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REDUCTION TECHNIQUES FOR DETAILED KINETICS MODELS: A NUMERICAL ASSESSMENT FOCUSED ON TRANSPORTATION FUELS

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Abstract. *Kinetics mechanism reductions using the directed relation graph (DRG) and directed relation graph with error propagation (DRGEP) are presented for two kinetics mechanisms for methane and one kinetics mechanism for PRF mixtures (mixtures of isooctane and n-heptane) using three threshold values: 0.1, 0.08 and 0.05. For methane, the Grimech3 mechanism with 53 species and 325 reactions and the San Diego mechanism with 48 and 303 reactions were reduced. The DRG-reduced mechanisms for methane with the threshold of 0.1 showed no differences in the calculation of Ignition Delay Time (IDT) and Laminar Flame Speed (LFS). The DRGEP-reduced mechanisms for methane with the threshold of 0.08 and 0.05 showed average errors of 27% for LFS relative to the detailed mechanism. For PRF mixtures, the POLIMI mechanism was used with 484 species and 19341 reactions. The reduced mechanism for PRF by the DRG method and the threshold of 0.08 presented 1% errors with the detailed mechanism for LFS, but did not perform satisfactorily for IDT values. The reduced mechanism for the PRF by the DRG method using the threshold of 0.1 presented IDT errors of 15% for lean and stoichiometric mixtures and 23% for rich mixtures, while being able to reproduce the NTC behavior for the PRF100.*

Keywords: Detailed Chemical Kinetics, CANTERA, Chemical kinetics mechanism reduction, DRG, DRGEP.

1. INTRODUCTION

The high environmental impact of fossil fuels used in transportation requires that their combustion be as efficient as possible in order to reduce their consumption and the generation of polluting gases. Tools such as CRFD have been fundamental for the design of more efficient and environmentally friendly engines. This CFD approach requires the implementation of kinetics models to calculate the burning of fuel and the production of emission gases. The detailed kinetics

mechanisms are basically a set of elementary species and reactions that represents the transformation from reactants (fuel and oxidant) to final products, taking into account intermediate species formed during this chemical transformation, managing to comprehensively describe the chemical process during the combustion phenomenon (Blurock and Battin-Leclerc, 2013). Detailed kinetics models usually have hundreds of species and thousands of chemical reactions, having no ceiling to it's size. Methane is one of the most studied hydrocarbons and different detailed mechanisms for its combustion have been proposed (Smith *et al.*, 1999), (UCSDMech, 2016),(Wang *et al.*, 2007),(Metcalfe *et al.*, 2013). In the present work, two mechanisms are used for methane combustion, the Grimech3 (Smith *et al.*, 1999) and the San Diego mechanism (UCSDMech, 2016). The Grimech3.0 has 53 species and 325 reactions and the San Diego mechanism has 58 species and 278 reactions. Since methane is the simplest hydrocarbon, its detailed mechanisms are relatively smaller compared to other hydrocarbons, even so, it is possible to perform reductions that improve the computational times required for its simulation (Hernández *et al.*, 2010), (Cazères *et al.*, 2021), (Lu and Law, 2008a). In CRFD simulations, in addition to the Navier-Stokes equations, it is necessary to solve a set of nonlinear equations associated with the kinetic mechanism. Therefore, the complexity of the problem and the computational resources often available make the use of detailed kinetic mechanisms unfeasible (Bortoli *et al.*, 2015). Therefore, it is necessary to reduce the number of species and reactions, but without greatly compromising their accuracy. For mechanism reduction there are currently multiple methods such as Sensitivity Analysis method - SA, Reaction-Diffusion Manifold - RDM, Computational Singular Perturbation - CSP, Directed Relation Graph - DRG, Directed Relation Graph with Error Propagation DRGEP, Level ofImportance - LOI and Rate-Controlled Cosntrained Equilibrium - RCCE, and others. In the present work, DRG (Lu and Law, 2006) (Zheng *et al.*, 2005) and DRGEP (Niemeyer and Sung, 2011) (Li and Yang, 2021) (D'Alessio *et al.*, 2020) (Wu *et al.*, 2020) reduction methods were used. The DRG method was initially proposed by Lu and Law Lu and Law (2005) and has been shown to be reliable in the reduction of large kinetics mechanisms (Lu and Law, 2006). Subsequently, the DRGEP method (Pepiot-Desjardins and Pitsch, 2008) was proposed based on the DRG but taking into account a geometric error propagation strategy obtaining only the most important chemical pathways of the mechanism within the evaluated domain.

1.1 Directed Relation Graph - DRG

The directed relation graph is a method that allows to identify which species of a detailed kinetics mechanism are really important for a group of initially established species, called target species, which have to be contained in the final mechanism (Lu and Law, 2005). Each node of the graph shown in the Fig. 1 represents a species and each line connects two species, e.g., there is a connection between A and B, only if species B is important for A, so that if B is removed the production rate of A would be significantly affected. The following expression is used to calculate the importance index between a non-target species B and a target species A.

$$I_{AB} = \frac{\sum_j |v_{Aj} w_j| \delta_{B,j}}{\sum_j |v_{Aj} w_j|} \tag{1}$$

Where w_j is the net reaction rate of reaction j, v_{Aj} is the stoichiometric coefficient of species A in reaction j and $\delta_{B,j}$ is a coefficient that is equal to zero if species B is not in reaction j and is equal to unity if species B is in reaction j. For this method it is necessary to establish a threshold value. If the importance index is higher than the threshold the species B is added to the list of important species (Ω). Figure 2 shows the algorithm applied in the DRG method. The importance index of a species B is evaluated for each species contained in the list of important (Ω) species and is considered the highest value of these indices. Each time a new species is added to the list of important species it is necessary to reevaluate the importance index for all non-target species.
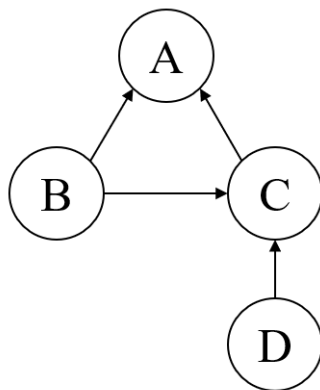

Figure 1. Example of a directed relation graph. From (Lebedev *et al.*, 2013)

1.2 Directed Relation Graph with Error Propagation -DRGEP

The Directed Relation Graph with Error Propagation method is a modification of the DRG method. In this method, the index of influence between two species is also analyzed, even if they are not directly related in the graph. For example in the Fig. 1, the importance index between the target species A and the non-target species D is calculated, taking into account for this calculation the importance index between A and C (Lebedev *et al.*, 2013). The importance index for DRGEP is calculated with the following expression:

$$I_{AB} = \frac{\sum_j |v_{Aj} w_j| \delta_{B,j}}{\sum_j |v_{Aj} w_j|} I_A \qquad (2)$$

The algorithm used for this method is shown in Fig. 2. Both methods have as input data the reaction rates **w**, the stoichiometric coefficients **v**, the list of important species (Ω) and the threshold value. As in the DRG method, if the importance index exceeds the established threshold value, the non-target species is added to the list of important species and the importance index of all the other non-target species must be reevaluated again until there are no more species to add to the list. The DRGEP method eliminates more unimportant species than the DRG method, thus generating higher reduction percentages. It should be noted that these two methods are based on species reduction and not on reaction reduction. These two methods have also been combined with the sensitivity analysis (SA) method in order to improve the reduction and eliminate even more unimportant species, being the DRGASA method (Lu and Law, 2008b; Zheng *et al.*, 2007; Tosatto *et al.*, 2013) and DREGEPSA method (Raju *et al.*, 2007; Niemeyer *et al.*, 2010; Xi *et al.*, 2020).
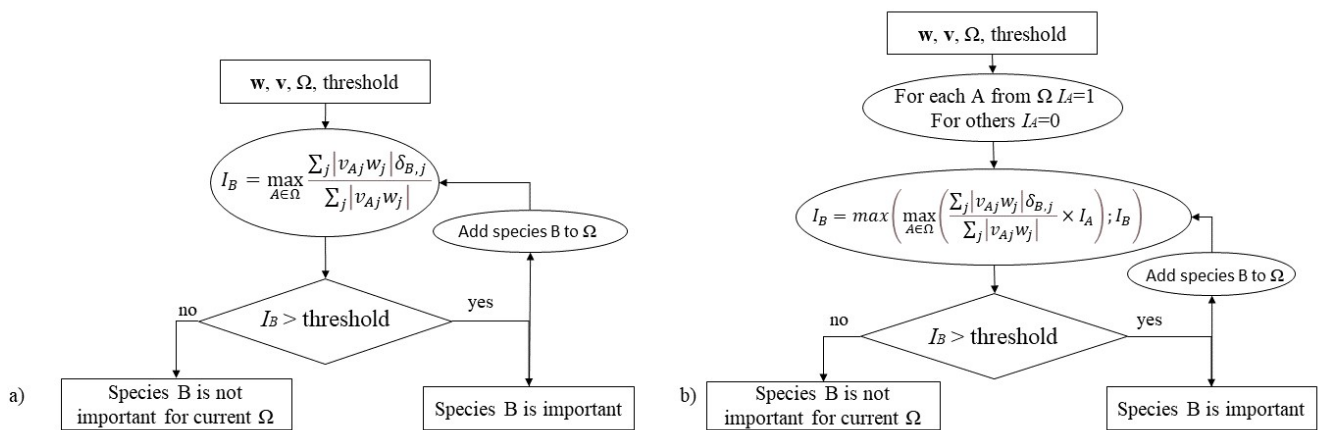

Figure 2. Algorithm of (a) DRG method, (b) DRGEP method. Adapted from (Lebedev *et al.*, 2013)

2. METHODOLOGY

2.1 The detailed chemical kinetics database available in the literature

For the development of this study we used the three kinetics mechanisms used by (Balestrin *et al.*, 2021) where the reduction of the mechanisms is performed using a cup ranking approach throughout the simulation process. The mechanisms used are shown in the Tab. 1. Two of the mechanisms are the GRIMech3.0 mechanism (Smith *et al.*, 1999) and the San Diego mechanism (UCSDMech, 2016), which are for methane. The third mechanism is the POLIMI (Ranzi *et al.*, 2012) for PRF blends as a gasoline surrogate.

Table 1. Detailed mechanisms used in this work

	Methane	Methane	Multi-Component Mixtures
Elements	5	6	6
Species	53	58	484
Reactions	325	270	19341
Reference	Smith *et al.* (1999)	UCSDMech (2016)	Ranzi *et al.* (2012)

2.2 The in-house code for mechanism reduction and The Cantera suite tools

In this work the Cantera 2.5.1 software was used. Cantera is an open-source suite of tools for problems involving chemical kinetics, thermodynamics, and transport processes (Goodwin *et al.*, 2021). In this work, two kinds of simulations of reactive systems where performed: (i) ignition delay time simulation on homogeneous adiabatic constant volume reactor and (ii) laminar free propagating flame speed. Additional information about Cantera can be found at the Cantera website. In the present study the DRG and DRGEP methods were used, it is possible to consult the performance of these methods in more depth in Pacheco (2016). The in-house code for mechanism reduction has been developed by the Combustion Research Group at LABCET/UFSC, in a collaborative effort by different users and researchers and it was adapted for the research proposed in this work. The DRG and DRGEP methods requires as input data: the kinetics mechanism to be reduced, the threshold value and the different states within which the reaction rates will be evaluated for the calculation of the importance index. The threshold value allows the method to be more or less restrictive in terms of the species to be retained; the higher the value, the fewer species the final reduced mechanism will have. In this case different values for the threshold were used, 0.05, 0.08 and 0.1. For the reduction of the mechanisms for methane using the DRG method, the threshold of 0.1 was used, while for the DRGEP method, the three values mentioned above were used. For mechanism reduction for PRF mixtures, the DRG method was used with the thresholds of 0.1 and 0.08, while the DRGEP method was analyzed only for the threshold of 0.1. The reductions were performed on the basis of both the ignition delay time (IDT) and the laminar flame speed (LFS). The states used for the analysis are defined by temperature, pressure and mass or mole fraction of each species. Figure 3 shows the procedure used for the mechanism reduction . Initially, the IDT and LFS were calculated for the detailed kinetics mechanism at different conditions of temperature, pressure and reduction equivalence ratio presented in the Tab. 2. Using an in-house routine in Python 3.8 using Cantera 2.5.1, the IDT for the detailed kinetics mechanism was simulated using a reactor with constant mass and pressure and adiabatic, from which the IDT values and the different TPY states (species composition in mass fraction) used for the reduction mechanism were obtained. On the other hand, the laminar flame velocity was calculated and the values of each TPY of a laminar free propagating flame from Cantera were obtained. The different state values obtained from IDT and LFS were analyzed together to obtain the list of important species of the final reduced mechanisms.
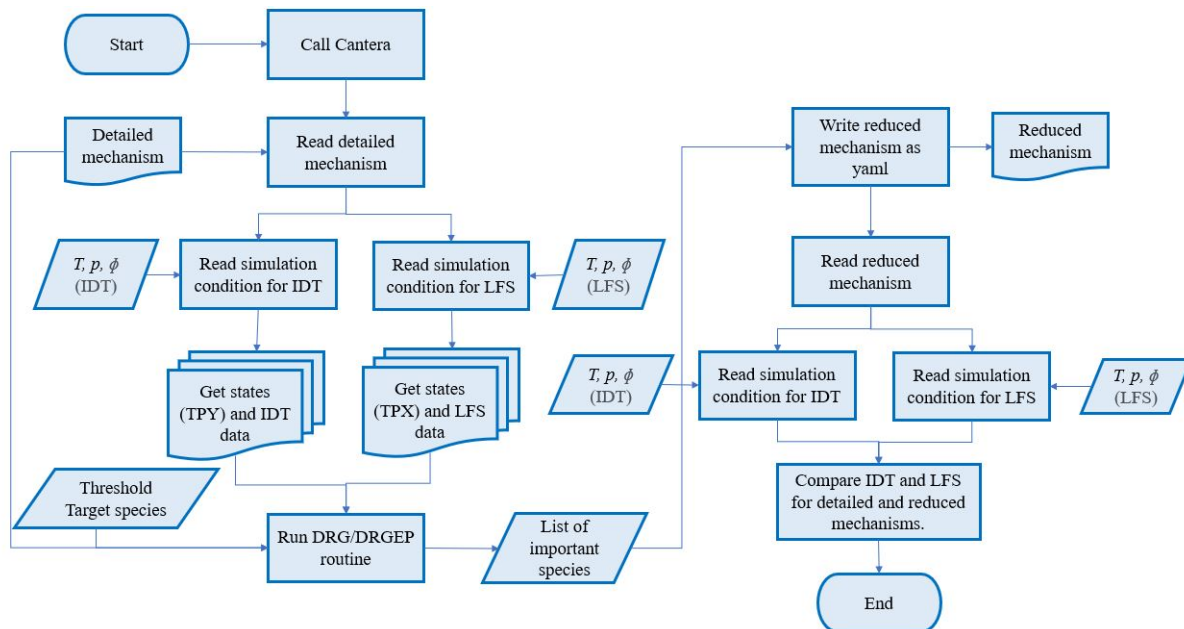

Figure 3. Flowchart implemented for detailed kinetics models reduction

Subsequently, from the list of important species given by the DRG or DRGEP routine, the kinetics mechanism is written in yaml format and Chemkin format. The reduced mechanism is now evaluated under specific evaluation conditions presented in the Tab. 2 and the IDT and LFS values are plotted and compared. Comparisons are made between the detailed kinetics mechanism, the results obtained for the mechanisms given by both DRG and DRGEP, as well as with the results obtained by the reduction performed by Balestrin *et al.* (2021) and the experimental data presented therein. The reduced kinetics models obtained in this work are available for download in the Internal Combustion Engines Laboratory - LABMCI/CTJ/UFSC in Cantera and CHEMKIN formats.

Table 2. Numerical and experimental conditions used for the reduction of the mechanisms

	Temperature [K]	Pressure [atm]	ϕ [-]
For reduction procedure			
Ignition delay time	1300, 1600, 1900	1, 5, 10	0.5, 1.0, 2.0
Laminar flame speed	300	1, 5, 10	0.7, 1.0, 1.3
Available data from literature (Hu *et al.*, 2015)			
Ignition delay time	$\sim$1300 to $\sim$1950	1, 3, 5, 10	0.5, 1.0, 2.0
Laminar flame speed	300	1, 2, 5, 10, 20	0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4
For reduction procedure			
Ignition delay time (PRF90)	1050, 950, 850, 750	40	1.0
Laminar flame speed (PRF90)	358	1	0.7, 1.0, 1.2
Available data from literature (Fieweger *et al.*, 1997; Bradley *et al.*, 1998; Van Lipzig *et al.*, 2011)			
Ignition delay time (PRF0/60/80/90/100)	$\sim$1100 to $\sim$750	40	1.0
Laminar flame speed (PRF0/50/90/100)	298, 338, 358	1	0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3

3. RESULTS AND DISCUSSIONS

Table 3 shows the size of the reduced mechanisms obtained for each detailed mechanism with the different threshold values used and the reduction percentages obtained. It is observed that the mechanisms obtained by the DRGEP method are smaller than those obtained by DRG, this is due to the fact that the method is more restrictive when taking into account the indirect importance indexes. The list of important species obtained for GRIMech 3.0 (Smith *et al.*, 1999) with DRGEP with the threshold of 0.08 and 0.05 increased by 2 and 11 species respectively, compared to the threshold of 0.1. This species difference increased the number of reactions by 25 and 93 for 0.08 and 0.05 respectively. In the reduced San Diego mechanism the amount of species obtained in the DRGEP method for a threshold of 0.08 and 0.05 was 5 and 8 respectively relative to the reduced mechanism for threshold of 0.01. This increase represented an increase in the number of reactions in comparison to the mechanism with the threshold of 0.01 of 20 and 40 reactions, respectively. This had a greater influence on the values obtained compared to the GRIMech 3.0 mechanism.

Table 3. Reduced kinetics mechanisms obtained from the kinetics mechanisms detailed in this work

	Elements	Species	Reduction in species (%)	Reactions	Reduction in reactions (%)	Reference
GRIMech 3.0	5	53	-	325	-	Smith *et al.* (1999)
Reduced DRG (0.1)	4	48	9%	303	7%	This work
Reduced DRGEP (0.1)	4	28	47%	129	60%	This work
Reduced DRGEP (0.08)	4	30	43%	154	53%	This work
Reduced DRGEP (0.05)	4	39	26%	222	32%	This work
San Diego 2016	6	58	-	278	-	UCSDMech (2016)
Reduced DRG (0.1)	4	52	10%	260	6%	This work
Reduced DRGEP (0.1)	4	28	52%	76	73%	This work
Reduced DRGEP (0.08)	4	33	43%	96	65%	This work
Reduced DRGEP (0.05)	4	36	38%	116	58%	This work
POLIMI	6	484	-	19341	-	Ranzi *et al.* (2012)
Reduced DRG (0.1)	4	265	45%	11447	41%	This work
Reduced DRG (0.08)	4	315	35%	15439	20%	This work
Reduced DRG (0.05)	4	403	17%	17253	11%	This work
Reduced DRGEP (0.1)	4	49	90%	205	99%	This work

Figure 4 shows the results for the laminar flame speed for methane using the detailed mechanisms and the reduced mechanisms with DRG with the threshold of 0.1 (G-drg and SD-drg) and DRGEP with the threshold of 0.05 (G-drgep and SD-drgep). In the LFS calculation, the reduced mechanism for the GRIMech 3.0 by the DRG method with a threshold of 0.1 (G-drg) did not present any error in relation to the detailed mechanism. With respect to the DRGEP method being a smaller mechanism, it presented higher errors, obtaining average errors of 47% with the threshold of 0.1, 27% for threshold of 0.08 and 0.05. The increase in the number of species and reactions between the use of the threshold of 0.05 and 0.08 did not show improvements in the accuracy of the reduced mechanism. The smallest differences occurred for

the pressure of 1 atm and increased for higher pressures.
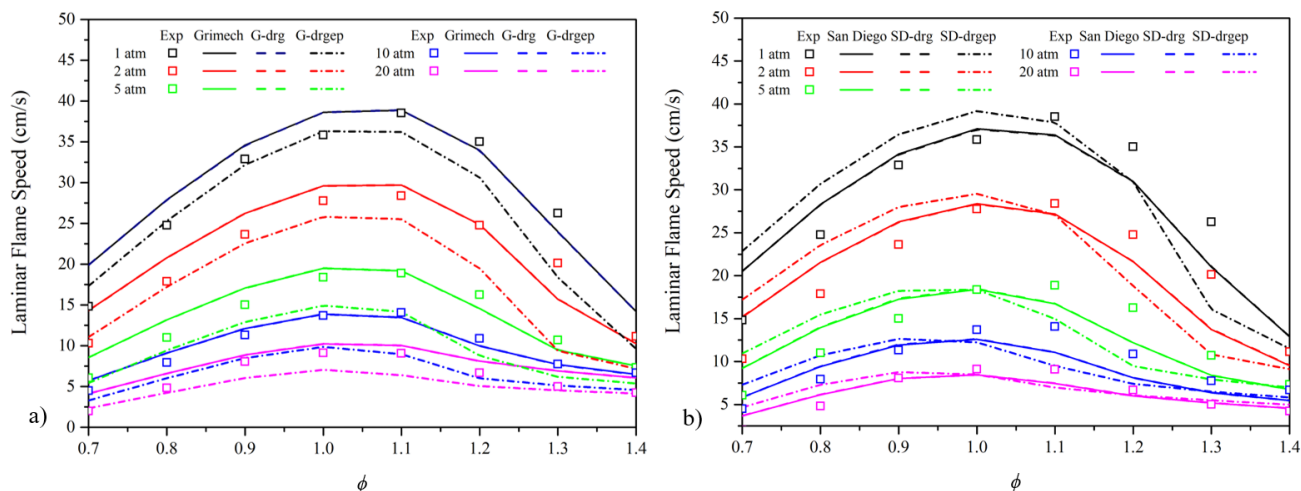

Figure 4. Laminar flame speed for methane/air mixtures. (a) GRIMech 3.0 (Smith *et al.*, 1999) solid lines, GRIMech reduced for DRG with threshold of 0.1 dash lines, GRIMech reduced for DRGEP with threshold of 0.05 dash-dot lines. (b) San Diego Mech (UCSDMech, 2016) solid lines, San Diego Mech reduced for DRG with threshold of 0.1 dash lines, San Diego Mech reduced for DRGEP with threshold of 0.05 dash-dot lines. Experimental data from (Hu *et al.*, 2015).

The reduced mechanism by DRGEP with the threshold of 0.05 (G-drgep) for GRIMech 3.0 (Smith *et al.*, 1999) underestimated in all conditions the LFS values given by the detailed mechanism and the G-drg mechanism and for most of the experimental data. For low pressures of 1 and 2 atm the prediction given by the G-drgep mechanism fitted the experimental data best at lean equivalence ratios. For laminar flame velocity values, again the mechanism reduced for the San Diego mechanism by the DRG method did not present errors relative to the detailed mechanism. On the other hand, the mechanisms obtained with the DRGEP method had smaller errors than those found for the GRIMech 3.0. On average for the DRGEP method, average errors of 20%, 13% and 9% were obtained, for the thresholds of 0.01, 0.08 and 0.05 respectively. Showing a significant decrease of the error in the LFS for the DRGEP method with the decrease of the threshold. In the SD-drgep mechanism the smallest differences were presented for the pressure of 20 atm and it was increasing for lower pressures. The mechanism reduced by DRGEP with the threshold of 0.05 (SD-drgep) for the San Diego mechanism (UCSDMech, 2016), over predicted the LFS data given by the detailed mechanism and SD-drg for lean mixtures, while for rich mixtures the behavior was the inverse. The experimental values are slower the predictions given by the models for lean mixtures and faster for rich mixtures. Although at high pressures the detailed mechanism and the SD-drg fitted the experimental data better.

Figure 5 shows the IDT values for the detailed mechanisms and the mechanisms reduced with DRG (threshold of 0.1) and DRGEP (threshold of 0.08) and experimental data available in the literature presented previously by Balestrin *et al.* (2021). For the two methane mechanisms the IDT values calculated with the DRG-reduced mechanisms with the threshold of 0.1 (G-drg and SD-drg) had no differences with the values obtained with the detailed mechanisms for all conditions. As for the DRGEP method for the GRIMech 3.0 mechanism, the reduced mechanisms with the three threshold values did not have good approximations in relation to the detailed mechanism, with very large error percentages for all pressures and stoichiometries, being the lowest for the threshold of 0.05; for the San Diego mechanism, the lowest error percentages were obtained with the threshold of 0.08, with an average error of 23%.

The mechanism reduced by DRGEP with the threshold of 0.05 (G-drgep) for the GRIMech 3.0 (Smith *et al.*, 1999) overpredicted in all conditions the values given by the kinetics mechanism, the G-drg mechanism and the experimental data. At a stoichiometric equivalence ratio and the highest analyzed pressure of 10 atm it is found that the G-drgep mechanism presents good approximations to the experimental data. The mechanism reduced by DRGEP with the threshold of 0.05 (SD-drgep) for the San Diego mechanism (UCSDMech, 2016), underestimates in most cases the values of the detailed kinetics mechanism, presenting smaller differences at higher temperatures. For 1 atm pressure, minor differences are observed between the SD-drgep mechanism and the experimental data compared to the detailed mechanism. For pressures of 3 and 5 atm the SD-drgep mechanism has better agreement with the experimental data. For 10 atm the detailed kinetics mechanism and the SD-drg mechanism presented lower percentages of error with the experimental data. Figure 6 shows the comparisons of the IDT values obtained with the detailed mechanism and the reduced mechanisms with the DRG method for the threshold of 0.1, P-drg(0.1), and with the threshold of 0.05, P-drg(0.05). The detailed mechanisms failed to reproduce the NTC behavior of the fuels, only good approximations were observed in low temperature areas for PRF100 with the P-drg(0.05) mechanism that captured this NTC behavior. For the other conditions with both reduced
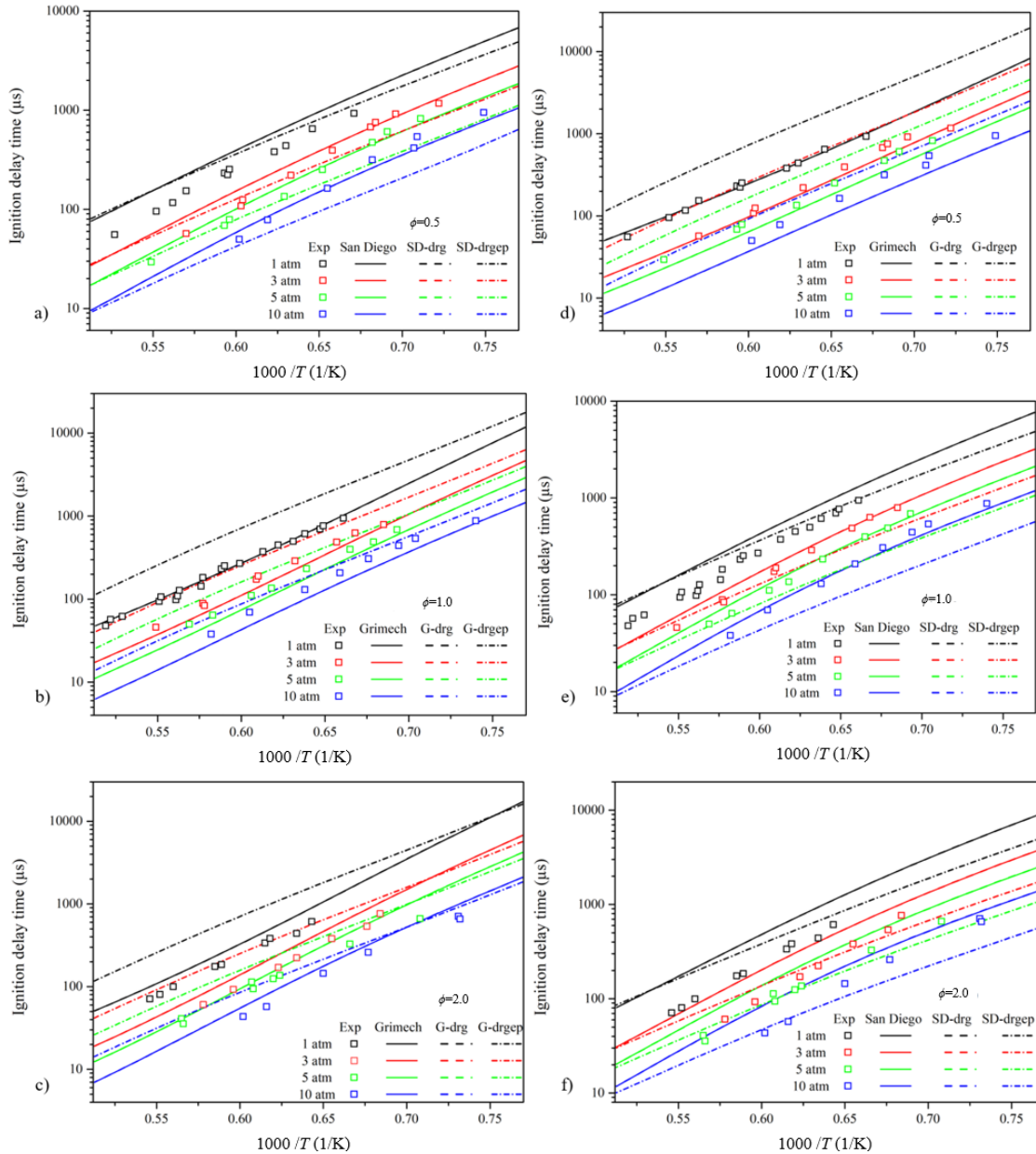
Figure 5. Ignition delay time for methane/air mixtures. (a), (b) and (c) GRIMech 3.0 (Smith *et al.*, 1999) solid lines, GRIMech reduced for DRG with threshold of 0.1 dash lines, GRIMech reduced for DRGEP with threshold of 0.05 dash-dot lines. (d), (e) and (f) San Diego Mech (UCSDMech, 2016) solid lines, San Diego Mech reduced for DRG with threshold of 0.1 dash lines, San Diego Mech reduced for DRGEP with threshold of 0.05 dash-dot lines. Experimental data from (Hu *et al.*, 2015).

mechanisms the IDT values were overpredicted. In general, the reduced mechanisms performed better in terms of IDT at higher temperatures. An error of 1% in IDT was obtained for the PRF100 between 1100 K and 1250 K with a threshold of 0.05 and 9% for this same range for the threshold of 0.01, with the DRG method. In a high temperature range from 1100 K and 1250 K the most approximate results were obtained by the DRG method with the threshold of 0.05 with 9% error, followed by the DRG application with the threshold of 0.08 with 10% error. Good approximations were not obtained with the reduced mechanism obtained with the DRGEP method with the threshold of 0.1.

In terms of laminar flame speed, the percentage error between the detailed mechanism and the reduced mechanism with DRG and the threshold of 0.1 (P-drg(0.1)) is approximately 15% for lean and stoichiometric ratios, while for rich stoichiometric ratios it is 23%. On the other hand, the mechanism obtained by DRG with the threshold of 0.08 (P-drg(0.08)) presented very small average errors of 1% and for the threshold of 0.05 (P-drg(0.05)) there was no difference with the values obtained with the detailed mechanism. The results obtained by the DRGEP method had large differences due to the high percentage of eliminated species and reactions. The reduced mechanism P-drg(0.08) was able to perform satisfactorily the LFS values having 168 species and 3909 reactions less than the detailed mechanism. Figure 6 (a), (b)

and (c) shows the values obtained for the laminar flame speed for the detailed mechanism and the reduced mechanisms P-drg(0.1) and P-drg(0.08), as well as experimental data for these conditions. For all conditions evaluated the reduced mechanism P-drg(0.1) overestimated the LFS values away from the experimental values. The numerical predictions best matched the experimental results for the 298 K and 338 K temperatures.
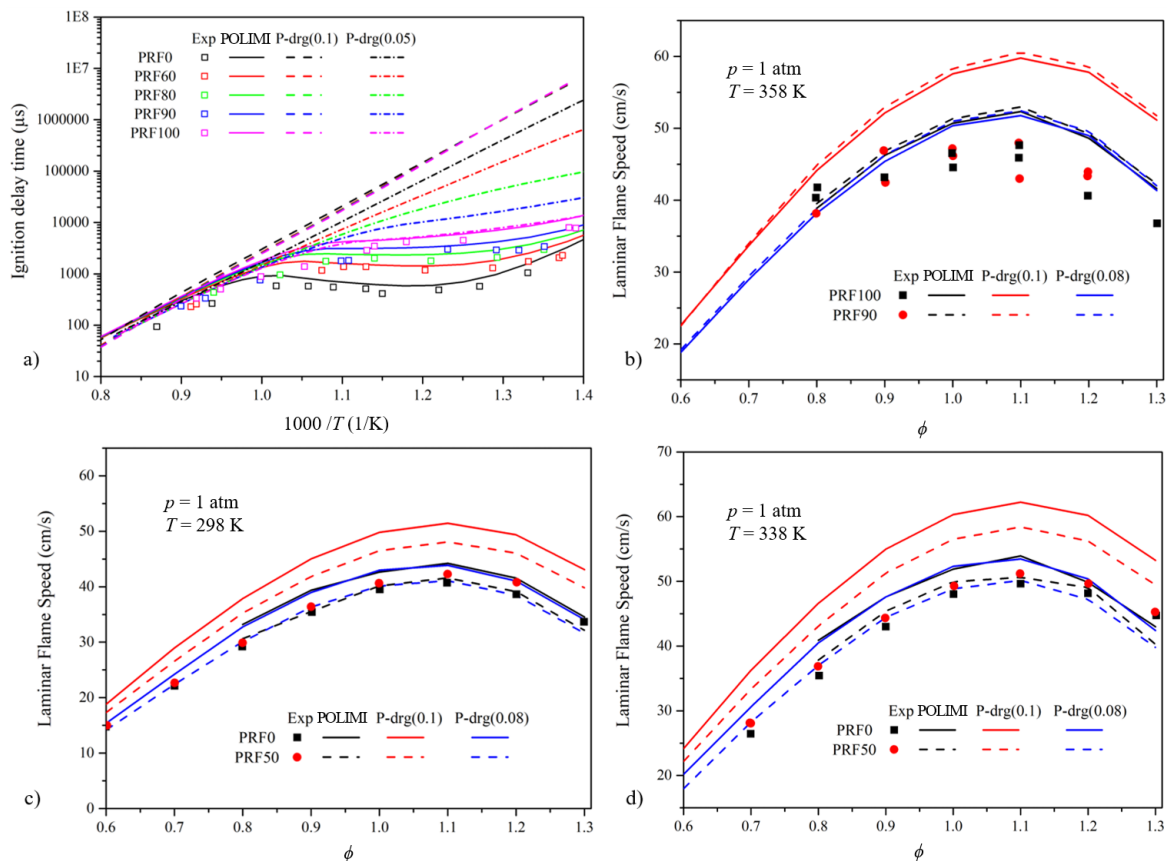

Figure 6. Ignition delay time for PRF / air mixtures. Experimental data from (Fieweger *et al.*, 1997). POLIMI (Ranzi *et al.*, 2012) solid lines, POLIMI reduced for DRG with the threshold of 0.1 dash lines, POLIMI reduced for DRG with the threshold of 0.05 dash dot lines.

4. CONCLUSION

The DRG and DRGEP methods are based on species reduction, being the DRGEP the most restrictive, obtaining significantly smaller mechanisms with this model. This greater reduction in the amount of species by the DRGEP method and therefore in the amount of reactions modified the behavior of the mechanism, this is better reflected in the reduction performed for the POLIMI mechanism that both the mechanisms reduced by DRG and DRGEP failed to capture the NTC behavior of the PRF mixtures of *i*-octane and *n*-heptane. The DRG-reduced mechanisms for methane had no difference in the behavior of both IDT and LFS due to the low reduction produced by this method. The DRGEP-reduced mechanisms for methane had acceptable error rates, being lower for the San Diego mechanism than for GRIMech 3.0, and had in some conditions good approximations with the experimental data.For LFS, the reduction with DRGEP of the San Diego mechanism presented errors of 9% for the 0.05 threshold. For IDT, the reduction with DRGEP of the San Diego mechanism presented the lowest errors using the threshold of 0.08, which was 23%. As the POLIMI mechanism is larger, the percentage of species reduction by DRG was higher being 45% for the threshold of 0.1 compared to the mechanisms for methane which using the same threshold, produced a 9% and 10% reduction. In general, the reduced mechanisms for the detailed POLIMI mechanism predicted more accurately the laminar flame speed values than the ignition delay time values. For LFS the error rates with the reduced mechanism P-drg(0.1) was approximately 15% for lean and stoichiometric mixtures and 23% for rich mixtures, but for the reduced mechanism P-drg(0.08) it was approximately 1%,hird while with P-drg(0.05) no differences were obtained. This contrasts with the predictions for IDT, where the reduced mechanisms did not capture the NTC behavior and presented larger differencesn due to the linear behavior presented. There was only representation of NTC behavior for thePRF100 simulation with the reduced P-drg(0.05) mechanism. It is worthwhile for future work to investigate the effect of the elimination of reactive third-body species that are not maintained by the applied methods. Likewise, it is also worthwhile to investigate the most optimal threshold value for each DRG and

DRGEP method. Both recommendations in order to adjust the errors of the reduced mechanisms in relation to the detailed mechanisms, and mainly the adjustment in the zone of NTC behavior of the PRF mixtures.

5. ACKNOWLEDGEMENTS

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