which have been shown to have an impact on soot precursors [24] Raj et al. [25] included notably the benzyl+propargyl pathway in a toluene reference fuels (TRF) mechanism (n-heptane/iso-octane/toluene) and modeled PAH formation up to pyrene in n-heptane/toluene and iso-octane/toluene diffusion flames. Zhang et al. [5] focused exclusively on benzene production in gasoline and kerosene flames but did not discuss the abovementioned naphthalene production paths. Blanquart et al. [26,27] and Wang et al. [10] included phenyl+vinylacetylene and cyclopentadienyl recombination pathways in their mechanisms but their study was restricted to TRF surrogates. Overall, the vast majority of detailed kinetic mechanisms of liquid transportation fuel combustion and PAH formation do not account for low temperature chemistry [28,29] thereby preventing their direct application to the design of emerging IC engine technologies [30,31].

In the present work, a new detailed chemical kinetic mechanism for the combustion of a multi-purpose liquid transportation fuel surrogate mixture including both low and high temperature chemistry was developed and validated over a wide range of operating pressures, temperatures, equivalence ratios, dilution and compositions. For the first time, three alternative naphthalene production paths, namely benzyl+propargyl, phenyl+vinylacetylene and dibenzofuran oxidation, were simultaneously considered in the same detailed kinetic mechanism, which allowed us to assess the impact of fuel formulation on the respective importance of naphthalene production pathways. The sequential occurrence of these paths was thereby evidenced and characterized.

2. Model development

2.1. Surrogate fuel formulation

Due to high complexity of liquid transportation fuels, surrogate mixtures composed of few hydrocarbons (from two to a dozen of components [32]) are often used to represent them. To reduce computational time (strongly dependent on the number of species to be transported) and simplify as much as possible the analysis and design of ever more complex engine technologies, combustionists desperately need flexible, simple and reliable chemical surrogate mixtures. As for most of the computational fluid dynamics (CFD) models, evaporation surrogates and chemical surrogates are still distinct, the choice was made to focus on the development of a purely chemical surrogate. A complete physico-chemical surrogate accounts for a number of important targets including H/C ratio, average molecular weight, autoignition quality, heat release rate, extinction, flame adiabatic temperature, sooting behavior, etc. A variety of surrogates formulations were proposed in the literature [33–37], but there is no one that models liquid transportation fuels with the same 3 components by varying their respective concentrations as a function of fuel type. The present ternary chemical surrogate does not aim to reproduce volatility nor H/C ratio nor PIONA (n-Paraffin, Iso-paraffin, Olefin, Naphthene, and Aromatic) composition, it was optimized to reproduces CN and TSI parameters accounting for both autoignition and soot production rate. We herein assess the robustness of this approach and PAHs formation during liquid transportation fuels combustion. Yang et al. [38] proposed that two global combustion parameters, namely the derived cetane number (DCN) and the threshold sooting index (TSI), could be considered for formulating a chemical surrogate. Based on these two global parameters, we considered a chemical surrogate for transportation fuels combustion composed of 3 components: iso-octane, n-decane and n-propylbenzene. The fractions of components in the surrogate mixture are provided in Table 1.

In terms of fuel composition representativity, n- and iso-paraffins are massively present in all liquid transportation fuels [34,41]. Aromatic compounds are also usually present in petroleum-based liquid transportation fuels [34,41,42] and have to be included in the blend to predict correctly soot volume fraction produced in fossil distillates combustion. N-propylbenzene was chosen as a good trade-off between light and heavier aromatics (from benzene to methylnaphthalene). Moreover, the combustion chemistry of n-decane, iso-octane and n-propylbenzene is presently relatively well modeled and several kinetic mechanisms have been validated over a wide range of conditions [43].

2.2. Development of a detailed chemical kinetic mechanism

A new detailed chemical kinetic mechanism describing the combustion of our and literature surrogates was derived from different subsets. Iso-octane and n-decane sub-mechanisms were extracted from Dooley et al. [33] and n-propylbenzene sub-mechanism comes from the study of Darcy et al. [31]. These 3 sub-mechanisms were merged to build a base mechanism. Whenever several thermokinetic data were present for the same reaction in both individual sub-mechanisms, those of Dooley et al. [33] were retained. The C_0, C_1, C_2 and C_3 sub models were extracted directly from the mechanism of Dooley et al. [33]. Reactions were subsequently added to improve agreement with experimental data obtained over a broad range of conditions such as ignition delay times, laminar flame speeds, PAH and important C_1–C_6 intermediates concentration profiles. Table 2 summarizes all mechanisms used for the model construction.

Reactions added for improving C_2 species (acetylene, ethylene, ethane) formation were taken from Alzueta et al. [57] and from AramcoMech [45]. For C_3 species (allene, propyne, propene), additional reactions were taken from Hansen et al. [46]. For C_4/C_6 species (butadienes, butenes, cyclopentadiene, benzene), reactions were taken from Wang et al. [48], Zeng et al. [49] and Colket et al. [47]. In addition to low temperature reactions from Dooley et al. [33], some additional n-heptane, iso-ocatne and n-decane low temperature reactions were extracted from the work of Ranzi et al. [50]. This low temperature subset allowed to improve ignition delay times predictions over the 600–900 K range, which is crucial in Diesel engine operation. For monoaromatic species (toluene, styrene, phenylacetylene), reactions were taken from Yuan et al.