Comparative study of detailed chemical kinetics models of soot precursors for ethylene/air combustion

Thiago Fabricius Konopka, konopka@petrobras.com.br
Petróleo Brasileiro S/A. Av. Henrique Valadares, 28 - Centro, Rio de Janeiro-RJ
Luís Fernando Figueira da Silva, luisfer@puc-rio.br
César Celis, cesar.celis@puc-rio.br
Pontifícia Universidade Católica do Rio de Janeiro, R. Marquês de São Vicente - Gávea, Rio de Janeiro - RJ

Abstract. *In this paper a comparative study is presented of four different detailed chemical kinetics models which include the main chemical species responsible for the process of nucleation, surface growth and oxidation of soot, i.e,. acetylene, propargyl, benzene, pyrene, molecular oxygen and hydroxyl. To this purpose, it is considered a perfectly stirred reactor model, which burns ethylene/air mixtures at equivalence ratios between 0.6 and 4 and residence times ranging from equilibrium to extinction. This model is chosen to both highlight the chemical kinetics effects on soot formation and represent turbulent combustion situations. The obtained results show that important discrepancies exist between the four kinetic mechanisms for all species analyzed. The study also uses the rate of production analyses to determine the most frequently reactionsthat control the formation of each considered species.*
Keywords*: soot precursors, propargyl, benzene, pyrene*

1. INTRODUCTION

Soot formation has been studied by several research groups in recent decades, but it is still not a fully understood problem due to its multi-scale nature and complex mechanisms. The reason why soot formation is still an open problem lies, partly, on the poor understanding of the mechanisms leading to the chemical species that constitute the soot precursors. Predicting and controlling soot is relevant for engineering applications including furnaces, internal combustion engines and gas turbines (Smooke et al., 2005). Soot is also a major pollutant that affects the environment and human health (Blacha et al., 2012).

Computational models for soot formation may use, for instance, detailed kinetic mechanisms involving the prediction of species responsible for soot formation and oxidation. Acetylene (C_2H_2) responds for two effects in soot formation models. First, this species is directly responsible for the soot formation (Kennedy, 1997). Second, it is associated with the surface growth of soot, which occurs after the nucleation phase and is concomitant with the coagulation phase of soot particles. Regarding soot oxidation, molecular oxygen (O_2) and hydroxyl radical (OH) are considered to be the predominant chemical species (Kennedy, 1997). Among the intermediate species involved in the formation of soot precursor species, propargyl (C_3H_3) plays an important role, because it is the main species responsible for the aromatics formation. For example, if the self-combination propargil reaction leading to benzene is not properly considered, discrepancies in aromatic species concentration may be significant (Blanquart et al., 2005). Some aromatic species such as benzene (C_6H_6), naphthalene ($C_{10}H_8$) and pyrene ($C_{16}H_{10}$) (Blacha et al., 2012) are often considered as soot precursors species. Precisely modeling of polycyclic aromatic hydrocarbons (PAH) concentrations is crucial to determining soot inception and growth (Slavinskaya et al., 2012), because PAH combinations create incipient soot particles taht aggregate into large structures. Regarding surface growth, PAH diffuse directly into the soot surface.

Recently, several studies have been published on ethylene counterflow non-premixed flames (Slavinskaya et al., 2012), on laminar flames (Slavinskaya and Frank, 2009), coflow diffusion flames (Dworkin et al., 2011), methane/air, ethane/air and ethylene/air co-flow laminar diffusion flames (Chernov et al., 2014). Indeed, literature is abundant as far as soot precursors and soot formation in laminar flames are considered. Nevertheless, fewer works may be found regarding soot formation turbulent flames (Blacha et al., 2012). In laminar flames, it is clear that diffusion plays an important role in smearing the differences among the various chemical kinetic mechanisms predictions. However, in turbulent flames, very fast mixing may enhance the chemical kinetics role on soot formation, when compared to laminar ones. Therefore, the limit case of very small Damkohler number leads to consider here the model of a perfectly stirred reactor for ethylene/air mixtures. Such a model reactor is used to determine the influence of the chemical kinetic model, mixture equivalence ratio, and reactor residence time on the chemical species involved in the soot formation. It is hoped that this investigation results could draw the attention to this simple configuration studied, which has led to significant advances on the understanding of chemical kinetics mechanisms.

Four chemical kinetic mechanisms were accounted for in this work. The first of these models was proposed by (Wang and Frenklach, 1997) and includes a sub-mechanism for the detailed kinetics of polycyclic aromatic hydrocarbons (PAH) formation. It involves 527 chemical reactions and 99 different chemical species. This mechanism was developed by using experimental results obtained from a shock tube, various configurations of ethylene and acetylene diffusion flames at low pressure, as well as results of models based on quantum mechanics. The second model

studied was proposed by (Appel et al., 2000) to better describe the soot formation process, and it represents an update of the model of (Wang and Frenklach, 1997). The updating essentially involved the modification of 24 chemical reactions to the model. The third chemical kinetic model is due to (Blanquart et al., 2009), which was designed to predict a wide range of hydrocarbon fuels (from C1 to C8), and is composed of 149 chemical species and 1651 chemical reactions. The model has been validated for the combustion of simple species, such as methane, passing through aromatic species like benzene and toluene, reaching the n-heptane and iso-octane. The construction of this kinetic mechanism was based on several others, each of which is valid for a given group of chemical species. The fourth chemical kinetic mechanism, which was designed by (Le Cong and Dagaut., 2007) for the combustion of fuels composed of up to three carbon atoms, is characterized by 99 chemical species and 743 reactions. The validation of this mechanism has been performed for the combustion of methane, syngas and mixtures of these two fuels. Note that this model was not developed with the aim of predicting soot formation, so it does not include PAH chemical kinetics.

The main focus in this work is to analyze how the main chemical species involved in soot production and oxidation behave during combustion and how different kinetic models describe them. The chemical species studied include: molecular oxygen, hydroxyl, propargyl, acetylene, benzene and pyrene. For this purpose, PSR computations of ethylene/air mixtures with equivalence ratios between 0.6 and 4 and residence times from ranging equilibrium to extinction are carried out.

Accordingly, following this brief introduction (Section 1), Section 2 describes the particular methodology utilized for obtaining and analyzing the different PSR results computed in this work. Next, in Section 3, PSR results of combustion of ethylene/air mixtures at different equivalent ratios, between 0.6 to 4, and residence times ranging from 100 ms to 0.1 ms are presented and discussed. Finally, Section 4 summarizes the main conclusions drawn from the main results obtained here.

2. METHODOLOGY

In this paper, a PSR based analysis of key chemical species involved in the soot formation process is carried out by examining the influence of both residence time (t_R) and mixture equivalence ratio (Φ) on soot precursors chemical species. The results are also compared to the chemical equilibrium composition of the mixture. Moreover, a reaction rate analysis is made to identify the main reactions and chemical paths for each chemical species analyzed in this study.

The PSR is an ideal reactor where all the chemical reactants are instantly mixed. This reactor is modeled by solving the conservation equation for chemical species, mass and energy, and also the equation of state. These equations are solved here under the hypothesis that the combustion is adiabatic, and it occurs at constant pressure and steady state. Therefore, the reactor composition for a given set of inflow equivalent ratio, pressure and temperature is solely controlled by the mixture residence time. The range of residence times studied covers the full range of steady state reactor operation, i.e., from equilibrium to extinction, which correspond to, respectively, for long and short residence times. In the former, the composition of the gas mixture should not depend on chemical kinetics. At the other extreme, when the residence time is small, i.e., close to the one where extinction is observed, chemical kinetics controls the combustion process. Throughout this paper atmospheric pressure combustion is considered.

The predictions obtained with different chemical kinetic mechanisms are compared on the basis of selected chemical species involved in soot formation and oxidation, i.e., molecular oxygen, hydroxyl, propargyl, acetylene, benzene and pyrene. More specifically, the computed molar fractions of these species as function of the mixture equivalent ratio for four t_R (100ms, 10ms, 1ms, and 0.1ms) are analyzed. The equivalence ratio of the ethylene/air mixture ranges from $\Phi = 0.6$ to 4, in order to cover the whole spectrum of possible situations.

In order to identify the origins of the molar fraction differences coming from the different chemical kinetic models utilized, a reaction rate analysis is performed for each chemical species involved in soot production and kinetic mechanism studied. The aim is to identify the main chemical reactions responsible for the formation of those chemical species. The reaction rate analysis provides all chemical reactions involved in the formation and consumption of these species.

The methodology of reaction rate analysis includes the following steps: First, the reaction rate is evaluated for several values of (Φ, t_R), which are specific to each chemical species; these values are shown in Table 1. In this table, A_1 represents benzene and A_4 represents pyrene. Second, up to the six main reactions for each value Φ, t_R, chemical species, and kinetic mechanism are identified. The arbitrary choice of this number of reaction intends to embrace the main reactions responsible for the species formation. As main reactions, are considered those ones which produces the largest amount of each chemical specie. Third, a table is prepared which summarizes the main reactions in order to consolidate the results. Since some reactions appear for a Table 1 single evaluation point only, whereas others do so for all of them – only those which are common to all evaluation points are retained. Fourth, in order to compare the various chemical reactions between the different kinetic models, the Arrhenius rate k (T) is evaluated at the typical temperature of 2000 K. The aim here is to quantify the discrepancies between the chemical kinetic mechanisms. Following, the main results obtained are presented and discussed.

Table 1. Parameter of Φ, t_R for reaction rate analysis for each chemical specie studied.

t_R (ms) / Specie	100	10	1	0.1
C_2H_2	Φ = 1.5 and 3.0	Φ = 1.5 and 3.0	Φ = 1.5	Φ = 1.5
C_3H_3	Φ = 1.8; 2.2; 3.6	Φ = 1.8; 2.2; 3.6	Φ = 1.8	Φ = 1.4
A_1	Φ = 2.2; 2.6; 3.5	Φ = 2.2; 2.6; 2.2	Φ = 1.9	Φ = 1.7
A_4	Φ = 2.4; 3.0; 3.5	Φ = 2.2; 2.6; 3,5	Φ = 2.1	-

3. RESULTS AND DISCUSSION

The present work aims to study in PSR based configurations the combustion of ethylene/air mixtures for different equivalent ratios, ranging from 0.6 to 4, as a function of different mixtures residence times, from extinction to equilibrium. The effects on selected soot related chemical species of these two parameters, according to the four different chemical kinetic models studied, are analyzed in the following sections. These chemical kinetic models are those described in (Appel et al., 2000), (Wang and Frenklach, 1997), (Blanquart et al., 2009), and (Le Cong and Dagaut, 2007). In Section 3.1, the results for temperature, hydroxyl, and molecular oxygen are presented. Indeed, the acetylene, propargyl, benzene, and pyrene in terms of molar fraction differences and the reaction rate analyzes, are analyzed in section 3.2. Finally, Section 3.3 presents the reaction rare analysis carried out for selected soot related chemical species.

3.1 Temperature and soot oxidizer species

Figure 1 presents the computed results of temperature, hydroxyl (OH), and molecular oxygen (O_2) molar fractions as function of the mixture equivalence ratio for the residence times of 100, 10, 1, 0.1 ms. Chemical equilibrium results are also shown in this figure. Concerning the temperature behavior first, for values of Φ < 2 and t_R = 100 ms, it may be observed that there is a suitable agreement between the PSR and the chemical equilibrium results, as it could have been expected. The reactor stable operation limits, in terms of equivalence ratio, are reduced for t_R = 0.1 ms (Φ_{min}, Φ_{max}) = (0.63, 1.84), when compared to that obtained for t_R = 100 ms, i.e., Φ (0.6, 4.0). It should be also noted in Figure 1 that the corresponding temperature evolution with Φ, which is classical, has a maximum of 2380 K near Φ ≈ 1 for the residence time of 100 ms. It may be observed as well that the maximum temperature (Φ ≈ 1) is reduced as residence time decreases. Reducing the t_R below 0.1 ms would lead the PSR to reach its extinction limit, where there is no enough energy release to promote the combustion within the reactor. Regarding the OH, the equivalence ratio corresponding to the maximum molar fraction varies in a small range of values as the residence time decreases, i.e., Φ = 0.99 for t_R = 100 ms and Φ = 1.05 for t_R = 0.1 ms. In addition, the value of the OH maximum mole fraction increases from $5.7x10^{-2}$ to $8.9x10^{-2}$ when t_R decreases form 100 ms to 0.1.

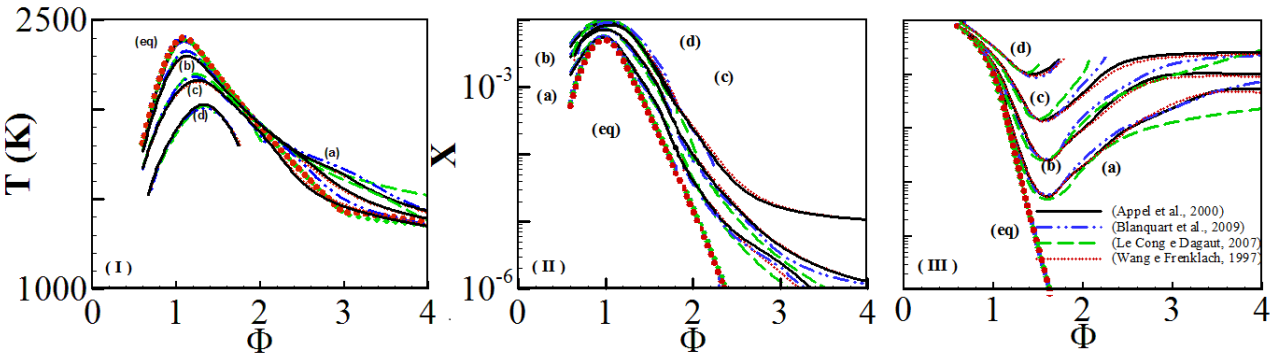

Figure 1. Temperature (I) and mole fraction of hydroxyl (II) and molecular oxygen (III) as a function of mixture equivalence ratio (Φ) for residence times of 100 ms (a), 10 ms (b), 1 ms (c) and 0.1 ms (d). Chemical equilibrium (symbols), chemical kinetic models result (lines).

For t_R = 1 ms and Φ > 2 the combustion stabilization is not possible with (Blanquart et al., 2009) and (Le Cong and Dagaut, 2008) mechanisms. Figure 1 show that the same does not occur for (Appel et al., 2000) and (Wang and Frenklach, 1997) models. Furthermore, when compared the (Appel et al., 2000) and (Wang and Frenklach, 1997) models, for Φ < 2 the maximum OH molar fraction differs 1.0%, and for values of Φ > 2, these discrepancies in OH molar fractions reach 8.5%. Comparing (Blanquart et al., 2009) to (Appel et al., 2000) for Φ < 2, the differences are more pronounced, reaching 10%. The (Le Cong and Dagaut, 2008) model is the one that exhibits the largest differences with respect to the (Appel et al., 2000) one, which reaches 26% for OH.

Upon analyzing the temperature evolution for Φ > 2 and t_R = 100 ms, it should be clear that discrepancies are observed with respect to the chemical equilibrium. Indeed the PSR does not reach the chemical equilibrium, which is

also evident by analyzing the results from chemical species OH and O_2. Indeed, Figure 1 also shows that both OH and O_2 exhibit concentration values higher than the chemical equilibrium corresponding ones. These differences increase as the mixture becomes richer by at least one order of magnitude.

Concerning the molecular oxygen (O_2), Figure 1 (III) shows a clear and systematic tendency for the four kinetic models, i.e., chemical equilibrium is not reached in the PSR. As the equivalent ratio is increased, oxygen molar fraction decreases until a minimum value, which is similar for the four kinetic models, and subsequently increases. On the other hand, the chemical equilibrium O_2 molar fraction tends to zero with Φ as it could be foreseen on thermodynamic bases. (Celis and Figueira da Silva, 2016) demonstrate that such non-equilibrium behavior is related to the high sensitivity to temperature of the backward reaction rate of reactions CO + O + M ⇔CO_2 + M and CO + OH ⇔ CO_2 + H.

3.2 Soot production related species

Chemical species responsible for the surface growth (acetylene) and inception (benzene and pyrene) of soot particles are analyzed in this section. In addition, propargyl is also studied due to its importance in formation of aromatic species.

In Figure 2 it is shown the variation with mixture equivalent ratio of the molar fraction of acetylene (C_2H_2), propargyl (C_3H_3), and benzene (A_1) as a function of the residence times of 100, 10, 1 and 0.1 ms, along with the corresponding chemical equilibrium concentration. It may be verified from Figure 2 (I) that acetylene does not have an easily noticeable extreme, such as that appearing in the oxidizing species. In addition, for a given (t_R; Φ) the acetylene molar fraction exhibits significant discrepancies with the choice of kinetic model. Another interesting feature of acetylene concerns the chemical equilibrium. For values Φ < 3 the chemical equilibrium molar fractions are negligible; whereas the PSR computed values are larger than 1 ppm for all models. This is also a strong evidence that chemical equilibrium is not reached in the reactor.

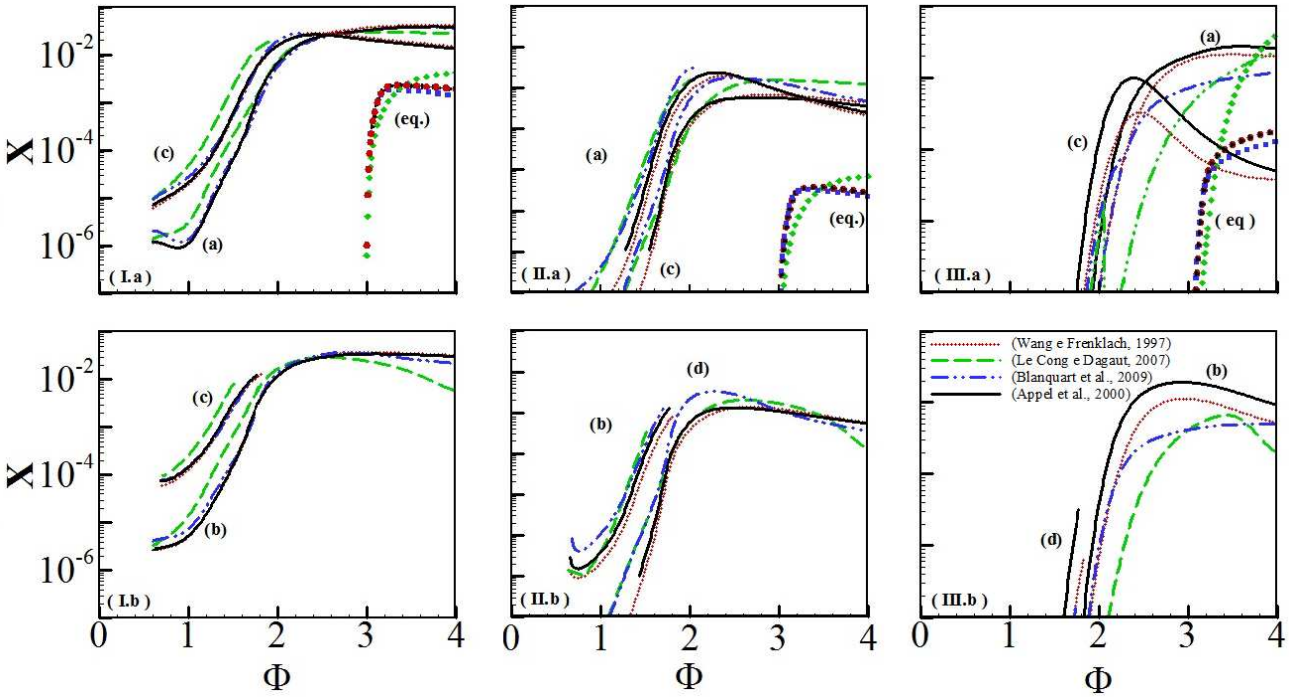

Figure 2. Mole fraction of acetylene (I.a and I.b), propargyl (II.a and II.b), and benzene (III.a and III.b), as a function equivalence ratio of the mixture (Φ) for residence times of 100 ms (a), 10 ms (b), 1 ms (c) and 0.1 ms (d). Chemical equilibrium (symbols), chemical kinetic models (lines). Top plots: Chemical equilibrium, t_R = 100 ms, and t_R = 1 ms. Bottom plots: t_R = 10 ms and t_R = 0.1 ms

Concerning the chemical kinetic models, Figure 2 (I) indicates that (Le Cong and Dagaut, 2008) model molar fractions diverges sharply from the others models results for the range of Φ and t_R studied, indicating conceptual mechanism differences for those chemical species. These molar fraction differences are 151% and 238% when this model is compared with the model of (Appel et al., 2000) for t_R = 0.1 ms and Φ = 1.4, and for t_R = 100 ms and Φ = 2.4, respectively. When compared the models of (Wang and Frenklach, 1997) and (Appel et al., 2000) the largest discrepancies observed are 13% when t_R = 0.1 ms and Φ = 1.4, whereas for t_R = 100 ms and Φ = 2.4 the discrepancy is 3,9%. Comparing the models of (Blanquart et al., 2009) and (Appel et al., 2000) for these same condition, the differences are 20% and 7%, respectively.

Figure 2 (II) also shows the obtained results for propargyl. It may first be noticed that the discrepancies between the four chemical kinetic models are more pronounced than the previous species studied, and that the differences with respect to chemical equilibrium are large. Indeed, for all t_R, a substantial increase in the molar fraction can be observed with a slight increment in Φ. As an example, the molar fraction increases four orders of magnitude when Φ goes from 1.5 to 2 for t_R = 100ms. However, for Φ > 1.8 this trend becomes a smoothing decreasing one, after the molar fraction reaches a maximum value. As already observed for acetylene, for Φ < 3 propargyl molar fraction at chemical equilibrium could be neglected, whereas in the PSR this species occurs in significant amounts. The discrepancies on molar fraction values for (Appel et al., 2000) and (Wang and Frenklach, 1997) models in the PSR have a very similar trend, even though these discrepancies are higher than those obtained for the acetylene. For Φ = 1.8 and 2.6, and t_R = 100 ms the molar fraction differences are -36% and 12%, respectively, and for t_R = 0.1 ms the molar fractions differences are 58%, for these two models. However, the differences between the other two models are even more significant. As an example, using the same values of Φ and t_R, i.e., Φ = 1.8 and 2.6 for t_R = 100 ms and Φ = 1.8 and 2.6 for t_R = 0.1 ms, the model of (Blanquart et al., 2009) has a relative difference in molar fraction with respect to the model of (Appel et al., 2000) of 129%, 201%, and 81%, respectively. Whereas, the (Le Cong and Dagaut, 2008) model has a molar fraction difference relatively to the model of (Appel et al., 2000), for the same values of Φ and t_R of 59%, 131% and 178%, respectively.

Figure 2 (III) shows the benzene PSR molar fractions as function of the mixture equivalence ratio for residence times ranging from 100 to 0.1 ms, and that associated with chemical equilibrium. At first glance, it is clear that discrepancies are much more severe than for the preceding species analyzed here. As for propargyl and acetylene, the benzene equilibrium molar fraction is negligible for Φ < 3.0. Nevertheless, the chemical equilibrium shows that, for Φ > 3.4, marked differences between (Le Cong and Dagaut, 2008) and the other models appear. Furthermore, the (Blanquart et al., 2009) model also has clear discrepancies over the (Wang and Frenklach, 1997) and (Appel et al., 2000); however, the overall trend is the same. This indicates that the chemical equilibrium for (Le Cong and Dagaut, 2008) is not the same than the others. Concerning the chemical kinetic models results, the differences between (Appel et al., 2000) and (Wang and Frenklach, 1997) models are the smallest; however, these differences are more significant than the others species analyzed. As an example, for t_R = 100 ms and Φ = 2.2 and 2.8, the molar fraction differences between the model (Wang and Frenklach, 1997) relative to the (Appel et al., 2000) one are 3.9 times and 1.2 times, respectively, and for t_R = 10 ms and the same values for Φ = (2.2 and 2.8) the molar fraction differences are 4.2 times and 1.8 times, respectively. The discrepancies are relatively higher between (Appel et al., 2000) model and (Blanquart et al., 2009). For t_R = 100 ms and Φ = 2.2 e 2.8, the models of (Blanquart et al., 2009) are a factor of 3.9 and 2.8. For t_R = 10 ms, and the same values of Φ the differences is a factor of 4.7 and 5.2, respectively. For the model of (Le Cong and Dagaut, 2008), t_R = 100 ms and Φ = 2.2 e 2.8, the differences are a factor of 231 and 9.3, respectively and for t_R = 10 ms and Φ = 2.2 e 2.8, the differences are a factor of 100 and 7.5.

Finally, Figure 3 shows the evolution of the pyrene (A_4) mole fraction as a function the equivalence ratio for residence times of 100, 10, 1 and 0.1 ms, and also the chemical equilibrium. Note that pyrene does not occur for t_R = 0.1 ms, and that the (Le Cong and Dagaut, 2008) model does not include chemical kinetic modeling for aromatic species higher than benzene. The depicted results show that the maximum mole fraction decreases with decreasing t_R, and that the equivalence ratio of this maximum shifts from 3 to 2.2 as t_R goes from 100 to 1 ms. This is the chemical species which has the most pronounced molar fraction discrepancies among all studied here. As an example, the relative differences between (Wang and Frenklach, 1997) model to (Appel et al., 2000) one for the t_R = 100 and Φ = 2.4 and 3.0, are a factor of 24 and 11, respectively and t_R = 1 ms and Φ = 2.1 is a factor of 37. For the same evaluation points, the differences of (Blanquart et al., 2009) model to (Appel et al., 2000) one are a factor of 16, 5.6, and 102 respectively.

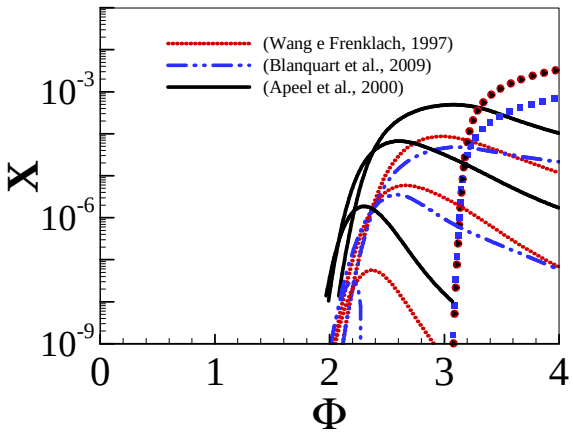

Figure 3. Mole fraction of pyrene as a function equivalence ratio of the mixture (Φ) for residence times of 100 ms (a), 10 ms (b), 1 ms (c) and. Chemical equilibrium (symbols), chemical kinetic models (lines).

3.3 Soot precursors reaction pathway

In order to understand the discrepancies presented in Section 3.2, reaction rate analyzes are performed for acetilene, propargyl, benzene, and pyrene so as to identify the main reactions and pathways responsible for these species. The main differences lie in the kinetic mechanisms design. Furthermore, in order to quantify these differences, the Arrhenius constant k (T) is evaluated at 2000 K. The main results from the referred analys are summarized in Table 2.

Concerning the acetylene, considering the models of (Appel et al., 2000), (Wang and Frenklach, 1997) and (Blanquart et al., 2009), the three main reactions are:

$C_2H_2+H(+M) \Leftrightarrow C_2H_3(+M)$ (3.1)
$C_2H_2+O \Leftrightarrow T\text{-}CH_2+CO$ (3.2)
$C_2H_2+O \Leftrightarrow HCCO+H$ (3.3)

whereas for (Le Cong and Dagaut, 2007) model, these are:

$C_2H_2+H(+M) \Leftrightarrow C_2H3(+M)$ (3.4)
$C_2H_2+O \Leftrightarrow HCCO+H$ (3.5)
$C_2H_4+(+M) \Leftrightarrow C_2H_2 + H_2 (+M)$ (3.6)

The main reaction pathway for the first three models shows a trend towards a common set of important reactions, only the (Le Cong and Dagaut, 2008) model exhibit discrepancies. When analyzing the Arrhenius reaction rates, k(T), (Wang and Frenklach, 1997) and (Appel et al., 2000) models do not exhibit significant differences. However, comparing (Blanquart et al., 2009) and (Appel et al., 2000) models, k(T) values are distinct. Factor of 44, 1.23 and 79 times larger are found for reactions 3.1, 3.2 and 3.3, respectively. Indeed, these two models have six reactions in common, but only one has the same value of k(T). Repeating the analysis for the (Le Cong and Dagaut, 2008) model, k (T) has factors of 0.38, 0.25 and 0.34 for reactions 3.1, 3.2, 3.3. Despite of not being an important reaction for this model, reaction 3.3 is in the scope of this kinetic mechanism. In addition, according to the reaction rate analysis, these models have three reactions in common but only one has the same value of k (T).

Regarding propargyl, the reaction rate analysis is performed according to the values Φ and t_R given in Table 1 for each chemical model. For the kinetic model of (Appel et al., 2000) and of (Wang and Frenklach, 1997) the main reactions are:

$C_2H_2 + CH_2 \Leftrightarrow C_3H_3 + H$ (3.7)
$C_3H_3 + OH \Leftrightarrow C_2H_3 + HCO$ (3.8)

Whereas, for the model of (Blanquart et al., 2009), the reactions are:
$C_3H_3 + H \Leftrightarrow P\text{-}C_3H_4$ (3.9)
$P\text{-}C_3H_4 + H \Leftrightarrow C_3H_3 + H_2$ (3.10)

and for (Le Cong and Dagaut, 2008) model one has:
$C_3H_3 + H \Leftrightarrow C_3H_2 + H_2$ (3.11)
$S\text{-}CH_2 + C_2H_2 \Leftrightarrow C_3H_3 + H$ (3.12)

It may be noticed that the main reactions of (Wang and Frenklach, 1997) and (Appel et al., 2000) models are identical. The only difference lies in the Arrhenius constants which lead to a different value of k(T) for reaction 3.7, in a factor of 2 for (Appel et al., 2000). Hence, the difference in mole fractions observed between the models of (Wang and Frenklach, 1997) and (Appel et al., 2000) are related to the update of other reactions, which modify the whole results. However, this does change significantly the results for the species studied so far. On the other hand, (Le Cong and Dagaut, 2008) and (Blanquart et al., 2009) models have no reactions in common in this analysis, underscoring an important difference in the reactions controlling the propargyl formation. When the kinetic model of (Blanquart et al., 2009) is compared with that of (Appel et al., 2000) reactions 3.9 and 3.10 are not among the main reactions for the second one. However, both models included these reactions in their models, and k (T) is different by a factor of 0.25 and 0.36, respectively for the (Blanquart et al., 2009) model in relation to (Appel et al., 2000) one. The same analysis has been made for (Le Cong and Dagaut, 2008) model; however, only the reaction 3.12 is in common with the model of (Appel et al., 2000) k(T) differs by a factor of 2 in relation to this model.

Table 2. Summary of the three major reactions for the formation of propargyl (C_3H_3), acetylene (C_2H_2), benzene (A_1) and pyrene (A_4) for the kinetic models of (Appel et al., 2000) (a), (Blanquart et al., 2009) (b), (Le Cong and Dagaut, 2008) (c), and (Wang and Frenklach, 1997) (d) and evaluation of Arrhenius rate k(T) at 2000 K.

		k(T)			
Item	**Chemical Reaction**	**(a)**	**(b)**	**(c)**	**(d)**
1	$C_2H_2+H(+M) \Leftrightarrow C_2H_3(+M)$	4,8E+12	2,3E+14	2,1E+12	4,8E+12
2	$C_2H_2+O \Leftrightarrow T\text{-}CH_2+CO$	3,6E+13	4,5E+13	7,3E+12	3,6E+13
3	$C_2H_2+O \Leftrightarrow HCCO+H$	3,6E+13	2,9E+15	9,6E+12	3,6E+13
4	$C_2H_4 (+M) \Leftrightarrow C_2H_2+H_2 (+M)$	1,1E+12	1,1E+12	2,5E+15	1,1E+12
5	$C_3H_3+OH \Leftrightarrow C_2H_3+HCO$	4,0E+13	-	-	4,0E+13
6	$C_2H_2+ CH_2 \Leftrightarrow C_3H_3+H$	1,6E+13	-	8,1E+12	8,1E+12
7	$C_3H_3 + H \Leftrightarrow P\text{-}C_3H_4$	3,0E+13	7,4E+12	-	-
8	$P\text{-}C_3H_4 + H \Leftrightarrow C_3H_3 + H_2$	1,4E+14	4,9E13	1,4E+14	9,1E+11
9	$C_2H_2+S\text{-}CH_2 \Leftrightarrow C_3H_3+H$	4,0E+13	1,9E+04	2,0E+13	8,1E+12
10	$C_3H_3+H \Leftrightarrow C_3H_2+H_2$	-	2,6E+13	-	4,1E+13
11	$A_1+H \Leftrightarrow A_1^-+H_2$	6,9E+13	8,5E+13	6,9E+13	6,9E+13
12	$A_1^-+H(+M) \Leftrightarrow A_1(+M)$	1,0E+14	-	-	1,0E+14
13	$C_3H_3 + C_3H_3 \Leftrightarrow A_1$	5,0E+12	1,1E+14	4,0E+12	2,0E+12
14	$A_1 \Leftrightarrow A_1^-+H$	-	2,1E+16	2,2E+14	-
15	$l\text{-}C_6H_6 \Leftrightarrow A_1$	-	-	6,49E+12	-
16	$A_4^-+H \Leftrightarrow A_4$	1,0E+14	1,5E+15	-	1,0E+14
17	$A_4+H \Leftrightarrow A_4^-+H_2$	9,6E+13	2,8E+14	-	9,6E+13
18	$A_3^{-4}+C_2H_2 \Leftrightarrow A_4+H$	1,8E+13	6,7E+12	-	9,2E+12
19	$A_4+OH \Leftrightarrow A_3^{-4}+CH_2CO$	6,9E+12	-	-	6,9E+12
20	$A_4+OH \Leftrightarrow A_4^-+H_2O$	7,1E+12	1,4E+13	-	7,1E+12
21	$A_4+O \Leftrightarrow A_3\text{-}4+HCCO$	1,7E+13	-	-	1,7E+13

Benzene is the next chemical specie analyzed. Thus, the three most important reactions for benzene, according to the reaction rate analysis, are shown below and the results for reaction rate are presented at the Table 2. For the models of (Appel et al., 2000) and (Wang and Frenklach, 1997), these are

$$A_1 + H \Leftrightarrow A_1^- + H_2 \quad (3.13)$$
$$A_1^- + H(+M) \Leftrightarrow A_1 (+M) \quad (3.14)$$
$$C_3H_3 + C_3H_3 \Leftrightarrow A_1 \quad (3.15)$$

for the model of (Blanquart et al., 2009),

$$A_1 + H \Leftrightarrow A_1^- + H_2 \quad (3.16)$$
$$C_3H_3 + C_3H_3 \Leftrightarrow A_1 \quad (3.17)$$
$$A_1^-+H \Leftrightarrow A_1 \quad (3.18)$$

and for the model of (Le Cong and Dagaut, 2008),

$$A_1 + H \Leftrightarrow A_1^- + H_2 \quad (3.19)$$
$$A_1^- + H \Leftrightarrow A_1 \quad (3.20)$$
$$l\text{-}C_6H_6 \Leftrightarrow A_1 \quad (3.21)$$

The most important reaction for benzene formation from smaller hydrocarbons is reaction 3.15, except for the (Le Cong and Dagaut, 2008) model. The reactions with propargyl could be expected due to its importance discussed in literature (Blanquart et al., 2009), (Appel et al., 2000), (Kennedy, 1997) assert that this reaction is the main responsible for aromatic species formation. It is surprising that for the (Le Cong and Dagaut, 2008) kinetic models this reaction has not been considered to be important in benzene formation, even if this reaction is included in the chemical kinetic mechanism. Moreover, analyzing the k(T) values at Table 2, it can be noticed that the four kinetic mechanisms present distinct values. Reaction 3.15 exhibits significant differences, being 13 times smaller for (Blanquart et al., 2009) model

and being 2.5 and 1.25 times smaller for the (Wang and Frenklach, 1997) and (Le Cong and Dagaut, 2008) models, respectively, when compared to the (Appel et al., 2000) model. For (Wang and Frenklach, 1997) and (Appel et al., 2000) models, the reaction constants and chemical reactions update processes are thus evident for benzene and has led to a significant influence on the results obtained.

Furthermore, the (Blanquart et al., 2009) model shows reaction pathway similar to the (Wang and Frenklach, 1997) and (Appel et al., 2000) models, insofar as the reaction 3.16 and 3.17 are common to them. However, examining more closely the (Blanquart et al., 2009) model, among the 5 most important ones, the two reactions that are important in benzene formation and are exclusively present in this kinetic model are:

$$A\text{-}C_3H_5 + C_3H_3 \Leftrightarrow A_1 + H_2 \quad (3.22)$$

$$C_5H_4CH_3 \Leftrightarrow A_1 \quad (3.23)$$

According to (Blanquart et al., 2009), these 2 reactions are on attempt to better describe A_1 in combustion. Thus, it is evident that these two reactions play an important role for this species formation in the PSR. In the case of model of (Le Cong and Dagaut, 2008) model, it is interesting to note the absence of the reaction 3.15, which should be the main reaction responsible for benzene formation. In addition, the value of k(T) for this mechanism is quite similar to the others. So, the differences can be related to the absence of the properly reaction pathway to the formation of C_3H_3 in this mechanism.

Finally, the pyrene reaction rate analysis is presented. A congruency in the reaction for pyrene may be observed for all kinetic models. Indeed, only Table 2 reactions 19 and 21 are not common for all three models. However, there are significant differences in the Arrhenius constants which imply different values of k(T). Indeed, the process of updating (Wang and Frenklach, 1997) to (Appel et al., 2000) model included changes in reaction constants for reaction 18 only. Regarding the (Blanquart et al., 2009) model the values of the reaction rates are different for all reactions; that is, the largest difference occurs for the reaction 16, where the reaction rate is 7 orders of magnitude smaller when compared to the (Appel et al., 2000) model. The reaction rate values for the other reactions exhibit the same order of magnitude that (Appel et al., 2000) model. Therefore, despite the kinetic models presenting rather small differences between chemical reactions and reaction rates for the formation of pyrene, the differences between the computed molar fractions are very large.

4. CONCLUSIONS

A study of key chemical species involved in soot formation processes has been performed in order to compare the prediction capacities of four different chemical kinetics mechanisms, following PSR and chemical equilibrium computations. For some mixture equivalent ratios, chemical equilibrium is not reached in the PSR, even for high residence times. Residence times higher than 100 ms were not evaluated because it was not possible to achieve numerical convergence. So, this situation interferes significantly in the results for all chemical models and the chemical species studied. Moreover, significant differences between the results obtained from different kinetic models have been observed for propargyl and aromatic species. These divergences could lead to error propagation in many others species which are directly involved in the chemistry of soot. Since propargyl is crucial for aromatic species, any substantial difference in its pathway on its molar fraction affects the prediction accuracy as is seen in the benzene and pyrene results.

5. REFERENCES

Appel, J., Bockhorn, H., Frenklach, M., 2000. “Kinetic modeling of soot formation with detailed chemistry and physics: laminar premixed flames of C2 hydrocarbons” Combustion and Flame, Vol. 121, pp. 122 – 136.

Blacha, T., Domenico M., Gerlinger, P., Aigner, M., 2012. “Soot predictions in premixed and non-premixed laminar flames using a sectional approach for PAHs and soot” Combustion and Flame. Vol. 159, pp. 181–193.

Blanquart, G., Pepiot-Desjardins, P., Pitsch, H., 2009. “Chemical mechanism for high temperature combustion of engine relevant fuels with emphasis on soot precursors”. Combustion and Flame, Vol. 156, pp. 588-607.

Celis, C. and Figueira da Silva, L. F., 2016, “On the Non-Equilibrium Behavior of Fuel Rich Hydrocarbon/Air Combustion within Perfectly Stirred Reactors”, Combustion Science and Technology (under review).

Dworkin, S. B., Zhang, Q., Thomson, M. J., Slavinskaya, N. A., Riedel, U., 2011. “Application of an enhanced PAH growth model to soot formation in a laminar coflow ethylene/air diffusion flame” Combustion and Flame, Vol. 158, pp. 1682–1695.

Kennedy, I.M., 1997. “Models of soot formation and oxidation” Progress in Energy and Combustion Science, Vol. 23 pp. 95-132.

Le Cong, T. and Dagaut, P., 2008. “Experimental and detailed kinetic modeling of the oxidation of methane and methane/syngas mixtures and effect of carbon dioxide addition”. Combustion Science and Technology, Vol. 180 pp. 2046 – 2091.

Slavinskaya, N.A. and Frank, P., 2009. “A modelling study of aromatic soot precursors formation in laminar methane and ethene flames”. Combustion and Flame, Vol. 156 pp. 1705–1722.

Slavinskaya, N. A., Riedel, U., Dworkin, S. B., Thomson, M. J., 2012. “Detailed numerical modeling of PAH formation and growth in non-premixed ethylene and ethane flames”. Combustion and Flame, Vol. 159, pp. 979–995 .

Smooke, M.D., Long, M.B., Connelly, B.C., Colket, M.B., Hall, R.J. 2005. “Soot formation in laminar diffusion flames” Combustion and Flame, Vol. 143, pp. 613–628.

Wang, H. and Frenklach, M., 1997. “A detailed kinetic modeling study of aromatics formation in laminar premixed acetylene and ethylene flames” Combustion and Flame, Vol. 110, pp. 173 – 221.

V. Chernov, Murray J. T., S. B. Dworkin b, Nadezhda A. Slavinskaya, U. Riedel., 2014. “Soot formation with C1 and C2 fuels using an improved chemical mechanism for PAH growth”. Combustion and Flame, Vol. 161, pp. 592–601.

6. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.