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TUNING DETAILED KINETICS MODELS FOR LAMINAR FLAME SPEED AND NO$_X$ PREDICTIONS: A SYSTEMATIC METHODOLOGY USING SENSITIVITY ANALYSES

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Abstract. *NO$_X$ emissions are important parameters related to the pollutants released by systems that burn fossil fuels for power and work generation. Five known routes generate NO$_X$ compounds, these routes consider sequences of chemical reactions that best depict the evolution of the chemical species. Chemical kinetics mechanisms incorporate the chemical reactions, which are employed to better understand how the compounds are created along the combustion process. The kinetics mechanisms are important tools to understand the behavior of the chemical species; however, occasionally the mechanisms show some deviations in comparison to experimental data. These deviations resulted from the values used for the reaction rate coefficients, even though, it is necessary to verify which of the reactions most influences the result, and what is achieved using the sensitivity analysis. In this work, the A. Konnov's DKM mechanism is studied, a detailed kinetics model available in the literature for the combustion of i-propanol and n-propanol. The mechanism is analyzed by using sensitivity analysis strategies, that process involves the assessment of the aforementioned kinetics model comparing the numerical predictions to experimental data also available at the literature. Another aspect of interest is the influence of the radiative and diffusive effects in the solution of the one-dimensional free flame. Along the sensitivity analysis, the most influencing reactions are pointed out and of this form, and tuned, to better reproduce the experimental data. The brute-force sensitivity and normalized sensitivity analyses were used. The most influencing reactions for NO$_X$ mole fraction prediction in the post-flame region were then elucidated and tuned.*

Keywords: Nitrogen oxides, Detailed Chemical Kinetics, Brute Force Sensitivity Analysis, CANTERA

1. INTRODUCTION

Among the equipment used to generate power, the internal combustion engines (ICE) are the most common ones, which are mainly driven by the combustion of fossil fuels. Given the growing depletion of the natural reserves of these resources, along with the environmental impacts caused by the pollutants resulted from the combustion, there is a search to better comprehend how these pollutants are created, to still consume the fossil fuels in less damageable way (Lubrano

Lavadera *et al.*, 2021).

The pollutants can directly lead to environmental problems such as photochemical smog and acid rain, where the main ones are those related to the sulfur oxides, SO_X, and nitric oxides, NO_X, the latter one that is investigated in this study (Ali *et al.*, 2020). The more stringent regulations on pollutant emissions along with the environmental impact, fostered more interest in fully understanding the conditions and paths that favor the appearance of these substances. This interest is verified by noting that several researchers have focused their investigations on understanding how nitric oxides are formed during combustion reactions, among them: Watson *et al.* (2016); Maroa and Inambao (2020); Han *et al.* (2021); Lubrano Lavadera *et al.* (2021).

The combustion chemical reactions happen in a very small time step, and, depending on the thermodynamic conditions, the appearance of specific substances is favored. Basically, during the combustion many decompositions, combination, and recombination reactions happen, leading to the final products (Turns, 2013; Glassman *et al.*, 2014). The before-mentioned oxides are created through some specific paths during the chemical reactions, where, the nitrogen present in the air mixture, along with the nitrogen present in the fuel, are modified to the NO and NO_2 compounds, mainly into NO (Maroa and Inambao, 2020).

Nowadays, among the tools employed to project and analysis of internal combustion engines, the numerical simulation of the combustion reactions is a common one, where, kinetics mechanisms are used. The kinetics mechanisms rely on experimental data to properly reproduce the real trend of the combustion, that is, if the mechanism is not calibrated the results produced will not be accurate enough. In this sense, the sensitivity analysis is employed, which allows identifying the reactions that most influence the result of some variable (e.g. IDT, species concentration, adiabatic temperature, laminar burning velocity) (Capriolo *et al.*, 2021).

Another important issue in the numerical simulation concerns the phenomena that are considered in the mathematical model, namely the thermal diffusion and thermal radiative heat transfer in the combustion reactions. Basically, the tendency of a mixture to separate, creating a mass flux, caused by a thermal gradient (SAGHIR *et al.*, 2005; Srinivasacharya *et al.*, 2015; Mohamed and Paleologos, 2018). Regarding the thermal radiative heat transfer, it is related to an energy flux caused by a concentration gradient in the mixture (Srinivasacharya *et al.*, 2015).

Hereupon, the objective of this work is to perform sensitivity analysis in a kinetics mechanism to determine which are the most influencing reactions in the laminar burning velocity and NO mole fraction in the combustion products, aiming to properly tune the parameters of these reactions and enhance the prediction made by the numerical simulation. Moreover, the effects of the thermal radiative and diffusive in the sensitivity analysis is checked, namely, the most influencing reactions, with a posterior tuning of these reactions.

2. LITERATURE REVIEW

The present paper focuses on understanding which chemical reactions most influences the laminar burning velocity and the NO mole fraction prediction through the chemical kinetics simulation of a mechanism made by the Division of Combustion Physics - Prof. A. Konnov - research group. So, the five known NO_X formation routes are presented as well as the sensibility analysis methods, their differences, and capabilities. Also, the kinetics mechanism used, and the available experimental data employed are briefly commented.

2.1 NO_X Routes

The NO_X comes from five known routes, one involving different reactions. The first route is called the thermal NO route, which comes from the oxidation of nitrogen in the air at high temperatures. It was proposed by Zeldovich and it is the dominant source of NO at long residence times and high temperatures. Most of the NO formed in this route, according to Zeldovich, occurs after the complete combustion, with the rate of the combustion reactions being much faster than the reaction of the NO formation itself (Martins and Ferreira, 2010).

The immediate formation route was proposed by Fenimore, who observed that the NO formation rate at the flame front exceeded the predicted by the thermal route in fuel-rich mixtures close to stoichiometry. The NO formation can be broken down into two conditions, fuel-poor and fuel-rich, being more important under stoichiometric and fuel-rich conditions, once the CH conditions decrease under excess air conditions (De Soete, 1975; Martins and Ferreira, 2010). According to Konnov (2009) researchers discovered that there was a divergence between the thermal constant calculated and the experimental data for the initial step reaction, existing one more step reaction, which better describes the real behavior of the formation route.

The third route is known as the N_2O-mediated, which is triggered by the recombination of O atoms with N_2, generation N_2O. It has two different paths, depending on the equivalence ratio, namely, if the combustion is occurring at lean or rich stoichiometric conditions. The route becomes important under conditions of a high-pressure environment and excess air (Martins and Ferreira, 2010).

The most recent route is the NNH mechanism, proposed by Bozzelli and Deant (1995). In this path, the NNH reacts with oxygen atoms, forming $HNNO^*$ which dissociates into $NH + NO$ (Bozzelli and Deant, 1995). This route is

considered to be important in the NO_X formation for long-chain hydrocarbon fuels and in gas operating turbines (Bozzelli and Deant, 1995; Klippenstein *et al.*, 2011; Purohit *et al.*, 2021).

The last route is related to the nitrogen present in the fuel. In liquid fuels, the nitrogen compounds present in the composition of the fuel vaporize quickly while entering the combustion chamber. For this route, the formation of nitrogen atoms via $N_2 + O$ is much more energy costly than the production of nitrogen atoms in the flame front (Martins and Ferreira, 2010). According to Bowman (1973), the time scale of the combustion reactions is comparable to the rate of NO formation through the nitrogen of the fuel route.

2.2 SENSITIVITY ANALYSIS

In the detailed kinetics mechanisms, the Arrhenius rate expression is applied to calculate the reaction rate, where the constants of the equation are obtained through experimental tests. It happens that slight changes in these constants are capable of modifying the whole result of the numerical simulation.

Aiming to verify the influence of changes in model input parameters on the output of mathematical models, the sensitivity and uncertainty analysis methods are for. Since sensitivity analyses provide information about the most influential reactions in the results of simulations in kinetics mechanisms, these tools are essential for understanding and optimization of detailed kinetics models (Capriolo *et al.*, 2021; Cancino, 2009).

The method is applicable to reactive systems that involve the time-evolution of chemical species (e.g. auto-ignition of reactive mixtures in reactors). In this methodology, it is necessary that at least one of the dependent variables is set as the target (e.g. reaction rate of chemical species or sensitivity to temperature). On the other hand, independent variables cannot be directly set as targets, in this case, it is necessary to use an indirect approach. The best way to explain this is using the ignition delay time example, where, it is well known the hydroxyl radical affects both the temperature increase and the fuel depletion, thereby, the target of the analysis is set as the sensitivity on the concentration of the hydroxyl radical (Cancino, 2009). Among the sensitivity analysis methods, normalized sensitivity analysis (NSA), and brute-force sensitivity analysis (BFSA) were chosen to be used, with both being explained in the sequence.

2.2.1 Normalized sensitivity analysis (NSA)

Sensitivity coefficients obtained with normalized first-order sensitivity analysis are used in combustion to show kinetics insight into the model capacity regarding the experimental data. This method is useful because it is a starting point for model analysis and identification of main parameters (Tomlin, 2013).

The fluctuation in the concentration of a given chemical species over time can be described by a nonlinear mass conservation equation, which will depend on the species concentration and the rate coefficient. The concentration itself is a vector dependent on the time and the vector rate coefficient, so, to solve the problem a first order coefficient is defined in Equation 1:

$$\frac{\delta c_i}{\delta k_j}(\mathbf{k}, t) = \frac{\mathbf{c}_i(k_j + \Delta k_j, t) - \mathbf{c}_i(k_j, t)}{\Delta k_j} \tag{1}$$

the equation describes the change in the concentration of the specie c_i at time t as a function of a fluctuation in the jth rate parameter. Making a Taylor expansion of the concentration equation at point t, $k + \Delta k$, where, on the first order term appears the local sensitivity matrix (Turányi, 1997). To numerically solve the integration to calculate the changes in $c_i(t)$ is a difficult and computationally expensive process, being necessary to normalize the problem, using the sensitivity matrix, as depicted in Equation 2.

$$S = \frac{\partial \left[ln \left(c_i(t) \right] \right.}{\partial \left[ln \ k_j \right]} \tag{2}$$

The normalized sensitivity coefficient, S, shows the change of the model solution due to an alteration in the parameter value, that is, the magnitude of S regards the relative importance of the reaction j^{th} in affecting the concentration of the chemical specie i^{th} at time t.

2.2.2 Brute-force sensitivity analysis (BFSA)

The procedure called the brute force sensitivity analysis is a simple method, however, it may result in inaccurate results, and be inefficient. Basically, to apply this method, in the first place it is necessary to have the original solution of the problem, and after, the new solutions are calculated again, but this time, each solution is done with a perturbation in the reactions parameters, one by one, that is, there will be m new solutions, where m is the number of reactions in the kinetics mechanism, and a total of $m + 1$ solutions (Cancino, 2009). As said, the main advantage of this method is its simplicity and ease to be implementation, what is the main reason for its use in this work.

3. METHODS

In a recent work by our research team Bonini *et al.* (2021), the NO formation and consumption from propyl alcohol fuels were evaluated, based in two kinetics mechanism for *n*-propanol and *i*-propanol combustion. The laminar burning velocity and NO mole fraction predicted by the mechanisms were compared with experimental data from Capriolo *et al.* (2021) (NO and laminar burning velocity measurements in the post-flame region were done). Laminar flame speed simulations (burner stabilized flat flame reactor) were performed in order to numerically assess the kinetics model's performance. In Bonini *et al.* (2021) work, the authors verified that the A.KONNOV's DKM mechanism showed some differences when the effect of the diffusive and radiative thermal effects was analyzed, namely, the predictions for laminar burning velocity (LBV) and NO concentration in the combustion products were better when the effects were disabled. The A.KONNOV's DKM mechanism is proposed for the combustion of C_3 alcohols, and it is composed of 6 elements, 206 species, and 2295 reactions. It was tested for flow and well-stirred reactors, ignition delay times, and flame structure, admissibly reproducing the experimental values. In this context, the present work aims to investigate which reactions most influences the results and tune their rate constants, in order to make better predictions with the chemical kinetics mechanism.

The numerical simulations in this work were done using the Cantera 2.4.0 toolkit with an in-house Python 3.6.13 script. Cantera is an open-source suite of tools for solving problems involving thermodynamics, chemical kinetics, and transport processes. The toolkit has pre-defined functions, used to solve combustion problems applied to reactors, flames, and chemical equilibrium[1]. To perform the simulations, a workstation with an Intel Core i7-7700 processor with 3.60 GHz and 16GB of memory RAM was used, in which, the average simulation time, for each fuel equivalence ratio was 65 hours.

Regarding the configuration of the simulation, the adiabatic, one-dimensional free flame[2], it was used, considering the combustion of two propyl alcohols: *n*-propanol, C_3H_7OH, and *i*-propanol, $(CH_3)2CHOH$ at an initial pressure of 1 atm and temperature of 373 K and equivalence ratio of 0.7-1.5.The refine criteria are: ratio of 3, the slope of 0.1, and curve of 0.1, and the multicomponent model was selected as transport model. The effects of the diffusive mass fluxes, Soret effect, and radiative heat transfer, were investigated, in this sense, two cases were simulated, one with the radiative and diffusive effects disabled, and another with the effects enabled.

Two sensitivity analyses were done, the brute force sensitivity analyses, in which the perturbation of 2 was adopted and a threshold enough to get a representative quantity of reactions in each analysis. Concerning the variables studied, the NO mole fraction in the products and the laminar burning velocity were considered. Along with the BFSA analysis, the normalized sensitivity analysis for laminar burning velocity was done.

In the context of the sensitivity analysis, both methods (BFSA and NSA) were performed for two different situations, namely, the first with the radiative and diffusive thermal effects enabled, and the second condition for which the refereed effects were enabled. In this sense, to better visualize how the nitrogen reacts within the mechanism, the nitrogen route inside the A.KONNOV's DKM mechanism is depicted in Figure 1, completely, in Table 1 NO_X formation routes and its constant values for A.KONNOV's DKM mechanism are outlined.

Table 1. Reactions from NO_X routes and respective constant values for A.KONNOV's DKM mechanism.

Label	Reaction	A mole-cm-sec-K	n -	E_a cal/mole
R-NO1	$O + N_2 \rightleftharpoons NO + N$	9.400E+12	0.14	0
R-NO2	$N + O_2 \rightleftharpoons NO + O$	5.850E+09	1.01	6200
R-NO3	$N + OH \rightleftharpoons NO + H$	2.800E+13	0	0
R-NO4	$CH + N_2 \rightleftharpoons NCN + H$	3.00E+13	0	22157
R-NO5	$NCN + H \rightleftharpoons HCN + N$	1.890E+14	0	8425
R-NO6	$C + N_2 \rightleftharpoons CN + N$	5.200E+13	0	44700
R-NO7	$O + N_2 + (M) \rightleftharpoons N_2O + (M)$	9.900E+10	0	57900
R-NO8	$N_2O + O \rightleftharpoons NO + NO$	9.150E+13	0	27680
R-NO9	$N_2O + O \rightleftharpoons N_2 + O_2$	3.690E+12	0	15940
R-NO10	$N_2O + H \rightleftharpoons N_2 + OH$	2.200E+14	0	16750
R-NO11	$N_2O + H \rightleftharpoons NH + NO$	6.700E+22	-2.16	37155
R-NO12	$N_2O + OH \rightleftharpoons N_2 + HO_2$	1.000E+14	0	30000
R-NO13	$O + NNH \rightleftharpoons NO + NH$	1.700E+16	-1.23	500

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[1]Additional information about Cantera can be found at Cantera website.

[2]The description of this function can be found in the documentation available at Cantera website.

Figure 1. Simplified schematizing of the nitrogen path within the A.KONNOV's DKM mechanism.

4. RESULTS AND DISCUSSION

This section of the paper is divided into three parts, firstly the sensitivity analysis results for LBV are shown, pointing out the reactions that most influence each of the fuels for both enabling and enabling the diffusive and radiative thermal effects. In the sequence, the procedure is repeated for the results concerning the NO mole concentration in the products. Finally, yet importantly, the tuning process is performed for the reactions found in the sensitivity analysis, and the new results are compared with the experimental data, and with the default case.

4.1 SENSITIVITY ANALYSIS FOR LBV

To better observe how the two fuels can be influenced by different reactions, the results for LBV are shown separated, in first place for *i*-propanol, and after for *n*-propanol. Additionally, in each of the sections, the effects of the radiative and diffusive thermal effects in the solution are also studied.

4.1.1 *i*-Propanol

As can be checked in Bonini *et al.* (2021) the biggest differences occurred for an equivalence ratio of 1.05, being the case that will be studied in depth, and for which, the results are presented in this section. In the first place the results for the BFSA analysis will be presented, followed by the NSA results. The top reactions found are related to the well comprehended and studied mechanisms, for which the reaction rates give no space for further modifications (the H_2O_2

and CH_4 reactions). The top 18 reactions for *i*-propanol and equivalence ratio of 1.05 are presented in Figure 2.
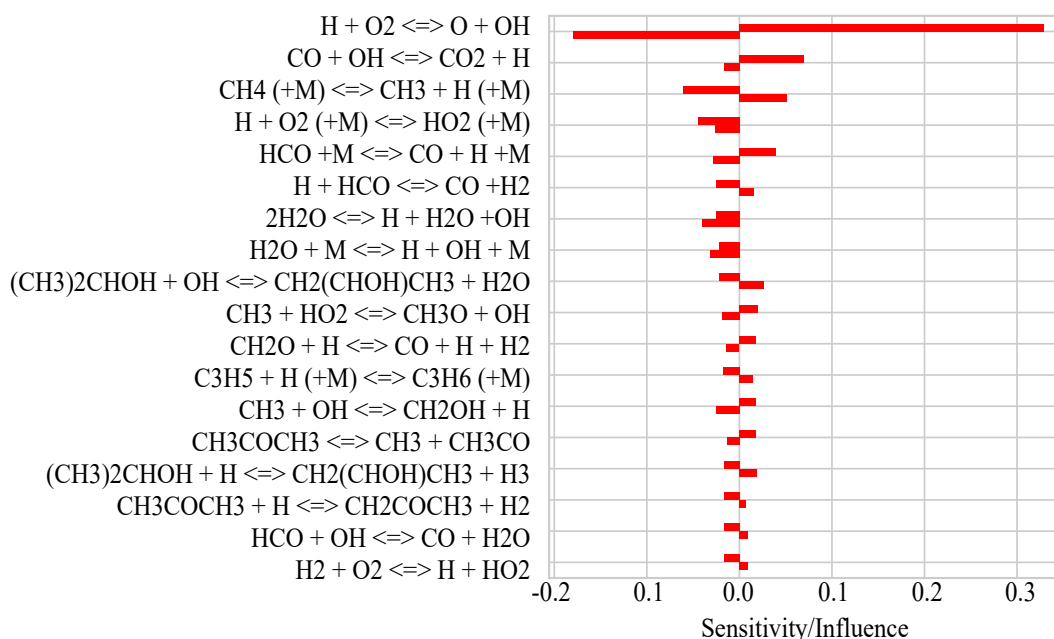

Figure 2. Sensitivity analysis obtained through the BFSA method using the detailed kinetic model from Capriolo *et al.* (2021) for laminar flat flame of (a) *i*-propanol. Unburned gas conditions: T = 323 K and p = 1 atm.

The reactions seen in Figure 2 are similar to the general result found for all the equivalence ratios analyzed. There are two reactions that always appear in the first and second places, being, firstly the $H + O_2 \rightleftharpoons O + OH$ reaction, and secondly the reaction $CH_4(+M) \rightleftharpoons CH_3 + H(+M)$, and, with the top 3 reactions being the same for all ratios. Attention must be taken when analyzing the reactions that most influence the results, the H_2O_2 reactions are a system exhaustively studied, so, the reaction rates are in the best state of the art, which also happens for the CH_4 decomposition reactions. The H_2O_2 system of reactions is always going to appear, regardless of the variable analyzed, because these reactions are basic kinetics of combustion. For the adjustment, those reactions are not modified, once their coefficients were confirmed by much evidence. Some trends observed are the increasing influence of the reaction $2H_2O \rightleftharpoons H + H2O + OH$ with the increase of the equivalence ratio up to 1.3, and decaying towards higher values, and, the growing influence of the dissociation reactions of larger fractions of carbon chains on the results with the increase of the equivalence ratio.

In Figure 2 R-9 is representative of a significant group of reactions that are very important in the chemical development of the combustion is the primary fuel decomposition reactions. Exploring deeper, more two reactions were found, with the group being present for almost all the equivalence ratios analyzed, which makes them strong candidates for the tuning process.

Performing the BFSA analysis with the radiative and diffusive effects disabled similar results were found, that is, the reactions have the same impact on the result (positive or negative). The primary fuel decomposition reactions appeared again, with similar values as those verified when the radiative and diffusive thermal effects were enabled. Table 2 summarizes the influences for the equivalence ratio of 1.05.

The first noticeable difference is the absolute value of the influence of each reaction in the results, which slightly changed from one case to another, also, the places between reactions R-8 and R-9, with reaction R-8 reducing its influence. Regarding the difference in the absolute values there is not a noticeable trend, that is, for some their values rose, and for others, they drooped. For the top 10 reactions presented in Table 2 the largest increase was of 3.3167% for the Reaction R-8 , and the largest reduction, of 2.146% occurred for Reaction R-3.

Regarding the NSA results, the same trend for BFSA was verified for both when the radiative and diffusive thermal effects were enabled and disabled, with slight differences in the absolute values of the influences, which, in some cases changed the position of the reactions, but, the same top 5 reactions were noticed for all the equivalence ratios analyzed. Specifically for $\phi = 1.05$, the absolute values for the top 10 reactions that most influenced were higher for those found for the BFSA analysis, for the effects enabled, they are higher at an average of 20%, with a maximum of 38% and a minimum of 3%, for the effects disabled, the average is 22%, the maximum of 41% and a minimum of 5%.

4.1.2 *n*-Propanol

In the present section, an analogous analysis as the one done in the previous section will take place here, but, at this time considering the combustion of *n*-propanol. The equivalence ratio of 1.05 is chosen again, once it showed the higher

Table 2. Reactions with the greatest influence on laminar flame speed for n-propanol combustion, obtained through BFSA.
Radiative and diffusive effects disabled. Unburned gas conditions: T = 323 K and p = 1 atm, $\phi = 1.05$.

| Label | Reaction | A | n | E_a | Influence |
		mole-cm-sec-K	-	cal/mole	-
R-1	$H + O_2 \rightleftharpoons O + OH$	1.040E+14	0	15286	0.312249
R-2	$CO + OH \rightleftharpoons CO_2 + H$	2.230E+5	1.9	-1160	0.0805209
R-3	$CH_4 + (M) \rightleftharpoons CH_3 + H + (M)$	2.100E+16	0	104913	-0.0588397
R-4	$H + O_2 + (M) \rightleftharpoons HO_2 + (M)$	4.660E+12	0.44	0	-0.050896
R-5	$HCO + (M) \rightleftharpoons CO + H + (M)$	4.750E+11	0.66	14870	0.0415273
R-6	$H + HCO \rightleftharpoons CO + H_2$	1.200E+14	0	0	-0.0245293
R-7	$2H_2O \rightleftharpoons H + H_2O + OH$	1.00E+26	-2.44	120160	-0.0233625
R-9	$(CH_3)2CHOH + OH \rightleftharpoons CH_2(CHOH)CH_3 + H_2O$	4.62E+0	3.7	-2946	-0.021515
R-8	$H_2O + (M) \rightleftharpoons H + OH + (M)$	6.060E+27	-3.312	120770	-0.0211555
R-10	$CH_3 + HO_2 \rightleftharpoons CH_3O + OH$	1.000E+12	2.0	-300	0.0206588

difference between the LBV predicted with and without the thermal radiative and diffusive effects enabled. It was noticed that again some primary decomposition reactions took place.

The NSA results found for n-propanol are very similar to those obtained for i-propanol, for the whole equivalence ratio simulated, for the radiative and diffusive thermal effects were enabled, there is an average difference of 25%, with a maximum of 40% and a minimum of 7%, for the effects deactivated the average is also of 40%, maximum of 40% and a minimum of 9%.

4.2 SENSITIVITY ANALYSIS FOR NITROGEN OXIDE CONCENTRATION IN THE PRODUCTS

The NO mole fraction on the products is heavily dependent on the NO formation routes, yet, for the different fuels and equivalence ratios, it is expected that the influence of each path is different, as will be demonstrated. It is important to point out that in Bonini *et al.* (2021) work, it was found that the greatest difference between the results predicted by the mechanisms with and without the thermal radiative and diffusive effects for the two fuels occurred at an equivalence ratio of 1.0. In this way, the results that will be analyzed in depth will be those of the aforementioned equivalence ratio.

4.2.1 *i*-Propanol

As a general trend, for equivalence ratio from 0.8 to 1.1 the reactions that most influenced the NO mole fraction in the combustion products were respectively Reaction R-NO-1 and Reaction R-NO-13 presented in Table 1. The aforementioned reactions do not contribute to the NO mole fraction for an equivalence ratio higher than 1.2. It is verified that the reactions from the N_2O route also follow this trend, becoming less influencing as the equivalence ratio grows, with no apparent contribution for equivalence ratio higher than 1.2.

The Immediate formation route is present across the whole spectrum of analyzed equivalence ratios, being the only NO_X formation route presented for $\phi = 1.4$. As long as the higher difference observed by Bonini *et al.* (2021), was for the equivalence ratio of 1.0, the BFSA results for NO mole fraction for this ratio are shown in Table 3.

Table 3. Reactions with the greatest influence on NO mole fraction for i-propanol combustion, obtained through BFSA.
Radiative and diffusive effects enabled. Unburned gas conditions: T = 323 K and p = 1 atm, $\phi = 1.0$.

Place	Reaction	Route	Influence
1	$N + NO \rightleftharpoons N_2 + O$	Thermal	0.51842
2	$NNH + O \rightleftharpoons NH + NO$	NNH	0.198563
3	$H + O_2 + (M) \rightleftharpoons HO_2 + (M)$		-0.182748
4	$CH + N_2 \rightleftharpoons H + NCN$	NO-prompt	0.115493
5	$CH_4 + (M) \rightleftharpoons CH_3 + H + (M)$		0.0476459
6	$CH + H_2 \rightleftharpoons CH_2 + H$		0.0457701
7	$CH_3 + O \rightleftharpoons CH_2O + H$		-0.0437135
8	$H + N_2O \rightleftharpoons NH + NO$	N_2O	0.0359713
9	$CO + OH \rightleftharpoons CO_2$		-0.0314738
10	$N_2O + (M) \rightleftharpoons N_2 + O + (M)$	N_2O	0.0308262

Table 3 shows that, from the top 10 reactions, half of them are related to some of the NO_X generation routes. The Thermal and NNH paths lead the list, with one reaction from the NO-prompt route, and two reactions concerning the N_2O path.

When the diffusive and radiative thermal effects were disabled, small differences between the reactions that most influence the NO mole fraction prediction was observed. Nevertheless, the general trend is the same, for equivalence ratio between 0.8 and 1.1 the thermal and NNH routes are most influenced, and, for equivalence ratio above 1.2 these routes do not contribute anymore, with the Immediate formation route being the only NO formation path present.

4.2.2 *n*-Propanol

The same analysis performed in the last section is going to be done here, aiming to check which chemical reactions most influence the prediction of the concentration of NO in the combustion products. In this manner, the general trend of the NO formation routes through the equivalence ratio observed for the combustion of *i*-propanol, where, a prevalence is observed in the presence of thermal and NNH routes for equivalence ratios between 0.7 and 1.1.

For equivalence ratio higher than 1.2 the Immediate formation route was the only NO formation path present. However, for the combustion of *n*-propanol, again, as seen for the LBV analysis, chemical reactions involving the basic decomposition of the fuel took place for equivalence ratios from 0.8, as can be seen in Table 4.

Table 4. Chemical reactions that influenced on NO mole fraction for *n*-propanol combustion, that concerns the decomposition of the fuel. **Radiative and diffusive effects enabled**. Unburned gas conditions: $T = 323$ K and $p = 1$ atm.

Number	Reaction	Influence $(.10^{-2})$						
		0.9	1.0	1.05	1.1	1.2	1.3	1.4
1447	$C_3H_7OH + H \rightleftharpoons H_2 + CH_3CH_2CHOH$	-1.23	-1.80	-2.21	-2.84	-4.21.	-5.67.	-6.17
1445	$C_3H_7OH + H \rightleftharpoons H_2 + CH_2CH_2CH_2OH$	1.06	1.32	1.47	1.75	2.46	3.47	4.00
1451	$C_3H_7OH + H \rightleftharpoons H_2 + CH_3CHCH_2OH$	-	-	-	-	2.30	2.30	2.58
1446	$C_3H_7OH + OH \rightleftharpoons CH_3CH_2CHOH + H_2O$	-1.02	-1.21	-1.34	-1.56	-	-2.39	-2.36

It is noticeable that when the equivalence ratio rises, the influence of reaction 1447 falls down, on the other hand, reaction 1445 had its influence increased. Reaction 1446 appears to have similar behavior as presented by reaction 1447, decreasing its influence for rising values of the equivalence ratio, but, it was not found a contribution of the reaction for the equivalence ratio of 1.2, for which further investigation must be done.

4.3 TUNING OF THE REACTION RATES

As discussed, the A.KONNOV's DKM kinetics mechanism is accurate, displaying minor differences for some results. After the sensitivity analysis, it was verified the presence of primary fuel decomposition reactions in the reactions that most influenced the results. In this sense, the aforementioned reactions for the combustion of *n*-propanol are going to be investigated, and a tuning process is going to be employed aiming to enhance the accuracy of the results.

From the results for *n*-propanol in Table 4, we have four primary fuel decomposition reactions. There are more reactions that influenced the results, but they are not in the scope of this work. The four reactions have a constant behavior through all the equivalence ratios simulated, that is, reactions number 1447 and 1446 had a negative influence while reactions 1445 and 1451 had a positive influence. Once, the four reactions only appeared simultaneously for $\phi = 1.3$, herewith, for reactions 1447 and 1446 the pre-exponential coefficient is going to be reduced to 40% and 25% respectively. For reactions 1445 and 1451 it will be enhanced by 25% and 50%, respectively.

Employing the tuning in the aforementioned reactions, the problem is simulated again and the results obtained are compared to the experimental data presented by (Capriolo *et al.*, 2021). The mechanism originally resulted in a value 14% higher than the experimental one (it is out of uncertainty data) and the tuned simulation predicted a value 0.0013% higher than the experimental (within the uncertainties of the measured data). On the other hand, the tuning deteriorated the prediction of the laminar burning velocity. Initially, the under-prediction was in the order of 0.41%, and after the tuning, it became an over-prediction in the order of 8.83%. Therefore, is evident that the tuning done is fair to enhance the result for the nitric oxide in the combustion product while it is not good for the laminar burning velocity.

5. CONCLUSION

The A.KONNOV's DKM kinetics mechanism is a very rich source of information that allows many analyses of different variables inherent to the combustion process and pollutants generation. The process carried out in this paper aimed to identify any patterns in the results that explain the divergences found in the previous paper published by our research team (Bonini *et al.*, 2021).

Performing the sensitivity analysis, it was verified which reactions were most influenced in each variable, LBV and NO concentration in the post-flame area. Concerning LBV, a group of similar reactions was found for both fuels, except for the primary fuel decomposition reactions, which were different for i-propanol and n-propanol. The NSA analysis resulted in the same reactions with slight differences in the absolute value of the influences of the reactions.

Furthermore, amongst the chemical that most influenced the NO results, it was found that, for equivalence ratio from 0.8 to 1.1 the reactions that most influenced the NO mole fraction in the combustion products were related to the Thermal and NNH paths, and, for higher equivalence ratio, the Immediate formation route took places. Moreover, it was observed that the main reactions were not always those linked with the five known paths.

An important aspect observed is the presence of primary fuel decomposition reactions influencing both variables for both fuels. We assessed a tuning process aiming to enhance the accuracy of the predictions made by the kinetics mechanism. From the 52 primary decomposition reactions for n-propanol, the four that most influenced were tuned. It was shown that the tuning for $\phi = 1.3$ improved the prediction of NO mole fraction in the products of the combustion, although the laminar burning velocity prediction became worse. In this sense, a suggested approach is to manipulate the pre-exponential coefficients of the reactions according to the equivalence ratios, namely, setting functions dependent on the equivalence ratio for each one.

As exposed, it remains clear how complex and tricky the tuning process is, being necessary a process that considers the differences: equivalence ratios, temperatures, pressures, and result variables. In this sense, it is presented that a substantial gap could be fulfilled if a proper method of configuring the pre-exponential coefficients of the reactions is presented. In the end, some interesting information arose from the analysis, even though, more questions showed up related to the chemical kinetics mechanism and how to do the tuning in an optimal way, which requires further specific analysis to be fully answered.

6. ACKNOWLEDGEMENTS

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