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# An upgraded chemical kinetic mechanism for *iso*-octane oxidation: prediction of polyaromatics formation in laminar counterflow diffusion flames

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#### ABSTRACT

*Iso*-octane is widely recognized as a prominent candidate to represent the oxidation of *iso*-alkanes within jet fuel and gasoline surrogates. This work evaluated a chemical kinetic mechanism for *iso*-octane focusing on the model's capability to predict the formation of polycyclic aromatic hydrocarbons (PAHs). As the model is intended to be further coupled with soot models, the chemical kinetic mechanism must supply good predictability of the formation and consumption of PAHs considered as major soot precursors. A first validation of the *iso*-octane sub-model as incorporated within ESTiMatE-Mech, using experimental data from literature, reveals the need to improve the submodel. Considerable deviations were observed in the prediction of the PAHs, although concentration profiles of major

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species and fundamental combustion properties, here ignition delay time and laminar flame speed, were accurately predicted. Through rate of production and sensitivity analyses of the mechanism, nine reactions were identified to have a strong impact on the (over)prediction of the PAHs. These reactions have been modified based on information gathered from literature resulting in an updated version of the mechanism called ESTiMatE-Mech\_mod. Simulation results with this modified mechanism showed that this updated mechanism is now capable of predicting well the targeted PAHs, while retaining the good initial prediction of the major species concentration profiles as well as of laminar flame speeds and ignition delay times.

Keywords: iso-octane, PAHs, chemical kinetic mechanism, jet engines, kerosene, flames, ignition, speciation

#### INTRODUCTION

Understanding of pollutants formation processes is an essential step towards the reduction and control of emissions generated by conventional and future combustion technologies. The aviation sector, which uses (fossil stemmed) Jet A-1 as well as sustainable aviation fuels (SAF) in blends with Jet A-1 according to the existing jet engines specifications [1], plays an essential role as part of the efforts to meet the global emissions reduction goals [2].

Soot is a crucial pollutant to evaluate considering its potential impact on the environment and climate [3, 4]. Therefore, reaching a deeper understanding of the soot formation pathways within the combustion of Jet A-1 and SAF is essential to speed up the development of cleaner combustion technologies. Soot models such as *e.g.*, the sectional approach [5-6] and the method of moments [7, 8] are being continuously developed to model soot particle formation in aero-engine combustors. The interface between a chemical kinetic mechanism and a specific soot formation model is achieved by the transition from polycyclic aromatic hydrocarbons (PAHs) from the gas-phase to soot particles. Therefore, a chemical kinetic mechanism must supply adequate predictability of the formation and consumption of PAHs before being coupled with a soot model.

The modeling of the combustion process of real multi-component fuels such as jet fuels is commonly performed using a fuel surrogate [9, 10]. Therefore, the development of their detailed chemical kinetic mechanisms follows the same approach. A surrogate is composed of a few hydrocarbons selected from different chemical families, representing

the major components of each chemical family and their fractions in a given fuel. *Iso*-octane is widely recognized as a good candidate to represent the oxidation of *iso*-alkanes within jet fuel and gasoline surrogates. Therefore, *iso*-octane has been proposed as part of the formulation of a Jet A-1 surrogate in the frame of the EU Horizon 2020 Clean Sky project ESTiMatE [11]. Within ESTiMatE, a major goal is to achieve a deeper understanding of the combustion of Jet A-1, in particular, of the soot formation and destruction network.

To the best of the authors' knowledge, the validation of chemical kinetic mechanisms for *iso*-octane – as a singlecomponent fuel and not as part of a surrogate – has been conducted using experimental laminar flame speeds [10, 12, 13], ignition delay times [10, 13, 14], and species concentration profiles [15-18]. To illustrate some examples, laminar flame speeds were considered from the work of Kathrotia *et al.* [10] and Kumar *et al.* [12] done at 1 bar: At a preheat temperature of 473 K in a wide fuel equivalence ratio ( $\varphi$ ) regime ranging from 0.6 <  $\varphi$  < 2.0 [10], and within a preheat temperature range from 360 K to 640 K for fuel-air ratios between 0.7 and 1.4 [12], respectively. Liu *et al.* [13] evaluated the effect of pressure on laminar flame speeds considering a pressure range from 1.0 MPa to 2.5 MPa. All ignition delay times considered were reported for pressures above 10 atm [10, 13, 14]. Also, species concentration profiles were considered mainly for species up to one aromatic ring [15-18]. Bakali *et al.* [15] and Dagaut *et al.* [16] measured important intermediate species, such as allene, propyne, and benzene representing the first aromatic ring molecule, at high [15] and intermediate temperature conditions [16]. Malewicki *et al.* [17] evaluated speciation in a high-pressure shock tube; however, no measurements of aromatic species were reported. Zhao *et al.* [18] evaluated the oxidation of *iso*-octane occurring in a counterflow burner, with focus on the analysis of benzene formation.

Recently, Vlavakis *et al.* [19] presented, as elaborated within the ESTiMatE project, a data base for *iso*-octane non-premixed counterflow flames, where PAHs concentration profiles such as benzene, toluene, styrene, ethylbenzene, indene, and naphthalene were measured [11, 19]. Major species concentration profiles (*i.e.*, CO<sub>2</sub>, CO,  $H_2$ , and  $C_2H_2$ ) and temperature profiles were also considered. Counterflow burners are very appropriate for combustion modeling since the stabilized planar flame allows the simplification of the problem to one dimension. Thus, this new experimental data set further allows validating the PAHs profiles for chemical kinetic mechanism development.

In the present work, a chemical kinetic mechanism called ESTiMatE-Mech [20] was further developed and optimized to allow its description of the combustion of *iso*-octane for different reactor conditions. ESTiMatE-Mech is

a compact mechanism suitable for modeling jet fuels surrogates. Targeting the mechanism's capability and performance to describe PAHs formation, the mechanism was validated against the experimental data presented by Vlavakis *et al.* [19]. Additionally, the performance of the *iso*-octane mechanism has been investigated by referring to experimental data gathered from literature [10, 19]. Targeted data included laminar flame speeds and ignition delay times. Required modifications of the model are introduced to achieve good predictability of the PAHs concentration profiles.

#### **EXPERIMENTAL DATA**

Table 1 presents the experimental data [10, 19] for *iso*-octane combustion at different pressures and temperature conditions selected here for the validation of the *iso*-octane model. These data were classified based on the type of measurements: Species concentrations profiles in a counterflow burner [19], ignition delay times [10], and laminar burning velocities [10]. The data from Vlavakis *et al.* were selected considering the goal of this work to validate the model regarding PAHs formation [19]. The experiments on ignition delay time and laminar flame speed [10] were incorporated to evaluate these global combustion properties in a summarized form.

As the main focus of this paper is the validation of the reaction model against species concentration profiles, the experimental conditions to measure these flames are briefly described here. *Iso*-octane flames [19] were measured in a non-premixed counterflow burner for different fuel mass fractions from 0.35 up to 0.60 and strain rates of 60, 100, and 120 s<sup>-1</sup>. The flame structure was investigated by measuring temperature using an S-type thermocouple and analyzing major and minor species along the flame axis obtaining the profiles as a function of the distance from the fuel duct. Gaseous species were quantified with gas chromatography using in-situ probe sampling [19]. Major species concentration profiles included CO<sub>2</sub>, CO, H<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub>; aromatics and PAHs included benzene, toluene, ethylbenzene, styrene, indene, naphthalene, acenaphthylene, phenanthrene, and pyrene.

Six *iso*-octane flames were considered for validation of the *iso*-octane sub-model with the ESTiMatE-Mech studies for different mass fractions (Y) and several strain rates ( $\alpha_2$ ). The notation set for these flames in this paper is as follows: 'I' for *iso*-octane, 'Y##' for the mass fraction, and 'S##' for the strain rate. The 's' is to clarify if the flames

are sooting or non-sooting. Non-sooting flames are expected to have less influence from the soot formation on the prediction of the PAHs. Therefore, the differentiation is included here. These flames are:

- I-Y35-S60: Y = 0.35,  $\alpha_2 = 60 \text{ s}^{-1}$ . Non-sooting flame
- I-Y47-S60\_s: Y = 0.47,  $\alpha_2 = 60 \text{ s}^{-1}$ . Sooting flame
- I-Y50-S60\_s: Y = 0.50,  $\alpha_2 = 60 \text{ s}^{-1}$ . Sooting flame
- I-Y60-S60\_s: Y = 0.60,  $\alpha_2 = 60$  s<sup>-1</sup>. Sooting flame
- I-Y60-S100: Y = 0.60,  $\alpha_2 = 100 \text{ s}^{-1}$ . Non-sooting flame
- I-Y60-S120: Y = 0.60,  $\alpha_2 = 120 \text{ s}^{-1}$ . Non-sooting flame

Experimental data for laminar flame speeds and ignition delay times from literature [10] were also exploited to evaluate these fundamental fuel properties. The burning velocities of *iso*-octane were obtained by using the cone angle method [21] at 1 atm at a preheat temperature of 473 K, for fuel equivalence ratios from 0.6 to 2.0. Ignition delay times were obtained in a high-pressure shock tube at  $\varphi = 1$ , p = 16 bar, and a 1:2 dilution (N<sub>2</sub>).

#### CHEMICAL KINETIC MECHANISM AND MODELING APPROACH

#### Detailed chemical kinetic mechanism

The experimental data for species profiles measured in a counterflow burner as well as for laminar flame speeds and ignition delay times will be used for checking the performance of the reaction model ESTiMatE-Mech [20]. ESTiMatE-Mech contains 214 species and 1586 reactions. It is a compact mechanism that includes all important molecular classes required for the detailed surrogate modeling of various fuels used in aviation and road transportation. It was developed on the basis of the recently developed reaction mechanism DLR Concise that contains the kinetics of many *n*-, *iso*- and *cyclo*-paraffins and aromatics [22, 23]. Later on, this model (ESTiMatE-Mech) will be developed and optimized further, resulting in an updated reaction mode called ESTiMatE-Mech\_mod.

#### **Modeling Approach**

The counterflow flame data provided by Vlavakis *et al.* [19] have been simulated using Cantera [24], an open source code for the simulation of ideal chemical reactors and reactive 1D flows. It computes the diffusion flame between two opposite burners solving for the temperature, species fractions, velocities, and pressure gradients using a common set of governing equations within a 1D flow domain. The gas energy equation was solved accounting for the thermal radiation, and the species diffusive mass fluxes were computed according to multicomponent formulation. The numerical modeling of ignition delay times and laminar flame speeds were also performed using ESTiMatE-Mech\_mod. at different pressure and temperature conditions with Cantera [24]. For the modeling of laminar premixed flames, a freely propagating flame was assumed; the multicomponent diffusion model and thermo-diffusion were considered. Ignition delay times were done with a homogeneous constant pressure adiabatic reactor selecting the ignition criteria of the experiments, peak CH\* emission.

#### **RESULTS AND DISCUSSION**

Results and discussion are centered in two section. In the first one, a preliminary validation using ESTiMatE-Mech [20] is given. In the second one, the procedure to update the mechanism is explained based on a thorough analysis of the mechanism; then, finally, the results are shown for ESTiMatE-Mech\_mod.

#### Preliminary validation with ESTiMatE-Mech

An example of modeling results obtained for the counterflow flames I-Y35-S60 is presented in Fig. 1. For this flame, the experimental data were generated at atmospheric conditions and an inlet temperature of 393 K in the fuel side and 293 K in the oxidizer side [19]. Figures 1a to 1c show the species concentrations (%molar) obtained with ESTiMatE-Mech for *iso*-octane, O<sub>2</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, and CH<sub>4</sub> *vs*. distance from the fuel duct. ESTiMatE-Mech allows a good predictability of the *iso*-octane and oxygen consumption as it can be observed in Fig. 1a. Major species, such as CO and CO<sub>2</sub> (Fig. 1b) and C<sub>2</sub>H<sub>2</sub> and CH<sub>4</sub> (Fig. 1c), are also well predicted. Figure 2 presents the results of the temperature profile for the flame I-Y35-S60 calculated using ESTiMatE-Mech. The results from ESTiMatE-Mech

regarding the prediction of the temperature profile show good agreement with the experimental data as clearly to be seen.

As the main focus of the current paper is on the analysis of the PAHs, Figure 3 presents the modeling results for the aromatics and PAHs formation for the two non-sooting flames I-Y35-S60 and flame I-Y60-S100 using ESTiMatE-Mech [20]. Figures 3a to 3i show the species concentration profiles *vs.* temperature profiles for: Benzene (A1), toluene  $(C_7H_8)$ , ethylbenzene (ebz), styrene  $(A1C_2H_3)$ , indene, naphthalene (A2), acenaphthylene (A2R5), phenanthrene (A3), and pyrene (A4). Even with no experimental data points reported for phenanthrene and pyrene because they were below the detection limits, they are presented here as they are important soot precursors need to be considered. Figure 3 shows for both flames, I-Y35-S60 and I-Y60-S100, a considerable overprediction of the PAHs. Additionally, for pyrene (Fig. 3a), the concentrations observed within the simulation were considerably higher than the experimental detection limits [19].

In order to evaluate the deviation of the experimental concentration profiles with the simulated results, the concentrations peaks of different species predicted by the simulations were compared with the concentration peaks from experimental data. This comparison for the six flames evaluated is presented in Fig. 4 as percentage of deviation at concentration peak. This figure shows that there is a considerable overprediction of the PAHs for all flames. The overprediction for benzene and toluene is around 100-150%. Considerable deviations were observed in the prediction of larger PAHs: For styrene, indene, naphthalene, and acenaphthylene, the simulated peak concentration profiles show an average overprediction of up to a factor of five.

Figure 5 presents the results of the laminar burning velocity calculated using ESTiMatE-Mech [20]. In general, the results obtained by using ESTiMatE-Mech show a good agreement with the experimental data, particularly, for fuel equivalence ratios between 0.60 and 1.40. However, predicted flame speeds at very rich conditions ( $\varphi > 1.5$ ) obtained with ESTiMatE-Mech are below the measured values. The discrepancy in the calculated and the measured data at those conditions could be related with uncertainties associated with the flame measurements, *e.g.*, due to aerodynamics effects promoted by flame stretch which are not accounted for in the model. Additionally, a possible soot production in very rich flames might promote an increase in flame temperature, which strongly influences the

flame speed. Here, it is important to mention that the ESTiMatE-Mech is capable to accurately reproduce the temperature profile measured in the counterflow burner as shown in Fig. 2. Considering the strong correlation between flame speed and temperature, it allows to assume in general a good evaluation of the heat release and flame speed by the mechanism.

Ignition delay times were also evaluated with ESTiMatE-Mech for *iso*-octane at  $\varphi = 1$  and p = 16 bar. The results are presented in Fig. 6. In general, ignition delay times are well predicted with ESTiMatE-Mech, mainly at high temperature conditions. A precise prediction of the ignition delay times is not expected for temperatures below 1000 K because the model does not include the kinetics for low temperature peroxy-chemistry. At some intermediate points within 1000 K < *T* < 1200 K, the absence of larger aldehydes *e.g.*, C<sub>x</sub>H<sub>2x</sub>O may have some effect in making the chemistry slower and less reactive. However, the deviation at intermediate temperatures is considered acceptable.

#### ESTiMatE-Mech\_mod. - Mechanism update to improve PAHs prediction

Here, the further optimization of the base mechanism as done in the present work is described. A sensitivity analysis of the PAH peak concentrations with respect to the pre-exponential factors (A) of the Arrhenius equation was conducted with ESTiMatE-Mech, to investigate the peak overpredictions. The results are presented in Fig. 7. The PAHs considered for this analysis were: Benzene (A1), toluene ( $C_7H_8$ ), ethylbenzene (ebz), styrene (A1 $C_2H_3$ ), indene, naphthalene (A2), and acenaphthylene (A2R5). Figure 7 only shows sensitive reactions from the PAH sub-model, for which the parameters have been reviewed in this work. Modifications to the core model and to further sub-models of the mechanism are not considered here, as these parts were validated in our prior work [22, 23].

As it can be observed in the sensitivity analysis for A1, the mechanism assigns a major role to the stabilized radicals *iso*-butadienyl (iC<sub>4</sub>H<sub>5</sub>) for benzene formation via the reaction  $iC_4H_5 + C_2H_2 \rightleftharpoons A1 + H$ . The kinetic rate coefficients for this reaction were assumed similar to the one of *n*-C<sub>4</sub>H<sub>5</sub> with acetylene [25]. However, the rate coefficient for *n*-C<sub>4</sub>H<sub>5</sub> + C<sub>2</sub>H<sub>2</sub> is considerably larger than that for *i*-C<sub>4</sub>H<sub>5</sub> + C<sub>2</sub>H<sub>2</sub> (at least two orders of magnitude) [29, 30], which may cause overproduction of benzene. Therefore, the kinetics of these reactions were updated following the work from Senosiain *et al.* [26].

The kinetic parameters of five reactions were updated based on the kinetics presented in the KAUST mechanism [27] that has shown a good prediction of PAHs when used for simulation of those gasoline surrogates that includes *iso*-octane [27]. The following five reactions have been updated:

(1)  $iC_4H_5 + C_4H_4 \rightarrow A1C_2H_3 + H$ . Reaction (1) was updated because of its relevance for styrene prediction. Also, previously, this reaction was found to have the reaction rate expression associated to the reaction of the  $nC_4H_5 + C_4H_4$  $\Rightarrow A1C_2H_3$ , not to the reaction involving the  $iC_4H_5$  radical. Having updated this reaction, a better prediction of ethylbenzene, toluene, and benzene was obtained.

(2) C<sub>7</sub>H<sub>7</sub> + H ≒ C<sub>7</sub>H<sub>8</sub>. Reaction (2) strongly influences the overprediction of toluene and A2R5 as shown in Fig.
7.

(3)  $ebz \rightleftharpoons C_7H_7 + CH_3$ . This reaction (3) is an important path within the mechanism for ethylbenzene according to Fig. 5.

(4) Indenyl +  $C_3H_3 \rightleftharpoons A2R5 + H_2$ . The reaction (4) is the most sensitive reaction regarding the overprediction of A2R5.

(5) A1- + CH<sub>3</sub>  $\rightleftharpoons$  C<sub>7</sub>H<sub>7</sub> + H. The kinetics update of this reaction, with A1- (phenyl) involved, helped to reduce the overprediction of several PAHs, although this reaction was not identified as the most sensitive ones and thus, not included in Fig. 7.

In addition, three reactions were removed from the mechanism. First of all, the reaction (a)  $A2R5 \rightleftharpoons A1C_2H + C_4H_2$ , which was identified as one of the main reactions contributing to the overprediction of acenaphthylene, A2R5. This decision was taken based on the fact that no experimental data nor calculated kinetic coefficients were available in literature to compare the kinetics values included in ESTiMatE-Mech. Thus, the overprediction of A2R5 is completely reduced. Furthermore, a better prediction is also obtained for those species, where A2R5 is playing a major 10

role within their reaction pathways. The reaction (b)  $iC_4H_5 + A1 \rightarrow A2 + H_2 + H$ , which contributes to the overprediction of naphthalene, A2, was also removed. Valencia-Lopez *et al.* [28] have analyzed the convenience of this reaction as part of mechanisms to model counterflow burner experiments and identified the effect of removing this reaction as a way to achieve better prediction of aromatic species. Finally, the reaction (c)  $A1C_3H_4 \rightleftharpoons$  indene + H was removed considering that – based on a literature mechanism [29] – the main  $A1C_3H_4$  reaction paths involved  $A1CH_2$ ,  $A1C_3H_5$ , and A1, but not indene.

This version of the optimized mechanism with inclusion of all the modifications mentioned before, is denoted here as ESTiMatE-Mech\_mod. With this new version, all the experimental data presented before, were modeled and compared with the preliminary mechanism (ESTiMatE-Mech [20]). The results are presented in Fig. 8. For simplification purposes, only the results for two of the major species concentration profiles (*iso*-octane and O<sub>2</sub>) as well as of the laminar flame speed and ignition delay times are given. As shown in Fig. 8, the newly obtained ESTiMatE-Mech\_mod. is able to retain the initial good prediction of the major species profiles as well as of the laminar flame speeds and ignition delay times.

Figure 9 presents the percentage of deviation at the experimental concentration peak with the results obtained with ESTiMatE-Mech\_mod. (similar to the one presented in Fig. 4). As can be observed, the overprediction is now considerably reduced for the six flames evaluated.

Additionally, Fig. 10 shows the results of the calculated PAHs concentration profiles using ESTiMatE-Mech\_mod. [p.w.] and ESTiMatE-Mech [20] for the two flames I-Y35-S60 and I-Y60-S100. For species, such as benzene and toluene, the new version of the mechanism (ESTiMatE-Mech\_mod.) reduces their overprediction considerably, from about 130% deviation to about 30 to 50% (concentration deviation @ peak values). However, these new values of the overprediction are assumed 'normal' considering the uncertainties of this kind of experiments. It is well known that the uncertainties of larger aromatics can be roughly a factor of 2 and even higher if measured in flames and at flow reactor conditions where no direct calibration is available. On the other hand, from the modeling side, model uncertainties resulting e.g., from inappropriate reaction rate expressions, might also be a possible source

of errors. Also, further studies should focus on an analysis of the mechanism to identify the influence of intermediate species that might enhance the prediction of the PAHs.

A remarkable reduction of the overprediction is seen for the larger PAHs, except styrene. Additionally, the peak value of pyrene is now, as expected, at least close to the detection limits of the experiments (1 ppm). However, without experimental data, no further comparison related to pyrene is possible. Styrene and acenaphthylene need to be further analyzed to reach a better prediction of their concentration profiles.

Clearly, the updated mechanism, ESTiMatE-Mech\_mod. improves considerably the prediction of the PAHs. These results are important considering the relevance of the need of a good prediction of the PAHs for soot modeling.

#### SUMMARY AND CONCLUSIONS

Within this work, an updated chemical kinetic mechanism for *iso*-octane oxidation called ESTiMatE-Mech\_mod. has been developed starting from the previously described reaction mechanism called ESTiMatE-Mech [20]. The newly developed model was evaluated against new experimental speciation data from *iso*-octane counterflow flames at atmospheric conditions [11, 19]. With a focus on the mechanism's capability to describe PAHs formation, the results were evaluated against experimental data of PAHs concentration profiles, *here* benzene, toluene, styrene, ethylbenzene, indene, naphthalene, and acenaphthylene [11, 19]. Major species concentration profiles and temperature profiles from the counterflow flames and literature data for laminar flame speeds and ignition delay times were also considered.

The initial check of the *iso*-octane sub-model shows already a good prediction of the concentration profiles of major species (such as, CO, CO<sub>2</sub>,  $C_2H_2$ , and CH<sub>4</sub>) as well as of ignition delay time and laminar flame speed. However, considerable deviations were observed in the prediction of the PAHs: Simulated peak concentration profiles of specific aromatic showed an average overprediction of up to a factor of five.

Hence, rate of production and sensitivity analyses were used to gain detailed insights into the ESTiMatE-Mech performance regarding PAHs formation. Nine reactions were identified to have a strong influence in the (over-)prediction of the PAHs. Consequently, the kinetic rate expressions of six reactions were updated, and three reactions were removed. Thus, an optimized reaction model has been obtained within the present work called ESTiMatE-Mech\_Mech\_mod.; its prediction quality has been demonstrated by comparing the simulation results for the experimental data base.

The ESTiMatE-Mech\_mod. is capable of predicting the concentration profiles of the targeted PAHs while retaining the initial already good prediction capabilities of ESTiMatE-Mech for the other experimental data. For benzene and toluene, the percentage of deviation (percentage of deviation @ peak values of simulated and experimental results) was considerably reduced from an overprediction of about 130% to about 30%. A remarkable improvement is achieved for some of the larger PAHs, ethylbenzene, indene, and naphthalene. For these species, the deviation is now only about 40% on average; thus, substantially lower compared to the initial deviations which were up to 20 times larger. For styrene and acenaphthylene, the deviations were successfully reduced, too, although there is room for improvement.

This new version (ESTiMatE-Mech\_mod.) of the previous mechanism (ESTiMatE-Mech) allows good predictability of the PAHs profiles during the combustion of *iso*-octane. This is essential when considering the integration of the mechanism with soot models to evaluate soot formation. Future efforts will focus on the modeling of PAHs formation in a Jet A-1 surrogate, as *e.g.*, the one proposed within ESTiMatE [11].

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#### Nomenclature

р	Pressure
Т	Temperature
Y	Mass fraction
S	Sooting flame
C <sub>max</sub>	Peak concentration of a given specie
$A_{\rm r}$	Pre-exponential factor of the reaction r

#### Greek letters

$\alpha_2$	Global strain rate at the oxidizer side
$\varphi$	Fuel equivalence ratio

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#### LIST OF FIGURE CAPTIONS

**FIGURE 1**: *Iso*-octane/air counterflow Flame I-Y35-S60: Comparison between measured [19] (symbols) and calculated (curves) species concentration profiles – ESTiMatE-Mech [20], p = 1 atm,  $T_{inlet} = 393$  K (fuel side), T = 293 K (oxidizer side).

**FIGURE 2**: *Iso*-octane/air counterflow Flame I-Y35-S60: Comparison between measured [19] (symbols) and calculated (curve) temperature profile – ESTiMatE-Mech [20], p = 1 atm,  $T_{inlet} = 393$  K (fuel side), T = 293 K (oxidizer side).

**FIGURE 3:** *Iso*-octane/air counterflow flames I-Y35-S60 and I-Y60-S100: Comparison between measured [19] (symbols) and calculated (curves) PAHs concentration profiles – ESTiMatE-Mech [20], p = 1 atm,  $T_{inlet} = 393$  K (fuel side), T = 293 K (oxidizer side).

**FIGURE 4:** Major products and PAHs deviation of concentrations peaks of simulated results compared with those of experimental results for six *iso*-octane non-premixed counterflow flames. Simulated results obtained with ESTiMatE-Mech [20].

**FIGURE 5**: Laminar flame speed for *iso*-octane – comparison between experimental [10] and calculated data with ESTiMatE-Mech [20] at p = 1 atm and a preheat temperature of 473 K for several fuel equivalence ratios.

**FIGURE 6**: Ignition delay times for *iso*-octane – comparison between experimental [10] and calculated (curve) data with ESTiMatE-Mech at  $\varphi = 1$ , p = 16 bar, and 1:2 diluted with N<sub>2</sub>.

FIGURE 7: Sensitivity coefficients calculated for selected PAHs for *iso*-octane/air flame I-Y35-S60 [19] by using ESTiMatE-Mech [20].

**FIGURE 8:** Comparison between the measured and simulated results for: *iso*-octane and O<sub>2</sub> concentration profiles (top), laminar flame speeds (medium) and ignition delay times (bottom) using: ESTiMatE-Mech [20] and ESTiMatE-Mech\_mod. [*p.w.*].

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**TABLE 1:** Experimental data available in the literature for *iso*-octane combustion used to validate and optimize

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 *iso*-octane model within ESTiMatE-Mech [20].

Measurement	<i>p</i> (atm)	<i>T</i> (K)	Method	Ref.
Species profiles	1	298-2000	Counterflow burner	[19]
Ignition delay times	16	800-1500	Shock tube	[10]
Laminar burning velocities	1	473	Cone angle method	[10]

Figures



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