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Use of Virtual Kinetics Chemistry for Ignition Delay Times Prediction for High Temperature and NTC behaviors

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Abstract. *The simulation of complex reactive flows, usually associated with the applications of combustion, generally requires a large amount of computational power, and the reactive part of the solution is usually the most time consuming. Detailed chemical kinetics mechanisms can reach up to tens of thousands species, while numerical simulations of complex reactive flows can handle mechanisms, at most, with a few hundred species. Virtual kinetic mechanisms are a very effective strategy to drastically reduce the computational time spent in the reactive part of numerical simulations. They are formed by artificial species and reaction paths, built from scratch, which are optimized to reproduce the important characteristics of a canonical problem of interest. This work presents the development of virtual mechanisms to reproduce ignition delay times and temperature profiles for high temperature as well as discussions over the low temperature and NTC behaviors. Methane and n-heptane were used as base models for the discussions however, the methodology can be extended to any other fuel. There are still limitations on using virtual chemistry, but the results present overall deviations much smaller than those obtained from reduction methods, such as DRG, when mechanism of the same size are used.*

Keywords: *virtual chemistry, auto ignition, NTC, kinetic mechanisms.*

1. INTRODUCTION

The simulation of complex reactive flows usually associated with the applications of combustion generally requires a large amount of computational power, and the reactive part of the solution is usually the most time consuming. Detailed chemical kinetics mechanisms can reach up to tens of thousands species, while numerical simulations of complex reactive flows can handle mechanisms, at most, with a few hundred species. Virtual kinetic mechanisms are a very effective strategy to drastically reduce the computational time spent in the reactive part of numerical simulations. They are formed by artificial species and reaction paths, built from scratch, that are optimized to reproduce the important characteristics of a canonical problem of interest. This work presents the development of virtual mechanisms to reproduce ignition delay times and temperature profiles for high temperature cases, as continuation of the studies presented by Pacheco *et al.* (2020) as well as discussions over the low temperature and NTC behaviors. Methane and n-Heptane were used as base models for the discussions however, the methodology can be extended to any other fuel. There are still limitations on using virtual chemistry, but the results can present errors much smaller than reductions methodologies, such as DRG, when mechanism of the same size are used.

The prediction of the chemical kinetics evolution of chemical species is one of the most time consuming operations in reactive flow simulations. Large mechanisms are required to describe with an adequate degree of accuracy the chemical kinetics paths and reactions for large molecules Lu and Law (2009). Although comprehensive mechanisms are needed to build understanding of the chemistry of combustion, their implementation in complex computational models is largely unfeasible. In order to accommodate the state of the art of kinetic mechanisms for large hydrocarbon molecules, e.g., the mechanisms of Naik *et al.* (2011) with 3,500 species and 17,000 reactions and Pei *et al.* (2015) with 2,885 species and 11,754 reactions, several simplification strategies were developed. Such methods can be classified accordingly to the final product and strategy used in schemes that produce skeletal mechanisms, strategies to create analytic mechanisms, and the tabulated strategies. Some of these strategies can also be used in on-the-fly reductions, when the simplification of the mechanism is done simultaneously and in fine tuning with the solution of the transport part of the problem.

Skeletal procedures search and remove unimportant components of the detailed mechanism and therefore reduce its size and complexity. Turányi (1990) published a study in which the importance of species are evaluated by means of removing the reactions where it participates. More recently, graph theory was introduced as a reduction technique by Lu and Law (2005) known as Direct Relation Graph (DRG). Each species is mapped as a node in a directed graph, and the reactions connecting species are mapped as edges. The importance of species in the graph is evaluated and species with negligible effect in the important ones are deemed as redundant and removed. Several studies expanded the basic DRG method, Pepiot-Desjardins and Pitsch (2008) introduced error propagation (DRGEP), and importance index variations, such as the path flux analysis (PFA), proposed by Sun *et al.* (2010). Presently, a large number of variations exist and several authors studied their applicability and efficiency on reducing very large mechanisms, an activity known as Computer Assisted Reduction Mechanism (CARM). Another application of these methods are the on-the-fly reduction schemes, such as the one proposed by Tosatto *et al.* (2011).

The main goal of the analytic methods of reduction is to divide the dynamics of the species transformation into fast and slow domains. Analytic reductions aims at reducing the stiffness of the mechanisms by searching for Quasi Steady State (QSS) candidates to be removed from the system, replacing partial differential by algebraic equations. One of the basic methods is the Computational Singular Perturbation (CSP), proposed by Lam (1985). One of the main advantages of such strategies is the accuracy and robustness of the final mechanism, since the species are not actually removed, but accounted for through QSS relations.

Tabulated chemistry relies on the fact that the chemical trajectory during a combustion process is in a great extent defined by a smaller sub-space, named a manifold. Such space can therefore be solved in advance, the solution is stored as a table and retrieved during the combustion simulation. The density of the table and the number of inputs needed to retrieve a given information is dictated by the complexity of the problem to be solved.

Despite the reduction techniques have achieved several orders of reduction of complex detailed mechanisms, a limit is always reached, when the accuracy would degenerate at a larger rate than the reduction itself. This limit is intrinsically related to the structure of the detailed mechanism and can hardly be circumvented, even using a combination of strategies.

A strategy proposed by Cailler *et al.* (2017) aims at surpassing this limitation. Contrary to the reduction methodologies that work down from the detailed mechanism, by removing species and reactions as the method advances, the virtual chemistry method builds a virtual mechanism from the ground up, such that the virtual mechanism reproduces the same effects as the detailed mechanism. The final mechanism provided by such methodology can be as accurate as desired, and can predict not only the thermodynamic behavior, but different aspects of the detailed chemistry (Cailler *et al.* (2017); Maio *et al.* (2019); Cailler *et al.* (2020)). Additional information can be added further and then, the final mechanism can be composed only by the necessary or desired modules for the current problem.

This work develops an application of virtual schemes to describe the temperature evolution and the ignition delay time for the thermal ignition of homogeneous, constant mass, constant pressure, adiabatic, fuel-air mixtures. Several strategies and their potential to use as a way to describe Negative Temperature Coefficient (NTC) behavior for complex fuels are evaluated. The methane-air system is used as an example of the high temperature cases while the NTC discussions are presented based on the nheptane fuel.

2. METHODOLOGY

Before addressing the virtual chemistry procedure, some considerations regarding the optimization are made. A genetic optimization was perform, mostly due to the nature of the problem. The optimization of kinetic parameters present a very complex solution surface, with a great amount of points where no solution can be achieved, by means of solver convergence problems or a bad combination of the parameters.

The development of a virtual chemistry requires, at least two steps to be used: Thermodynamic optimization and kinetic optimization. The first step focus on obtaining the optimized coefficients for the constant pressure specific heat function of the n virtual species, generally in the form of NASA-7 polynomials and the virtual species molar mass that better describe the detailed mechanism. The second step optimizes the kinetics parameters for virtual reactions. In addition to the prediction of the adiabatic flame temperature, additional targets and specific reactions can be added to describe different aspects of the combustion, such as pollutant formation or laminar flame speed. As the current work aims at expanding the use of the virtual chemistry as well as bringing more light into the NTC prediction, the practical discussion, i.e. mathematical development, can be found on the work of Pacheco *et al.* (2020) and only a brief description will be presented here.

The first step of the optimization is to proper model the thermodynamic properties, i.e enthalpy, constant pressure specific heat function and the mixture molar weight. The first two are usually implemented in the form of NASA-7 polynomials. Moreover, each species requires the definition of a MW. With this, a virtual species require at minimum, seven parameters to be optimized (six NASA coefficients and the molar weight, with an additional stoichiometric coefficient for every condition used). The fitness function for this step can be summarized as

$$\epsilon_{thermo} = \sum_{i=1}^{N_c} (\Psi_{det}^{eq}(T, P, \phi)_i - \Psi_{vir}^{eq}(T, P, \phi)_i) \tag{1}$$

where N_c is the number of conditions used, $\Psi_{det}^{eq}(T, P, \phi)_i$ represents the current detailed parameter being optimized, being the equilibrium temperature or the molar weight for the condition i, and $\Psi_{vir}^{eq}(T, P, \phi)_i$ is the virtual counterpart.

For the detailed part, all the values are known and thus, this equation become the target for the optimization. For the virtual mechanism, some considerations can be done: there are some species that does not requires the optimization, such as the fuel, oxidizer and diluent as they can have the same properties of the detailed species. By doing this, the fitness calculation can be improved by removing the contribution of those species from the Ψ, which makes sure that the virtual species are optimized to match the properties of the burned composition. Therefore, we can rewrite the fitness function as

$$\epsilon_{thermo} = \sum_{i=1}^{N_c} \sum_{l=1}^{N_{thermo}} (\bar{a}_l^{vir}(T,P,\phi)_i - \delta_l^{det}(T,P,\phi)_i) \tag{2}$$

$$\delta_l^{det}(T,P,\phi)_i = \bar{a}_l^{det}(T,P,\phi)_i - \bar{a}_{l,A}^{det}(T,P,\phi)_i \tag{3}$$

$$\bar{a}_l^{vir}(T,P,\phi)_i) = \sum_{k=1}^{N_{vir}} a_{l,k}^{vir} \alpha_k^{vir} Y_P^{det}(T,P,\phi)_i \tag{4}$$

Where N_{thermo} is the number of thermodynamics coefficients of NASA, α_k^{vir} is the stoichiometric coefficient for the k virtual species, $a_{l,k}^{vir}$ is the thermodynamic parameter l of the virtual species k, A is the group of species which have identical counterparts in both, detailed and virtual schemes (fuel, oxidizer and diluent) and P represent all detailed species not include in A. The fitness function present yet another unknown variable, the stoichiometric coefficient for the virtual species. The direct inclusion of these coefficients in the optimization scheme requires a new set of $N_c \times (N_{vir} - 1)$ parameters to be optimized. To ease the problem, Cailler *et al.* (2017) further divided the problem in two parts, the first part consider that for every group of N_{vir} there is a subset of m coefficients that perfectly describe the detailed mechanism and can be expressed as

$$\begin{cases} \sum_{k=1}^{N_{vir}} a_{1,k}^{vir} \alpha_k^{vir} Y_P^{detd}(T,P,\phi)_i = \delta_1^{det}(T,P,\phi)_i & \text{(5a)} \\ \dots & \text{(5b)} \\ \sum_{k=1}^{N_{vir}} a_{m,k}^{vir} \alpha_k^{vir} Y_P^{det}(T,P,\phi)_i = \delta_m^{det}(T,P,\phi)_i & \text{(5c)} \end{cases}$$

Where m is limited by the number of the NASA coefficients optimized, i.e. bound to 1 and 6 in the case of NASA7 polynomials. If an additional consideration of $\sum_{k=1}^{N_{vir}} \alpha_k^{vir} = 1$ is made, we can rewrite the equations as

$$\begin{cases} \sum_{k=1}^{N_{vir}-1} \left[a_{1,k}^{vir} \alpha_k^{vir}\right] + a_{1,N_{vir}}^{vir} \Big(1 - \sum_{k=1}^{N_{vir}-1} \alpha_k^{vir}(T,P,\phi)_i\Big) = \frac{\delta_1^{det}}{Y_P^{det}}(T,P,\phi)_i & \text{(6a)} \\ \dots & \text{(6b)} \\ \sum_{k=1}^{N_{vir}-1} \left[a_{m,k}^{vir} \alpha_k^{vir}\right] + a_{m,N_{vir}}^{vir} \Big(1 - \sum_{k=1}^{N_{vir}-1} \alpha_k^{vir}(T,P,\phi)_i\Big) = \frac{\delta_m^{det}}{Y_P^{det}}(T,P,\phi)_i & \text{(6c)} \end{cases}$$

If $m = N_{vir} - 1$, the system present $N_{vir} - 1$ equations and unknown variables α_k^{vir}, and with a given set of thermodynamic coefficients $a_{m,k}^{vir}$, the system can be used to calculate the corresponding stoichiometric α_k^{vir}.

Therefore, the first step for the thermodynamics optimization can be modified and the new fitness calculation takes the form

$$\epsilon_{thermo,1} = \sum_{i=1}^{N_c} \sum_{k=1}^{N_{vir}} v_k \tag{7}$$

$$v_k = \begin{cases} 0 & \text{if } 0 < \alpha_k^{vir} < 1 \\ 1 & \text{otherwise} \end{cases} \tag{8}$$

where α_k^{vir} are obtained from the solution of the system. This first optimization stop when $\epsilon_{thermo,1}$ reaches zero. The new procedure is to guess a initial set of NASA parameters and calculate the stoichiometric counterparts, and finally, calculate the fitness value of the current guess. As soon as the fitnesses reaches zero, the second part of the optimizations takes place. The second part targets the last $N_{vir} - m$ parameters, using the following equation

$$\epsilon_{thermo,2} = \sum_{i=1}^{N_c} \sum_{l=m}^{N_{thermo}} (\bar{a}_l^{vir}(T,P,\phi)_i - \delta_l^{det}(T,P,\phi)_i) \tag{9}$$

And finally the molar weight optimization, equation 1 is used, with a the Ψ function being the mixture molar weight.

As for the kinetic optimization, the main targets are the ignition delay time and the temperature transient profile. The model used is a homogeneous, constant mass, constant pressure, adiabatic reactor and IDT was defined as the point where the temperature increases by 400 K.

Here, $\dot{\omega}_k$ is the net production rates for species k. The set of equations are solved using the SCIPY package (Virtanen *et al.* (2020)) while an in-house code handles the chemistry part. Virtual reactions are modeled following the elementary reaction structure. The rate constant of each reaction is modeled by an Arrhenius form (Eq. 10), therefore each reaction requires at least two parameters, the pre-exponential factor A and the activation energy E_a, while the b can be included or not. Aside from these parameters, the order of each reactant can be used as another optimization parameter.

$$k_r = AT^b exp(-E_a/RT) \tag{10}$$

$$q_r = k_r \prod_{r=0}^{n_{reactants}} [r]^{\alpha_r} \tag{11}$$

Additional intermediate species may also be used, which requires another set of NASA-7 parameters to be optimized. These new species are not considered in the thermodynamics optimization step as they are not desired to exists at the equilibrium state, therefore its NASA-7 coefficients are optimized with the kinetic parameters. To ease the optimization process, only the first five coefficients are optimized, being the sixth obtained from Eq. 12 as follows

$$a_6 = \frac{\Delta H_v}{R} - \Big(a_1 T_0 + \frac{a_2}{2}T_0^2 + \frac{a_3}{3}T_0^3 + \frac{a_4}{4}T_0^4 + \frac{a_5}{5}T_0^5\Big) \tag{12}$$

where ΔH_v is set to be the enthalpy of formation for the virtual species at a reference temperature. Also, a penalizing factor is added to the fitness calculations to ensure that all the intermediaries are consumed at the end of ignition.

The objective function has two components. The first is directly defined as the relative error between the IDT predictions with the virtual scheme and with the detailed mechanism as

$$u_{idt}^j = \frac{|\tau_d^j - \tau_v^j|}{min(\tau_d^j, \tau_v^j)} \tag{13}$$

where τ refers to the IDT and the subscripts d and v are used for detailed and virtual mechanisms respectively while j represent the condition. The minimum in the denominator is used to discourage the genetic optimization to be trapped in very fast ignition cases.

The second component is calculated from the error between the temperature profiles over a time domain normalized by the IDT (Eq. 14), to ensure that the shape of the temperature curve is taken into account separated from the effect of the IDT. This methodology helps to adjust of the time domain used for the optimization by using a normalization space and all the error integrals presented in Eq. 15 are performed between $0 <= t_{n,i}^j <= t_f$, where t_f used was 1.5 for the methane cases. A t_f between 1.5 and 2.0 ensures that the mixture reaches an equilibrium state even with very smooths temperature curves.

$$t_{n,i}^j = \frac{t_i}{\tau_j} \tag{14}$$

$$u_T^j = \sqrt{\int_{t_n=0}^{t_f} \Big(\frac{T^v(t_n) - T^d(t_n)}{T^d(t_n)}\Big)^2 dt} \tag{15}$$

The fitness calculation for each condition is calculated by Eq. 16, which couple both errors. The coupling of the temperature profile and IDT is to take the different time scales into account for the normalize procedure. The objective function is them defined as Eq. 17 using a mean square average and the optimization targets become the minimization of this function.

$$\epsilon_k^j = (1 + u_{idt}^j)(1 + u_T^j) - 1 \tag{16}$$

$$\epsilon_k = \sqrt{\frac{\sum_{j=1}^{n_{cond}} (\epsilon_k^j)^2}{n_{cond}}} \tag{17}$$

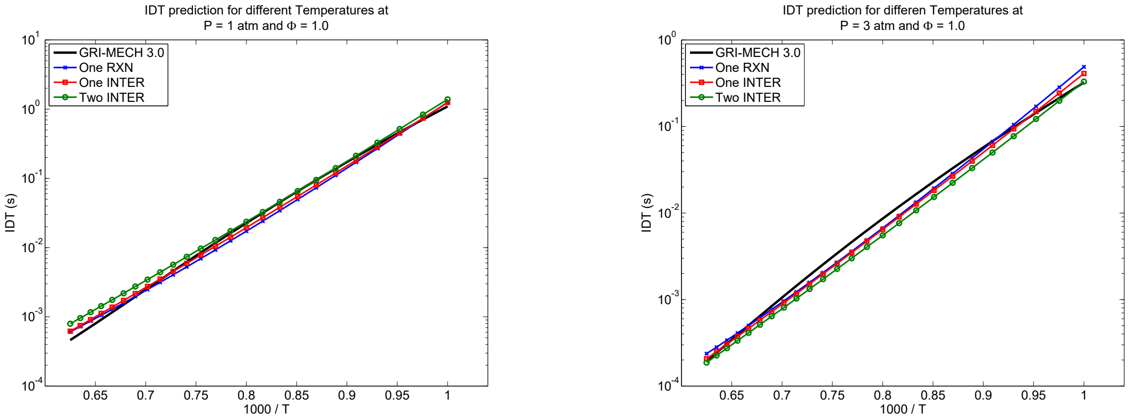
The next sections will show the capability of the method for prediction the methane IDT, as well as addressing some opportunities to improve said results and after that, a more theoretical discussion regarding low temperature ignition is presented, drawing some limitations and ways to ease the optimization step of the virtual chemistry implementation.

3. RESULTS

3.1 High Temperature Autoignition

Previous work on the high temperature autoignition, using methane as the target (represented as the GRI-MECH3.0 detailed mechanism, Smith *et al.* (2018)) is summarized in the following figures. A more extensive description of the virtual optimization for those cases can be found on Pacheco *et al.* (2020).

The basic of this optimization was a five virtual products optimization, with a plethora of different structure tested. Figure 1 shows IDT predictions for the initial structures, named: 1) One RXN, a global virtual mechanism; 2) One INTER, one intermediary between the fuel and final products and; 3) Two INTER, where two cases of One INTER are used with distinct intermediaries.



(a) (b)

Figure 1: IDT predictions of different basic virtual mechanism for methane-air systems at stoichiometric conditions for (a) 1 atm and; (b) 3 atm. **Source:** Pacheco *et al.* (2020)

The predictions shown here were obtained with the most simpler virtual structures possibles and as can be observed, the difference between the detailed mechanism and the virtual ones are very small, comparable to experimental data deviations. Additionally, the values are much on par with reduced mechanisms obtained from other methodologies, however the number of required species and reactions was at the worst case, less than ten species.

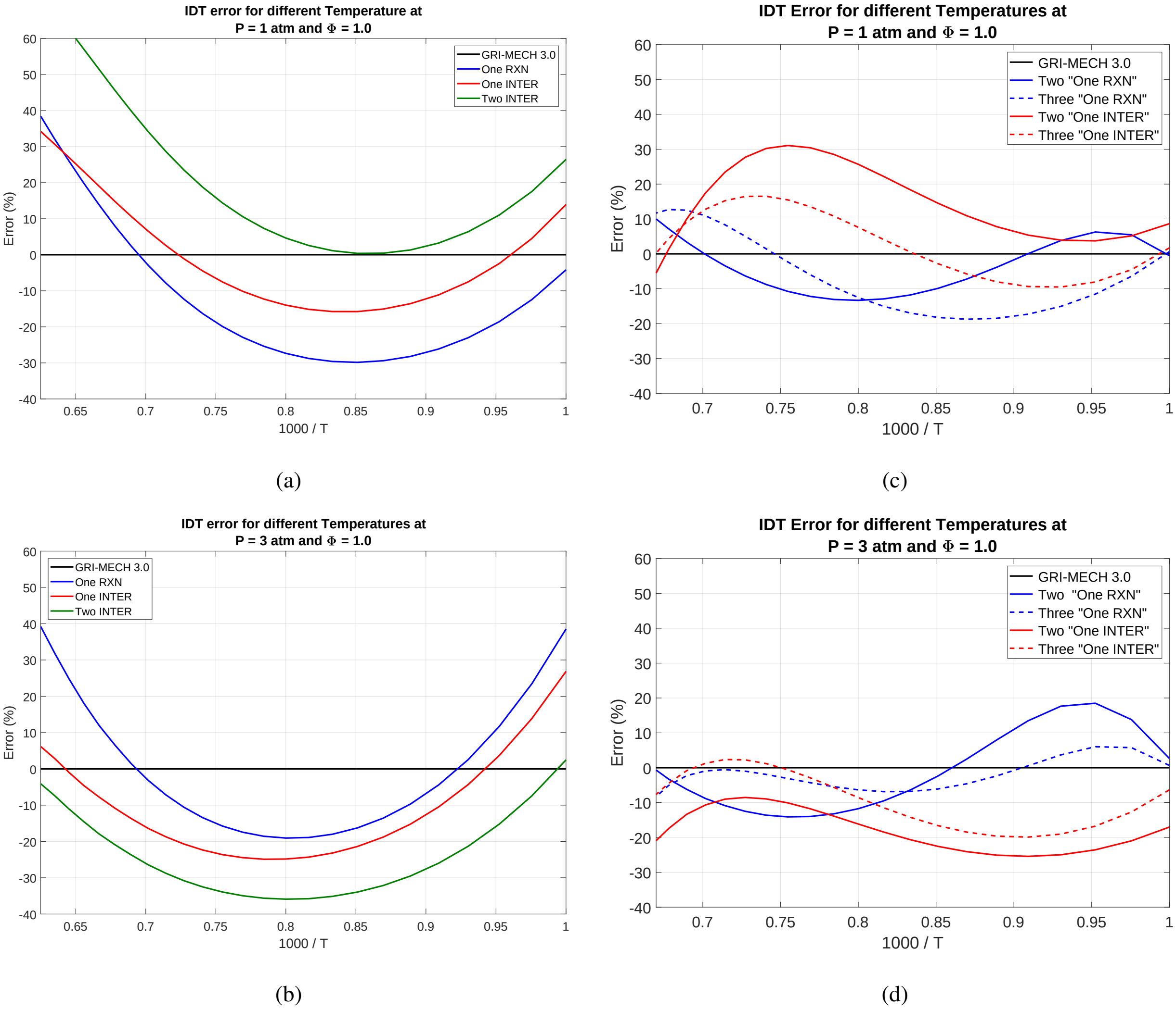
As for greater clarity, figure 2 presents the relative difference between the IDT prediction and the detailed mechanism prediction. The figures (a) and (b) are related to the same basic models presented in figure 1, and can be observed that even some results differs up to 60% at some cases, the overall predictions are very accurate.

Figures (c) and (d) present more elaborate mechanisms, named: a) Two "One RXN", where two globals reactions are used; b) Three "One RXN", similarly, three global reactions are optimized; c) Two "One INTER", two reactions are used to describe both the production and consumption of the intermediary species and; d) Three "One INTER", which is exactly like the last case with one additional reaction being added at each step. The additional reactions allows for more optimization parameters to be used, and the result is a better IDT prediction, as can be observed. With more optimization time or more complex virtual structures, the predictions could even further improved, however, the current solutions are a good proof of concepts of the method accuracy. As a final note of the high temperature ignition, the computational times of the virtual schemes, without any code optimization, were at the worst case, 50% of the detailed mechanism (at a much more optimized algorithm).

3.2 Low Temperature and NTC cases

Most of the transportation fuels present an exponent behavior of the IDT, with a direct relation with the unburnt temperature. Such behavior is relatively easily achievable, as the smallest mechanism (global reaction) is proven to reproduce such feature naturally as the results for the methane presented in the previous discussion have shown. The last section further demonstrate how the use of different simple virtual chemistry structure can improve the prediction. However, more complex phenomena, such as the NTC, presents a much more challenging behavior to emulate. Detailed mechanism for fuels that present such IDT curves, i.e. as the ones presented by the n-heptane (figures 3) generally present a very complicate structure only for the low temperature ignition and NTC region.

More complicate detailed mechanisms requires therefore more complex virtual structures to capture such details. Additional intermediaries and reactions are required, representing additional parameters to be optimized. The last statement

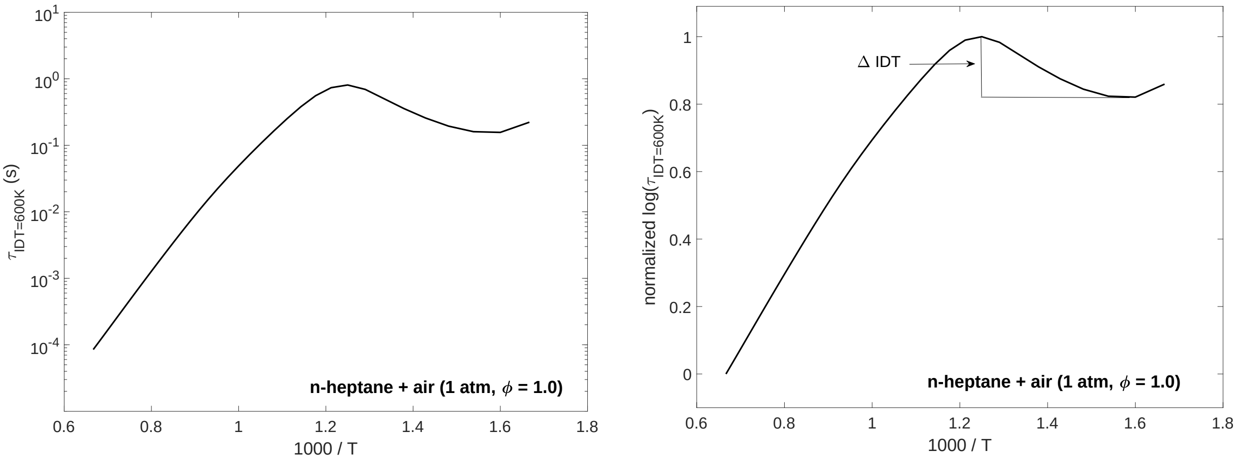


(a) (c)

(b) (d)

Figure 2: Temperature profile comparison between te detailed mechanism and the the virtual schemes.

describes the difficulty of optimizing a virtual mechanism, as how to obtain the most accurate mechanism with the least amount of parameters. The next few sections will discuss some strategies to alleviate the virtual optimization, mostly target to be used for fuels with an NTC.



(a) (b)

Figure 3: n-heptane IDT predictions for the mechanism of Mehl *et al.* (2011) (a) IDT (s); (b) normalized IDT.

3.2.1 Reactions and Thermodynamics Modeling

Regarding the thermodynamics properties for the intermediaries, the optimization could use one of two methods. The first one is to optimize five NASA parameters and calculated the last one based on the formation enthalpy of the virtual products as describe by Cailler *et al.* (2017); Maio *et al.* (2019); Cailler *et al.* (2020) and Pacheco *et al.* (2020). A second and more direct approach is to fully optimize the coefficients, however this adds additional solver problems on the energy equation that limits the optimization algorithm. Besides such issues, the potential for an improve temperature prediction is hard to quantify.

Not only how the properties should be optimize, one must account for the number of intermediaries, as every one could have one set of particular coefficients, adding more parameters to the problem. One solution is to mirror such properties, at least for the initial optimizations steps, up to the point where a solution could be found, being separate as the solutions improves.

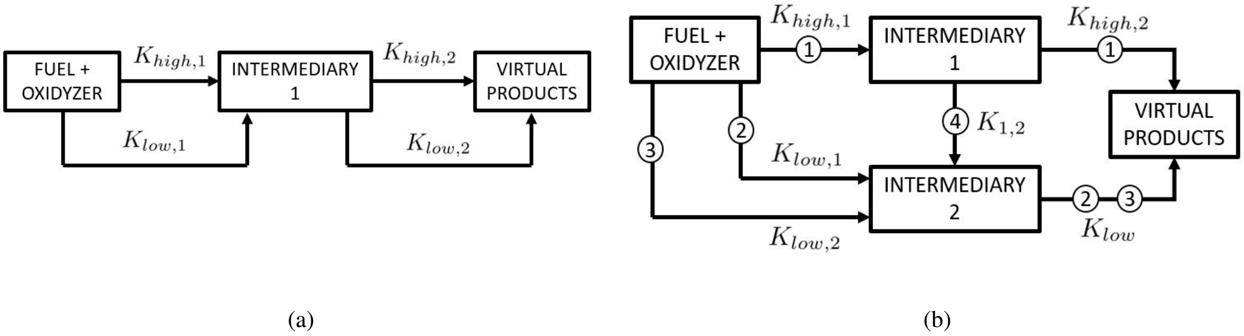
As for the reactions, the base equation used is the Arrhenius one, as it is the most used form to represent chemical reactions. Such implementation requires at least one order, the A parameter, the temperature coefficient b and the Activation Energy E_a. Here some more simplifications can be used to help the optimization. The first one is to proper address the requirement of the temperature exponent. Generally, chemical mechanism present a more direct reaction path, with a behavior that could be achieved without the use of the exponential parameter. As an initial solution, such reactions may not required that parameter, being optimized only at later stages. For NTC however, the easy way to obtain a reaction with a negative relation to the temperature is to use a b parameter with negative values. Identifying such reactions can help to produce valid solutions more easily.

The second one is related to the reaction orders. As for virtual chemistry, reaction orders has the main effect of adjusting the IDT behavior to other pressure levels, as generally no third body reaction is used. Additionally, for small fuel molecules, such as methane (CH_4), the stoichiometric coefficients for the fuel+oxygen reactions are on fifth order (four oxygens to one methane), which requires a concentration to the fifth power. As the fuel molecule sizes increases, i.e. n-heptane, the stoichiometric grows, up to eleven to one in this case, resulting in a concentration to the twelfth power. The instability of such high powers hinder even more the optimization. Therefore an effort to limit such values is a valid option, and a refinement of the final values being performed in an already optimization solution could be used.

3.2.2 Mechanism Structure

In order to ease the optimization targeting NTC behavior, the virtual structure has a major impact. Simpler solutions such as global reactions does not present the required behavior of an NTC autoignition curve. As studies have shown, low temperature ignition and NTC behavior are two very complex phenomenas that require much more effort to be modeled. As a fast way to test virtual structures, a small design of experiment (DOE) can be performed on a very simple virtual mechanism, using some simplifications: 1) no energy equation is solved; 2) the reactions rates are constant through each case and are defined based on the initial temperature tested; and 3) the IDT marker was set as the time required to produce a certain amount of virtual products.

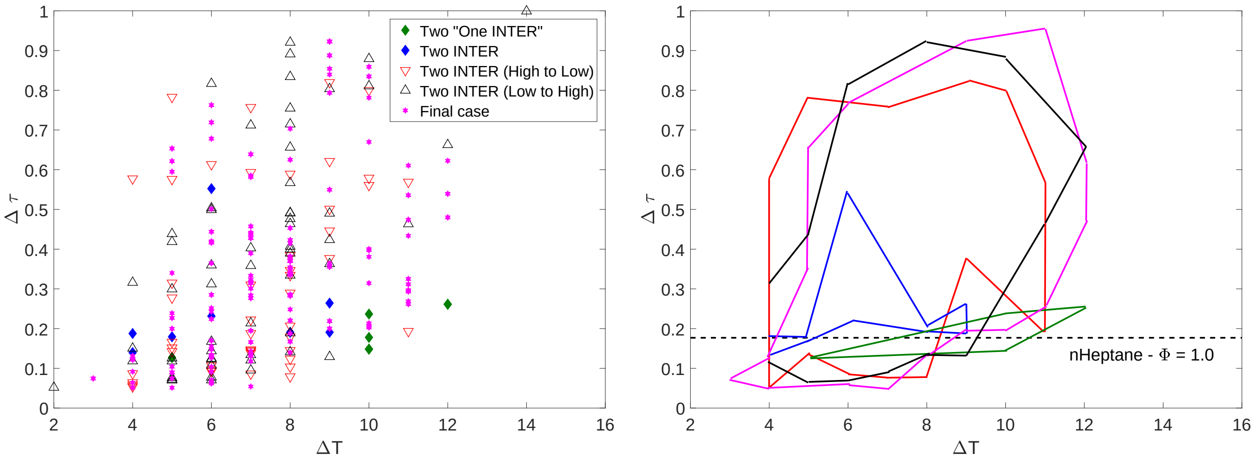
The two basic structures tested are shown in 4. Figure (a) represents one of the basic models to be used, where two reactions consumes the fuel and oxidizer to produce an intermediary, and another two produces the virtual products. A single reaction present several difficulties to represent a NTC as there are few parameters to be used. Such model is named as Two "One INTER" in the following discussions. As for more complex structures, figure (b) can be used. The first one is Two INTER, which can be achieved by turning off the reactions paths 3 and 4, the next one is the Two INTER (High to Low), which is represented by the paths 1, 2 and 4. The Two INTER (Low to High) is very similar, however the reaction 4 is changed to consume the Intermediary 2, producing the Intermediary 1. Finally, the Final case is the full model (paths 1 through 4), which added a better control of the fuel consumption than previous cases.



(a) (b)

Figure 4: Virtual mechanism structures. (a) Two "One INTER" and; (b) Two INTER, with all the reactions paths.

By solving the proposed models and plotting the cases whether a NTC was achieved, figure 5 can be produced. The y-axis represents the normalized logarithm time difference between the maximum and minimum points and the x-axis represents the initial temperature difference between said points. Figure 3 (b) shows the normalized IDT values for the n-heptane presented in the figure 3 (a) as an example. Figure 5 (a) shows the distribution of all the DOE valid cases. The number of points was directly related to the number of reactions, which is easily seen in the amount of points obtained with the Final case (purple dots) and the Two "One INTER" case (green diamonds). Figure 5 (b) shows the regions of the NTC points and, by optimizing the mechanisms parameters, any point inside said regions could be achieved.



(a) (b)

Figure 5: All NTC cases for the proposed model. (a) all points; (b) all regions.

The most important information of such DOE is how flexible every structure is in relation to NTC behaviors. The simpler model i.e. Two "One INTER" case, presents a very small window of NTC, which can be translated to a very difficult model to be used as NTC candidate when the energy equation is used as there are few opportunities to model and control the NTC. Similarly, the Two INTER model, even being the base for the last three structures, does not present a great NTC region. Here is worthy noting that the wider the region in the y axis the better, as it should present more opportunities for a NTC to appear. The last three structures present almost the same results, however the additional reaction on the Final case could help the optimization when solving the energy equation. As so, in order to obtain a valid virtual chemistry with a NTC prediction capability, a virtual structure similar to the Final case should be the best candidate.

4. CONCLUSION

The use of virtual chemistry is proven to be very interesting candidate as a mean to reduce the computational time for reactive flows. Results for the methane are shown to be in the same order of precision of several reduce mechanism but with a much smaller species pool. As for more complex behavior such as the one present by the autoignition of n-heptane, where a NTC is present, the virtual chemistry can present a series of difficulties to be used, as the higher complexity require a higher amount of parameters to be optimized which coupled with the solution surface, hinder the optimization process. Several discussions and analysis are presented to address the implementation and optimization of such problems in order to alleviate the optimization phase.

Additionally, although the concept of a virtual mechanism could bring several questions regarding the physical consistency of the proposed scheme, no violation occurs and the mass conservation for each reaction is strictly forced. The only point that is not assured is the conservation of the elemental composition, as the concept of chemical elements is present in the virtual species methodology.

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