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Reaction model development of selected aromatics as relevant molecules of a kerosene surrogate – The importance of m-xylene within the combustion of 1,3,5-trimethylbenzene

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ABSTRACT

The development of advanced reaction models to predict pollutant emissions in aero-engine combustors usually relies on surrogate formulations of a specific jet fuel for mimicking its chemical composition. 1,3,5-trimethylbenzene is one of the suitable components to represent aromatics species in those surrogates. However, a comprehensive reaction model for 1,3,5-trimethylbenzene combustion requires a mechanism to describe the m-xylene oxidation.

In this work, the development of a chemical kinetic mechanism for describing the m-xylene combustion in a wide parameter range (*i.e.*, temperature, pressure, and fuel equivalence ratios) is presented. The m-xylene reaction sub-model was developed based on existing reaction mechanisms of similar species such as toluene and reaction pathways

adapted from literature. The sub-model was integrated into an existing detailed mechanism that contains the kinetics of a wide range of n-paraffins, iso-paraffins, cyclo-paraffins, and aromatics.

Simulation results for m-xylene were validated against experimental data available in literature. Results show that the presented m-xylene mechanism correctly predicts ignition delay times at different pressures and temperatures as well as laminar burning velocities at atmospheric pressure and various fuel equivalence ratios. At high pressure, some deviations of the calculated laminar burning velocity and the measured values are obtained at stoichiometric to rich equivalence ratios. Additionally, the model predicts reasonably well concentration profiles of major and intermediate species at different temperatures and atmospheric pressure.

INTRODUCTION

To reach the emissions reduction targets as defined in the Paris Agreement, different challenges need to be tackled in many sectors. In this regard, the aviation sector is challenged by the increasing air traffic expected over the next 20 years, as the number of passengers is estimated to double [1-2]. Therefore, the aviation industry is investigating opportunities to achieve those targets. As an important approach to reduce emissions, modern numerically aided designs of new gas turbine engines running on kerosene and on sustainable aviation fuels (SAF) are inevitable. To evaluate the overall sustainability of these new technologies, life cycle assessments (LCA) need to be applied. One of the important parts of these LCA is fuel combustion process. In order to facilitate the engine design process, the development of advanced software tools for the prediction of pollutant emissions, *e.g.*, soot, besides others, in aero-engine combustors is playing a significant role. Such software development relies on a multidisciplinary approach based on chemical kinetics, computational fluid dynamics (CFD) modeling, and experimental validation.

Jet A-1 is the most common fuel in aviation [3]. Many efforts have been done on the development and improvement of accurate Jet A-1 combustion models, including NO_X and soot formation [4-7]. Those models could also be extended for SAF, which are allowed to be blended to Jet A-1 according to the respective specifications required to be matched.

In order to model Jet A-1 combustion, a detailed chemical kinetic mechanism is required. This is challenging due to its complex composition with up to hundreds of fuel species and the extensive chemical reaction network needed. Consequently, the combustion of Jet A-1 is modeled by means of a model fuel, also known as a surrogate; see *e.g.* [8-9] and refs. therein. A jet fuel surrogate contains a few hydrocarbons selected from the different chemical families representing the major components and their fractions in a given kerosene. A surrogate can be designed such that it will have physical and chemical properties similar to those of the actual jet fuel.

Recently, the EU Horizon 2020 Clean Sky project ESTiMatE [10] has proposed the formulation of a Jet A-1 surrogate with 1,3,5-trimethylbenzene as a component selected to represent aromatics. Within ESTiMatE, a major goal is to achieve a deeper understanding of the combustion of Jet A-1 and of the corresponding soot formation and destruction networks. ESTiMatE aims to study this soot process supported by CFD modeling tools.

The development of a kinetic mechanism for 1,3,5-trimethylbenzene implies, as a first step, the development of a mechanism for m-xylene [11-12]. M-xylene is not only relevant because it is a major intermediate within the oxidation of trimethylbenzene, but also because the species produced by the initial hydrogen abstraction and decomposition reactions of 1,3,5-trimethylbenzene are mainly radical species that have been reported as major species within the m-xylene oxidation [11].

Different reaction mechanisms for m-xylene have been proposed in literature. Battin-Leclerc *et al.* [13] developed a kinetic mechanism for the three isomers of xylene (ortho-, meta- and para-xylene), for which the relevance of the generation of a specific mechanism for each of the xylene isomers was additionally discussed, based on experimental data and modeling results. Gaïl and Dagaut [14] measured the oxidation of m-xylene in a jet stirred reactor and proposed a kinetic mechanism that represented well their measured data.

Narayanaswamy *et al.* [15] developed a kinetic reaction model to describe the combustion behavior of some substituted aromatic species (m-xylene among them) at moderate and high temperatures. This mechanism was validated against experimental data from literature for species profiles, laminar flame speeds, and ignition delay times. The mechanism validation showed good agreement with the experimental data available for species concentration

profiles (at $T = 1155$ K) and in general, reasonable agreement for ignition delay times and laminar flames speeds. The mechanism was used further in a more complete mechanism to model the combustion of a jet fuel surrogate [16].

Andrae [17] developed a m-xylene reaction model to describe the self-ignition behavior of low alkyl-benzenes at high pressure conditions. The validation of the mechanism showed good agreement with experimental data for ignition delay times and species concentration profiles at high pressure ($p > 8$atm). Gudiyella *et al.* [18] proposed a detailed chemical kinetic model to simulate stable species profiles for high pressure m-xylene oxidation experiments. Additionally, Diévart *et al.* [12] proposed a very detailed reaction model for 1,3,5-trimethylbenzene which includes a m-xylene sub mechanism. However, a specific validation for m-xylene oxidation was not provided.

To model 1,3,5-trimethylbenzene combustion, it is required to have first a reaction mechanism that can describe the m-xylene oxidation in a wide range of parameters. Targeting its use in CFD modeling, the mechanism should consist of a limited number of species that will allow an efficient analysis and reduction process while keeping a good prediction of the most important combustion properties of m-xylene and, in a further step, of 1,3,5-trimethylbenzene.

In this context, the main objective of this study is to present the development of a chemical kinetic mechanism for describing m-xylene combustion at various temperatures, pressures, and fuel-air ratios. The model is validated against existing experimental data and compared to m-xylene models available in literature. In future, the developed m-xylene sub-model will be used for the development of a complete model for 1,3,5-trimethylbenzene oxidation, and finally, for a jet fuel surrogate.

KINETIC MODEL

In the present work, a chemical kinetic reaction mechanism to describe the m-xylene combustion within a wide range of parameters (*i.e.*, temperature, pressure, and fuel-air ratio) is presented. The m-xylene sub-model developed in this work is added to the existing multi-component reaction mechanism [19] that will be referred as base mechanism within the present work.

The base mechanism [19] contains all important molecular classes required for the detailed surrogate modeling of various fuels used in aviation and road transportation as well. It is a single reaction mechanism that includes reactions for the comprehensive description of the oxidation of many n-paraffins up to C_{16}, as well as iso-paraffins of varying degree of branching such as iso-octane (2,2,4-trimethyl-pentane), one methyl branched $iC_{11}H_{24}$ (2-methyl-decane), as well as $iC_{10}H_{22}$ (2,7 dimethyl-octane), and farnesane $iC_{15}H_{32}$ (2,6,10-trimethyl-dodecane); furthermore, cyclo-paraffins, *e.g.* cyclohexane, propylcyclohexane, and bicyclic decalin, cyclo-aromatics, *e.g.* indane, indene, and tetralin, and aromatics, such as benzene, toluene, propylbenzene, styrene, naphthalene, methylnaphthalene, and biphenyl. All these hydrocarbons are validated as fuel compounds against data from various experimental setups. Over more, some higher PAHs up to C_{20} (*e.g.* phenanthrene, pyrene, chrysene) and polyynes up to C_{10} are implemented to represent a complete picture of soot precursors.

This base mechanism [19] is modular and contains a wide range of components, not all of which are important to model the surrogate proposed for the ESTiMatE project. Therefore, some of them (larger iso-paraffins iC > 8 and larger n-alkanes nC > 12) were removed in order to keep only those components necessary to model the Jet A-1 surrogate. This compact version of the base mechanism includes 191 species and 1464 reactions to which 9 species and 62 reactions are added as part of m-xylene sub-mechanism; thus, summing up to 200 species and 1526 reactions in total referred hereafter as ESTiMatE-Mech for convenience.

The development of the reaction sub-model for m-xylene is an iterative process that initially considers the fundamental understanding of decomposition and the proposition of a basic reaction path to describe m-xylene oxidation process. Further modifications to the reaction routes and their emphasis on different branching routes are optimized based on the experimental data. In this work, this is obtained based on the global combustion parameters such as ignition delay times, flame speeds, and a more detailed model refinement achieved by comparing speciation data obtained in a jet stirred reactor.

The different m-xylene mechanisms from literature, described in the previous section, were studied by exploiting the rate of production (ROP) and sensitivity analysis to identify some of (most) the reaction routes that are important

to consider within m-xylene combustion. Various considerations done during the mechanism development are discussed below.

Figure 1 presents the reaction pathway for m-xylene combustion considered in this work. The initial unimolecular decomposition of m-xylene ($A1CH_3CH_3$) yields the m-xylyl ($A1CH_3CH_2$), and the displacement reaction of one the methyl groups of m-xylene by an H-atom produces toluene ($A1CH_3$). This pathway was generated based on the analogous reaction of the toluene sub-model being already integrated in the base mechanism [19].

The additionally thermal decomposition of m-xylene to produce m-methylphenyl radical ($C_6H_4CH_3$) and CH_3 was included by following evaluated models from literature [12-15]. The integration of this reaction path allows a better prediction of the ignition delay times, mainly at high temperature conditions ($T > 1400$ K). The reaction pathway of $C_6H_4CH_3$ includes $OA1CH_3$ which decomposes to A1 (benzene) + CO + H as well as the reaction with H leading to toluene. These reactions were taken from the models of Diévart *et al*. [12] and Narayanaswamy *et al*. [15-16].

Further reactions of m-xylene include the H-atom abstraction by different species yielding to m-xylyl (*e.g.* $A1CH_3CH_3 + OH \leftrightarrows A1CH_3CH_2 + H_2O$ and $A1CH_3CH_3 + CH_3 \leftrightarrows A1CH_3CH_2 + CH_4$). The species included here were O, O_2, H, OH, HO_2, CH_3, C_2H_3, C_3H_3, C_3H_5, C_5H_5, C_6H_5O, HCO, iC_4H_5, and A1- (phenyl radical). These are the same species considered for H-abstraction from toluene in the base mechanism.

The reactions of $A1CH_3CH_2$ with O_2, O, OH, and HO_2 produce m-methylbenzaldehyde ($A1CH_3CHO$) which are reactions commonly included in m-xylene models [12-15]. A second reaction path for m-xylyl radical, here reactions with O, H, and HO_2 forming $C_6H_4CH_3$, was integrated to the model following the work of Narayanaswamy *et al*. [15] in which intermediate species that decompose rapidly were lumped.

The $A1CH_3CHO$ molecule reacts via two reaction routes with O, O_2, H, OH, and HO_2. The first route produces benzylic radicals with an aldehydic group ($A1CH_2CHO$) while the second one produces $C_6H_4CH_3$. The description of these reaction paths follows considerations as described within the work of Diévart *et al*. [12] and Narayanaswamy *et al*. [15].

Finally, A1CH$_2$CHO reacts with O, O$_2$, OH, and HO$_2$ to form m-phthalaldehyde (m-A1CHOCHO) which further reacts with those same species producing benzaldehyde (A1CHO). The termination path of benzaldehyde was taken from the mechanism of Andrae [17] and the POLIMI_HT mechanism [20-22] which included the intermediate formation of C$_6$H$_5$CO radical (which finally decomposes to A1- + CO) and the decay to benzene. Particularly, the integration of this reaction path to the m-xylene sub-model allows a better prediction of the laminar flame speeds (longer values of the flame speeds) for flame rich conditions.

METHODOLOGY

Experimental Data

Table 1 presents experimental data available in literature [13-14, 23-25] on m-xylene combustion at different pressure and temperature conditions which were selected for the validation of the kinetic mechanism developed in this work. The experimental data is classified based on the type of measurements: Ignition delay times [13, 23], laminar burning velocities [24-25], and species concentrations profiles [14].

Battin-Leclerc *et al*. [13] measured, using a shock tube, ignition delay times for m-xylene at pressures (p) from 7 to 9 atm, temperatures (T) from 1350 to 1700 K, and equivalence ratios (φ) from 0.5 to 2.0. The ignition delay time was defined as the time interval between the pressure rise due to the arrival of the reflected shock wave and the rise of the OH radical emission up to 10% of its maximum value.

Shen and Oehlschlaeger [23] evaluated ignition delay times in a shock tube at pressures from 9 to 45 atm, temperatures from 941 to 1408 K and equivalence ratios of φ = 0.5 and 1.0. In this case, the ignition delay time was defined based on the extrapolation of the maximum slope in the observed OH radical emission signal.

The laminar burning velocity of m-xylene was determined by Ji *et al*. [24] in a counterflow configuration at 1 atm and a preheat temperature of 353 K, for equivalence ratios from 0.7 to 1.5. Axial flow velocities were measured along

the stagnation streamline using digital particle image velocimetry (DPIV). Unstretched laminar flame speed values were extrapolated from the burned flame speed *vs.* strain rate data using a polynomial function.

Johnston and Farrell [25] presented laminar flame speeds for m-xylene at 450 K and 304 kPa over the equivalence ratio range 0.8 to 1.4. The laminar flames were measured in a constant volume combustion vessel using the outwardly propagating spherical flame configuration. The flame growth was estimated using high-speed Schlieren imaging. The data were corrected with linear regressions for flame stretch to yield unstretched laminar burning velocities.

Gaïl and Dagaut [14] investigated the oxidation of m-xylene in a jet-stirred reactor (JSR) at 1 atm and a temperature range of 900-1400 K. Concentration profiles of m-xylene, intermediates, and final products were obtained by low pressure sonic probe sampling followed by on-line and off-line gas chromatography analyses.

Modeling Approach

The numerical modeling for the experimental conditions listed in Table 1 has been performed using the open-source software Cantera [26]. For the modeling of laminar premixed flames, a freely propagating flame is assumed, and the multi-component diffusion model and thermo-diffusion were considered. The refine criteria "slope" and "curve" were set to 0.1 and in general, a mesh with about 100 points was obtained. Ignition delay time data were modeled using the approach of a homogeneous reactor with constant pressure. The criteria considered for the ignition delay times were the same as those of the specific experiments mentioned in Table 1. Measured pressure profiles have been used (when applied) in the simulation of ignition delay times to account for facility effects in shock-tube. The JSR conditions were simulated in Cantera [26] with a homogeneous reactor approach considering isothermal conditions that corresponds to the given reactor temperature. The details about the modeling approach are given in Table 2.

In addition to the mechanism developed in this work, four reaction mechanisms from literature (listed in Table 3) have been used: the reaction model from POLIMI at high temperatures (POLIMI_HT) [20-22] which includes m-xylene oxidation and three of the previously described ones for m-xylene, from Narayanaswamy *et al.* [15], from Andrae [17], and from Diévart *et al.* [12].

RESULTS AND DISCUSSION

Ignition delay times

Ignition delay times datasets for m-xylene at $\varphi = 1.0$, $p = 8$, 10, and 40 atm and $T = 1100 - 1680$ K [13, 23] are used to validate the kinetic mechanism developed in this work and are plotted in Figure 2. The experimental data from Battin-Leclerc *et al.* [13] (Fig. 2a) were generated at high temperatures and at very diluted conditions. Ignition delay times of a m-xylene/oxygen/argon mixture (m-xylene/O_2/Ar = 0.625/ 6.562/92.812 mol %) were measured at around 8 atm over a temperature range of 1350 to 1700 K. In these experiments, the ignition delay times ranged between 17 and 798 µs, depending on the temperature and pressure conditions. Shen and Oehlschlaeger [23] reported ignition delay times for mixtures of m-xylene/O_2/N_2 = 1.962/20.60/77.44 mol % at elevated pressures, $p = 10$ and 40 bar, and intermediate temperatures, $1020 < T < 1400$ K (Figures 2b and 2c). In this case, the ignition delay times ranged between about 100 and 1400 µs.

Figure 2 shows the results of the calculated ignition delay times using ESTiMatE-Mech at $\varphi = 1.0$ against experimental data of Battin-Leclerc *et al.* [13] and Shen and Oehlschlaeger [23]. Three different pressures are presented: 8 atm (Fig. 2a), 10 atm (Fig. 2b), and 40 atm (Fig. 2c) for temperatures ranging between $1020 < T < 1680$ K. Additionally, simulation results using POLIMI_HT [20-22] and the mechanisms of Narayanaswamy *et al.* [15] and Andrae [17] are included as reference. The measured ignition delay times are matched accurately by the modeling results obtained with ESTiMatE-Mech. Moreover, the temperature and the pressure dependencies are both well-captured. A reasonable agreement between measured and predicted ignition delay time data is seen for the other reaction models considered in this study (Fig. 2). The mechanism from Andrae [17] predicts precisely the ignition delay time for all evaluated conditions. This is expected because his mechanism was developed particularly to describe the self-ignition for small alkylbenzenes at high pressures. Other kinetic mechanisms show an over-prediction of the ignition delay times for $p = 10$ atm and $p = 40$ atm. This trend becomes considerably more evident at $p = 40$ atm and lower temperatures, as can be seen in Fig. 2c.

A linear brute force sensitivity analysis with respect to the pre-exponential factors (A) of the Arrhenius equation was applied to ESTiMatE-Mech in order to identify the key reactions leading to the changes of ignition delay time. The analysis has been performed for diluted stoichiometric conditions, similar to the experimental conditions from

Battin-Leclerc *et al.* [13]: m-xylene/O_2/Ar = 0.625/ 6.562/92.812 mol %, p = 8 atm and T = 1400 K. The ignition criterion was adopted from the experimental procedure and was defined by the time when 10% of the maximum concentration of the exited OH radicals was reached. The corresponding results are presented in Fig. 3. As can be seen, ignition delay times show a high sensitivity to the chain branching reaction $H+O_2\leftrightarrow OH+O$ followed by the initiation reaction of the m-xylene mechanism, mainly to the reactions $A1CH_3CH_3+O_2\leftrightarrow A1CH_3CH_2 + HO_2$. The ignition delay times are mainly sensitive to the kinetics of m-xylene sub-model.

Laminar Flame Speed

Figure 4a presents the results of the laminar burning velocity (Su) calculated using ESTiMatE-Mech, at different equivalence ratios, atmospheric pressure (p = 1 atm) and a preheat temperature T = 353 K, and plotted against experimental data of Ji *et al.* [24]. Additionally, simulation results using POLIMI_HT [20-22] and the mechanisms of Narayanaswamy *et al.* [15] and Andrae [17] are included as reference. In general, the results from ESTiMatE-Mech show a good agreement with the experimental data. Particularly, ESTiMatE-Mech predicts fairly well the measured values of the burning velocity in the lean and near stoichiometric equivalence ratios ($0.7 \leq \varphi \leq 1.05$), and highly rich conditions ($\varphi \geq 1.4$). Within the fuel air range $1.1 \leq \varphi \leq 1.3$, ESTiMatE-Mech slightly overpredicts the Su values. The referenced mechanisms from literature [15, 17, 20-22] predict well the variation of the laminar burning velocity with the equivalence ratio. The resulting curve using the mechanism of Narayanaswamy *et al.* [15] is slightly shifted towards lean conditions which results in an overprediction of the Su at lean equivalence ratios. Contrary, the resulting curve using the mechanism from Andrae [17] is shifted towards rich conditions underpredicting the Su values at lean conditions and overpredicting them at rich conditions.

Increasing the pressure to 3 atm and the preheat temperature to 450 K (Fig. 4b) results is an overprediction of the measured Su values as calculated with all the considered reaction mechanisms at stoichiometric and fuel rich conditions. At φ = 0.8 and 0.9, ESTiMatE-Mech and the mechanism of Diévart *et al.* [12] match the measured values. The discrepancy in the calculated and the measured data could be related to the use of the linear regression method for the stretch corrections of the experimental data of Johnston and Farrell [25]. Kelley and Law [27] reported that there is considerable uncertainty on the feasibility and accuracy of the method when linearly extrapolating unstretched laminar burning velocities.

For both pressure regimes, the peak values of the measured burning velocities are between about $\varphi = 1.0$ (Fig. 4a) and $\varphi = 1.05$ (Fig. 4b). However, the peak value calculated with ESTiMatE-Mech is located at $\varphi = 1.1$. The fact that the ESTiMatE-Mech is developed based on previous knowledge of the kinetics of an alkylbenzenes species (mainly toluene) and that previous experimental data for alkylbenzenes (*e.g.* toluene, propylbenzene) [28-30] have shown Su peak values at φ close to 1.1 may explain the tendency of ESTiMatE-Mech to peak at those values. Nevertheless, this requires further analysis and will be studied in future.

Sensitivity analyses of the m-xylene laminar flame speeds were conducted with ESTiMatE-Mech at $p = 1$ atm and a preheat temperature $T = 353$ K for three different conditions of equivalence ratio, $\varphi = 0.7$, 1.0, and 1.3. The normalized sensitivity coefficients are sorted according to average sensitivity considering the three values of φ. Figure 5 displays the 15 most sensitive reactions that strongly influence the calculation of the laminar burning velocity for m-xylene combustion at the selected equivalence ratios. At each condition, the chain branching reaction $H + O_2 \leftrightarrow O + OH$ and the chain termination reaction $H + O_2 (+ M) \leftrightarrow HO_2 (+ M)$ are two important ones. Clearly, the propagation of m-xylene flames is considerably sensitive to one of the initiation reactions of the m-xylene model: $A1CH_3CH_3 (+ M) \leftrightarrow A1CH_3CH_2 + H (+ M)$. The sensitivity analysis reveals that the equivalence ratio has a minimum influence in the direction (positive or negative) of sensitivity coefficients but that they are relevant regarding the magnitude of those values. For example, the reaction $H + O_2 (+ M) \leftrightarrow HO_2 (+ M)$ is particularly important at lean conditions due to the high oxygen content in fuel lean mixtures. At rich conditions ($\varphi = 1.3$), with a slight overprediction of the calculated laminar burning velocities, there is no evidence of particular reactions that affect specifically the calculation of the laminar flame speed at the selected conditions

Species Concentration Profiles

Figure 6 presents the modeling results using ESTiMatE-Mech of a jet stirred reactor study at atmospheric pressure and a temperature range $1000 < T < 1400$ K against experimental data of Gaïl and Dagaut [14]. Figures 6a to 6h show species concentration profiles *vs.* temperature profiles for m-xylene, CO, H_2, C_2H_2, CH_2O, benzene, toluene, and benzaldehyde, respectively.

The simulation results using the three literature mechanisms [12, 15, 17, 20-22] are also given. CO and H_2 were included because they are major products in the m-xylene oxidation. CH_2O and benzaldehyde were evaluated as major

intermediates within the m-xylene oxidation. Finally, C_2H_2, benzene, and toluene are studied as they play a major role as soot precursors.

ESTiMatE-Mech reproduces properly the m-xylene reactivity shown here as m-xylene consumption against temperature (Fig. 6a). Major species, such as CO (Fig. 6b) and H_2 (Fig. 6c), are correctly predicted, not only regarding the shape of the concentration profiles but also concerning their corresponding peak values. Besides these major species, other species like acetylene (Fig. 6d) and formaldehyde (Fig. 6e), are also predicted accurately. In the case of the aromatic species benzene, toluene, and benzaldehyde, the model properly predicts their concentration profiles, although the benzene and benzaldehyde profiles are slightly shifted to lower temperatures (Fig. 6f and 6h, respectively). The peak values of those aromatic species are, in general, well-predicted except the one of toluene which is underpredicted (Fig. 6g). The POLIMI_HT mechanism shows an accurate prediction of the m-xylene reactivity and the formation of some of the main species (*e.g.* CO, H_2, C_2H_2). The other literature models considered reveal a larger consumption of m-xylene at lower temperatures and, thus an earlier formation of the intermediates. As mentioned before, the ESTiMatE-mech is intended to be integrated with soot models to predict soot formation in conditions relevant for aeroengine operations. In that sense, the properly prediction of the aromatic species as well as the acetylene is considered a relevant result.

SUMMARY AND CONCLUSIONS

In this work, a chemical kinetic reaction mechanism for the oxidation of m-xylene, consisting of 9 species and 62 reactions (additional to the base mechanism), has been developed and incorporated into a compact version of the detailed reaction mechanism of Kathrotia *et al.* [19] that contains all the important molecular classes for modeling surrogates of aviation fuels. The resulting mechanism, called here ESTiMatE-Mech, has been validated for m-xylene combustion against experimental data taken from literature, at different temperatures, pressures, and equivalence ratios. The performance of the developed ESTiMatE-Mech was compared with several m-xylene models from the literature.

Overall, the presented m-xylene mechanism is a compact model that correctly predicts combustion properties of m-xylene. Ignition delay times at high pressures (up to 40 atm) and high temperatures (1020 K < T < 1680 K) can be accurately calculated for stoichiometric mixtures.

The ESTiMatE-Mech correctly predicts the laminar burning velocities of m-xylene/air mixtures at ambient pressure and different fuel equivalence ratios (lean, stoichiometric, and rich). However, larger deviations of the measured laminar burning velocity data were obtained for stoichiometric and rich equivalence ratios at higher pressure (3 atm). A reason for this might be the application of linear stretch correction approaches for the experimental data instead of a non-linear one. Further studies are required to improve the prediction of the laminar burning velocities of m-xylene at those high-pressure conditions.

Regarding species concentrations, the developed model predicts reasonably well the concentration of major and intermediate species at different temperatures and atmospheric pressure. Particularly, an accurate estimation of the concentrations of aromatic species and acetylene was achieved. This is essential for the envisaged integration of the ESTiMatE-Mech into soot models to study the soot emissions at conditions relevant for aero-engines when burning Jet A-1.

Future efforts will focus on extending the developed m-xylene mechanism to develop a complete kinetic model for 1,3,5-trimethylbenzene combustion, which can be used as the representative aromatic species in a surrogate formulation.

Acknowledgments

Nomenclature

p	Pressure [Pa, atm, bar]
T	Temperature [K]

| t | Time [s] |
| S_u | Laminar burning velocity [m/s] |

Greek letters

| φ | Equivalence ratio |
| τ | Ignition delay time |

Subscripts

| ign | Ignition |

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LIST OF FIGURE CAPTIONS

FIGURE 1   Reaction pathway for m-xylene oxidation.

FIGURE 2 Comparison between measured (symbols) and calculated ignition delay times (lines) of stoichiometric m-xylene-O_2-Ar/N_2-mixtures at p = 8 [13], 10, and 40 atm [23]. The calculated results were obtained with ESTiMatE-Mech and four mechanisms from literature [12, 15, 17, 20-22].

FIGURE 3   Sensitivity coefficients for ignition delay time (defined as $A/\tau *d\tau/dA$) of m-xylene calculated at p = 10 atm, φ = 1.0, and T = 1400 K using ESTiMatE-Mech.

FIGURE 4 Comparison between calculated laminar flame speeds of m-xylene/air mixtures at different equivalence ratios, along with measured burning velocities from literature (symbols) [24-25]. T = 353 and 450 K, p = 1 (top, a) and 3 atm (bottom, b). The calculated results were obtained with ESTiMatE-Mech and four mechanisms from literature [12, 15, 17, 20-22].

FIGURE 5   Sensitivity coefficients (defined as k/S*ds/dk) for laminar flame speed computed with ESTiMatE-Mech for m-xylene/air mixture at φ = 0.7, 1.0, and 1.3 at T = 353 K and p = 1 atm.

FIGURE 6   Comparison between calculated species concentration profiles (lines) and measured profiles [14] obtained during m-xylene oxidation in a jet stirred reactor at p = 1 atm, φ =1.0 and a residence time of 0.1 s.

LIST OF TABLE CAPTIONS

TABLE 1: Experimental data available in literature for m-xylene combustion

Measurement	p (atm)	T (K)	Experimental configuration	Ref.
Ignition delay times	7-9	1350-1700	Shock tube	[13]
Ignition delay times	9-45	941-1408	Shock tube	[23]
Burning velocities	1	353	Counterflow burner	[24]
Burning velocities	3	450	Constant volume combustion vessel	[25]
Species profiles	1	1050-1400	Jet-stirred reactor (JSR)	[14]

TABLE 2: Modeling approach followed for the experimental conditions used to validate the m-xylene mechanism.

Measurement	Reactor model approach	Main assumptions and modeling considerations
Ignition delay times	Homogeneous reactor	Homogeneous constant pressure adiabatic reactor
Burning velocities	Freely propagating flame	Multi-component diffusion model and thermo-diffusion
		Refine criteria: Slope=0.1 and curve=0.1
Species concentration profiles	Homogeneous reactor	Homogeneous constant pressure reactor under isothermal conditions

TABLE 3: Detailed kinetic models used in present work

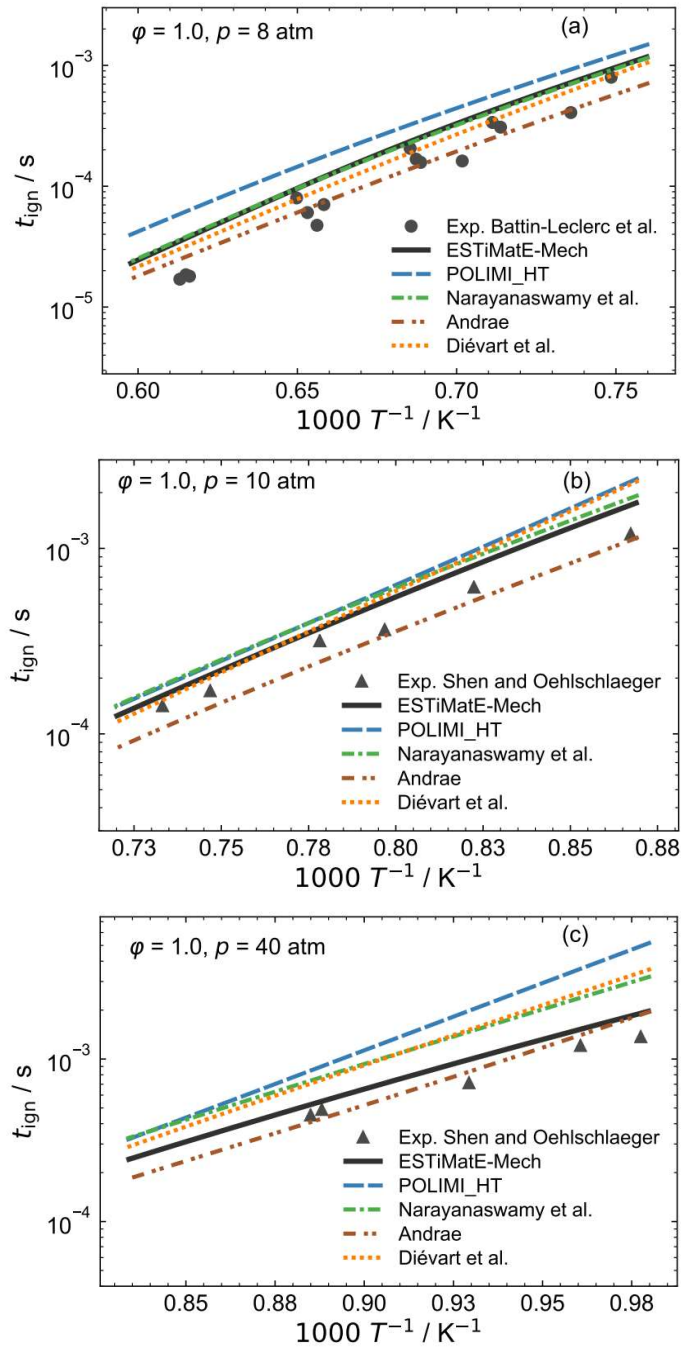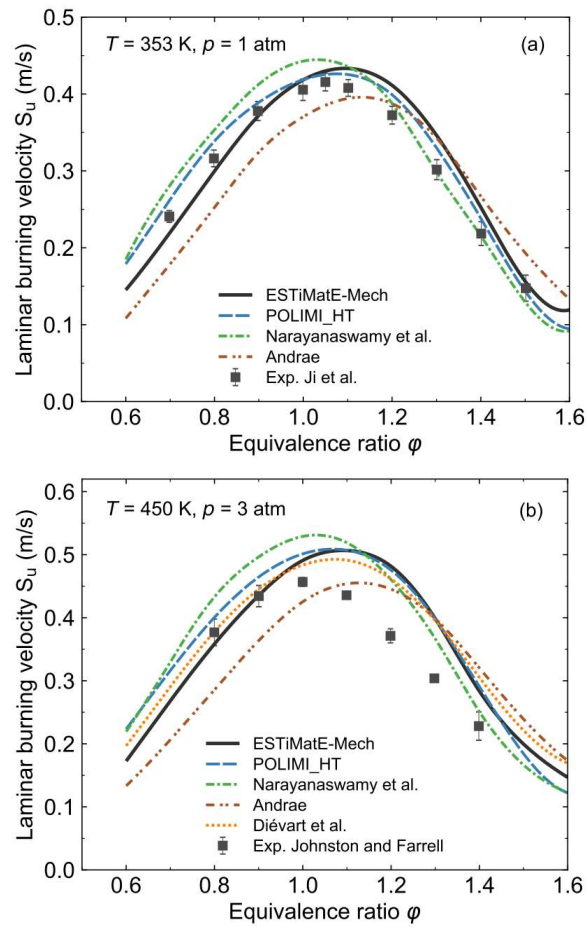| Reference	Species	Reactions
ESTiMatE-Mech	200	1526
POLIMI_HT [20-22]	368	14324
Narayanaswamy *et al.* [15]	158	1038
Andrae [17]	150	767
Diévart *et al.* [12]	450	2569

Figures
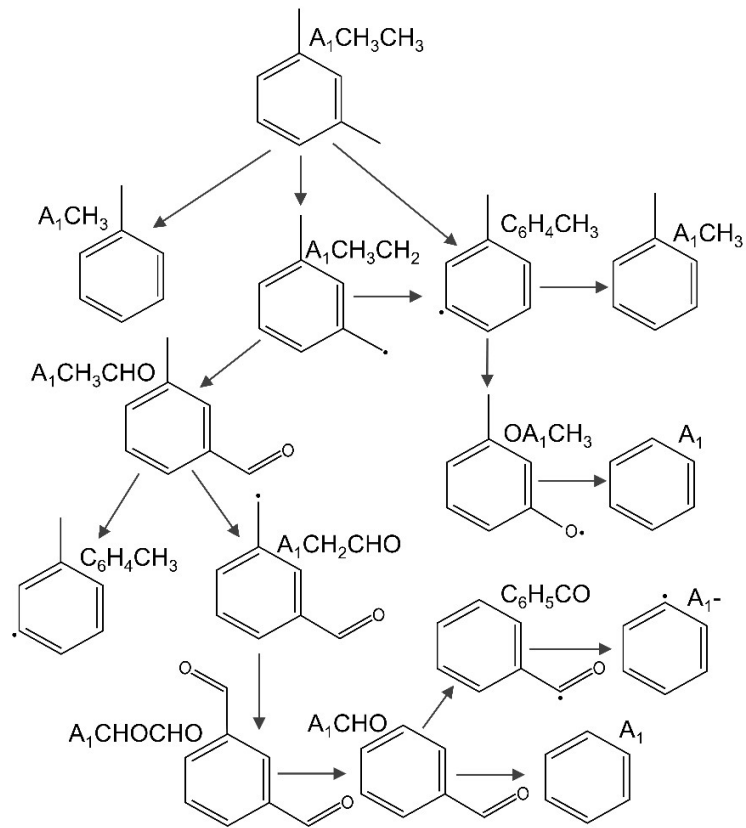
FIGURE 1: Reaction pathway for m-xylene oxidation.

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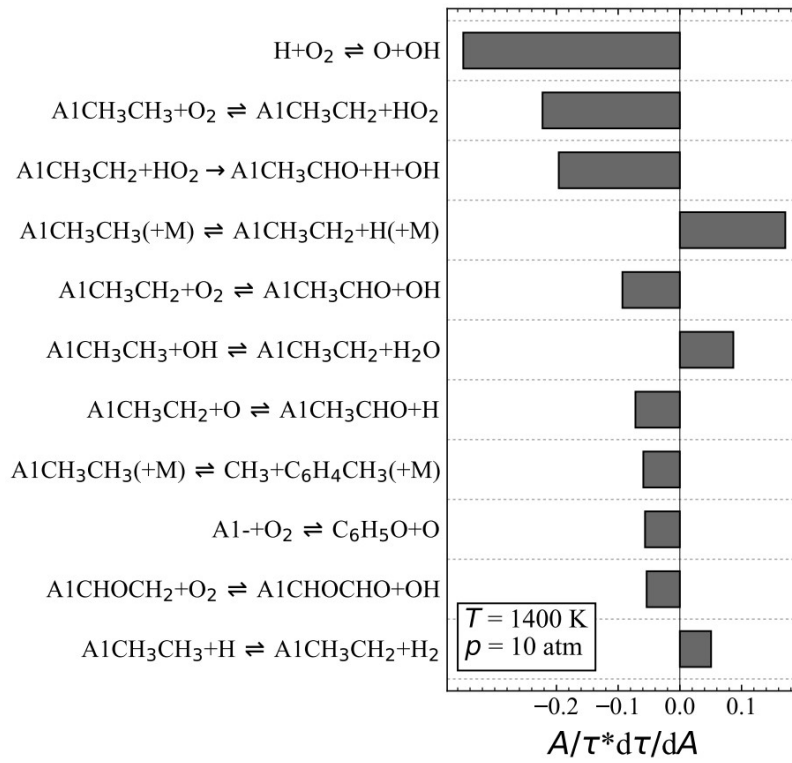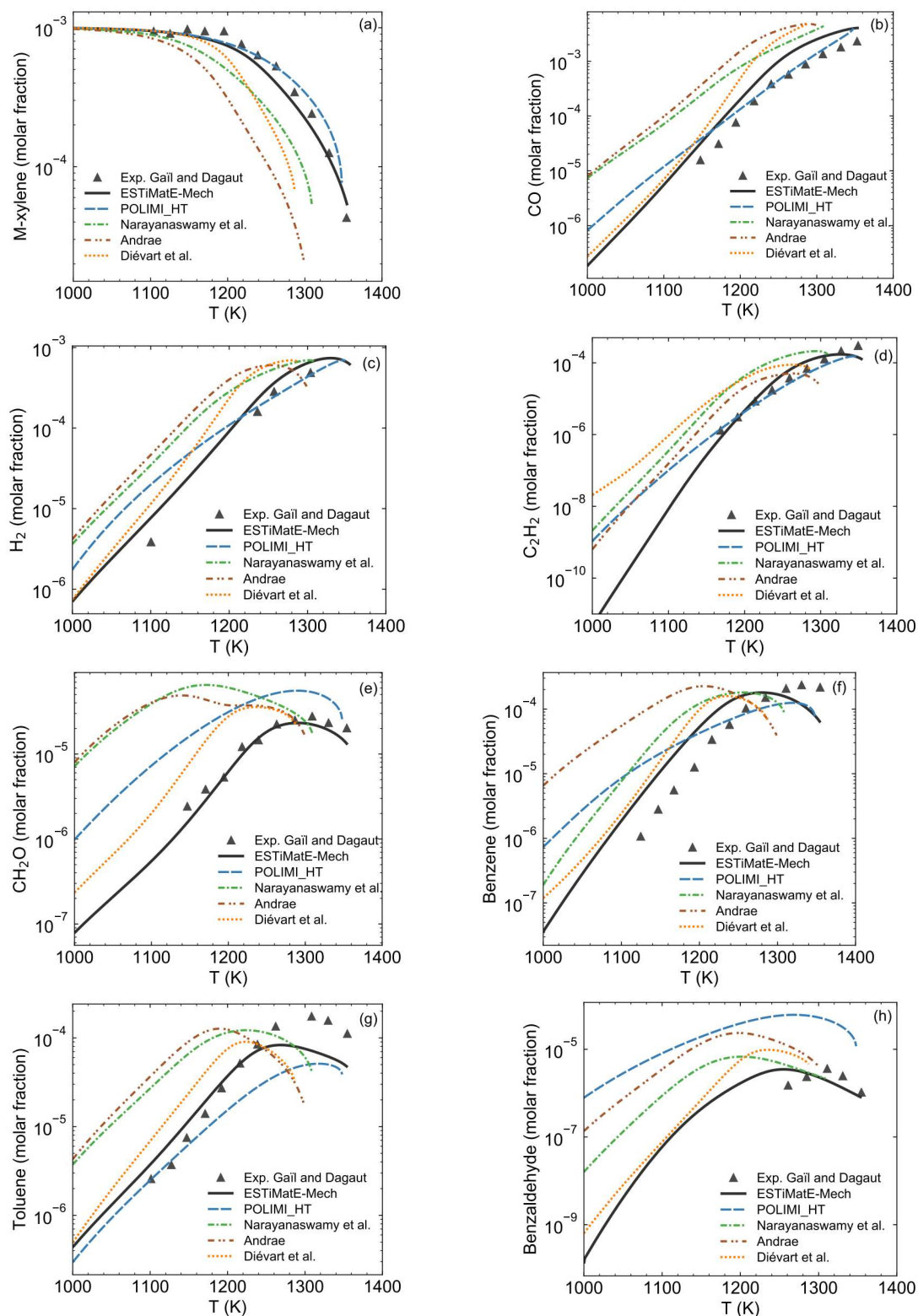
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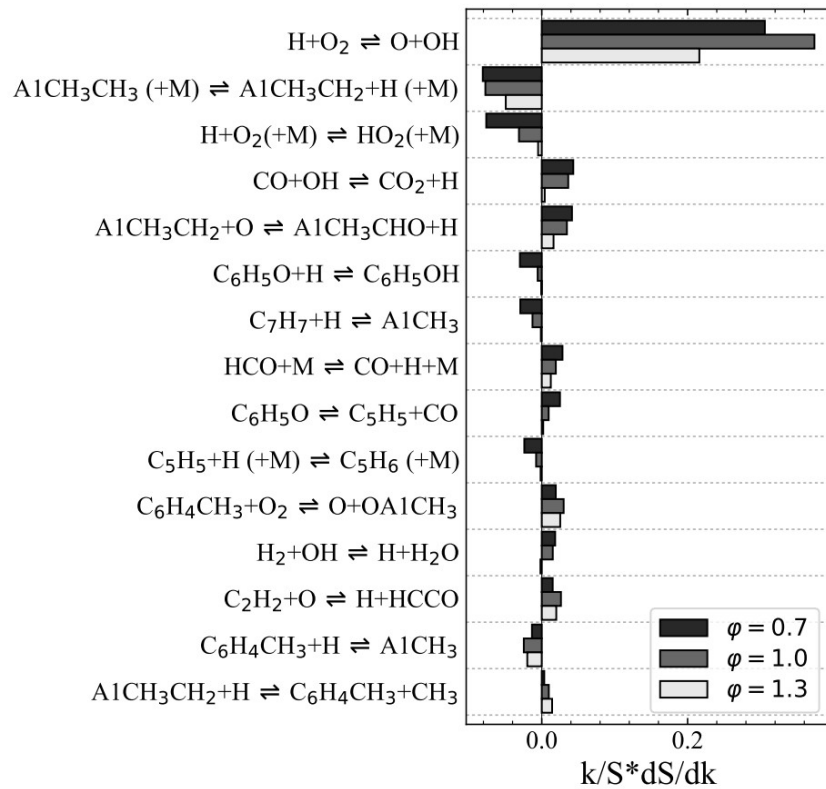
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