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REDUCED KINETICS MODELS FOR GASOLINE SURROGATES

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Abstract. *Due to environmental concerns, research has been carried out to increase the fuel's performance in internal combustion engines. Detailed kinetics models are composed of hundreds or thousands of chemical species with an extended sequence of chemical reactions, making the simulation process intractable with the employment of computational reactive fluid dynamics (CRFD). Methods to detailed kinetic mechanisms reduction are employed purposely to obtain more complete mechanisms than the global ones, with the capability to supply the required information with lower differences concerning the detailed, and mainly, reducing the computational cost. The main objective of this study is the development of reduced mechanisms by the systematic elimination of the low-ranked reaction-rate elementary reactions method. Three detailed chemical kinetics models were used as base-model and then reduced considering the numerical response of ignition delay time and laminar flame speed for fuel surrogates. Methane and binary Primary Reference Fuels mixtures were chosen as fuels for detailed kinetics mechanisms reduction. The results of IDT and LFS predictions showed accuracy comparing with those with detailed models. Moreover, the main observation was that the employment of the reduced mechanisms results in a higher variation in LFS than in the IDT prediction.*

Keywords: *Reduced kinetics models, Sensitivity analysis, Fuel surrogates.*

1. INTRODUCTION

Nowadays, numerical simulation using Computational Fluid Dynamics (CFD) for optimization processes is the standard method adopted even in the industry or academic research projects. This fact can be easily observed in the large (and augmenting) amount of research papers published in high-quality journals representing the impact of these simulation processes on people's daily lives, from sport to medicine (Oggiano *et al.* (2021); Lei *et al.* (2013); Anthony and Flynn (2006) and references therein) as well as in other aspects to reach a better life quality. More focused on research and industrial process involving combustion, the Computational Reactive Fluid Dynamics (CRFD) have been rising since the last decades fairly in companion to the rising in the materials science (superconducting materials as an example, Malozemoff (1988)), besides, the development of highly accurate numerical methods applied to large scale computation (high efficient solver algorithms), as an example the Guzik *et al.* (2016) study. Among several barriers in using CRFD for optimization processes, the "Achilles heel" is the number of chemical species and reactions involved in the choose

combustion model, depending on those numbers, the simulation process can be performed (or not) with the available computational resources and, on time for analysis. Combustion models can be classified in three groups according to Merker *et al.* (2012), as shown in Figure 1, depending on its approach: a) Thermodynamic (0D) models , b) Phenomenological (quasi-dimensional) models and c) CRFD (multidimensional) models.

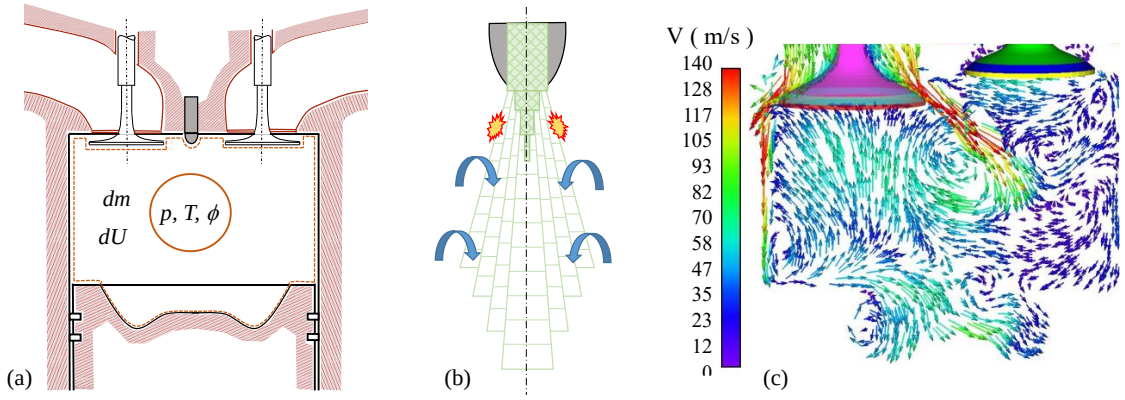

Figure 1. Combustion models - Adapted from Merker *et al.* (2012), figure (c) from Sánchez (2017)

The main difference observed is related to the spatial coordinates (dimensions) used for the solution. Concerning thermodynamics models (Figure 1(a)), there are no spatial coordinates involved, being the solution devoted to the temporal coordinate (time without transport properties) and the use of all the computational capability available solving only time-dependent simulation. For phenomenological models (Figure 1(b)) pseudo-coordinates (not spatial) related to the solution method and submodels can be involved. The CRFD approach (Figure 1(c)) demands spatial discretization of the physical domain (commonly called computational mesh) involving transport properties and using a considerable part of the available computational capability for the solution. It is clear that the available computational capability must be divided into all models used for the solution, in a discrete way in each cell at the domain, the computational domain being larger, meaning, increasing the cells within the domain, will demands higher of the computational capability to the solution. When the problem can be approached using a global or reduced kinetics model, the numerical solution can be performed for a high mesh resolution in the computational domain by using typical clusters for research (hundreds GB RAM and thousands of GB storage). The problem becomes intractable when is chosen a detailed kinetics model with a considerable number of chemical species and elementary reactions for the combustion model, and depending on spatial mesh resolution, at this point, should be necessary a computation infrastructure with thousands of of GB RAM and thousands of TB for storage. More details about the numeric combustion simulation process, in terms of computational viability, phenomenological complexity, the influence of the kinetics model on computational time related to computational resources can be found in Cancino (2009). The research related to the combustion of real fuels and their data are scarce, the main difficulty relies on their analysis in detail, as their composition being of hundreds of different species, making combustion modeling computationally impracticable. To overcome this limitation, the employment of fuel surrogates, a combination of different hydrocarbons species and classes that emulate real fuels, is proposed and used in combustion research. A fuel surrogate is a mixture composed of a reduced number of chemical species which must represent, in theory, all the physical, chemical, thermodynamic, and combustion properties of the real fuel. Fuel surrogates defined, kinetics models (global, detailed, skeletal, etc.) are used for numerical simulations. Due to the reduced number of species forming the mechanism, global kinetics models are commonly used. However, in some cases, more detail is needed to obtain satisfactory results of the ignition delay time (IDT), flame speed, and pollutants, which are important factors in fuel development. This work shows the capability of a simple methodology for detailed kinetics models reduction. As practical examples, three detailed chemical kinetics models validated against experimental data from the literature were then analyzed and reduced. Two of the before mentioned detailed kinetics model are consecrated in the scientific community for methane/air mixtures which are Smith *et al.* (1999) and UCSDMech (2016). The last one is a detailed kinetics model developed for multicomponent gasoline surrogates of real transportation fuels, from Ranzi *et al.* (2012).

1.1 Reduction methods for detailed chemical kinetics models

To handle the complex interaction between physical and chemical processes in reactive systems, it is necessary to find methods that simplify the modeling in such a way that it becomes both more understandable and practically useful, especially when optimization processes involving CRFD are required. In the literature can be found several reduction techniques as Reaction-Diffusion Manifolds - RDM (Neagos *et al.*, 2017), Computational Singular Perturbation - CSP (Zagaris *et al.*, 2004), Level Of Importance - LOI and Rate-Controlled Constrained Equilibrium - RCCE (Rigopoulos and Løvås, 2009), Quasi Steady State Assumption - QSSA (Bond *et al.*, 1998), Directed Relation Graph methodology - DRG

(Lu and Law, 2005), Sensitivity Analysis - SA (Zhu *et al.*, 1993) and Reaction Flow Analysis - RFA (Merker *et al.*, 2012), among other less reported in the literature. In this work, a simplistic way for elementary reaction low-ranked reaction rate elimination was used. In order to develop this elimination, it is necessary to systematically manipulate the set of elementary reactions in the detailed kinetics model in the appropriate software. All the proceedings are explained in the methodology section.

2. METHODOLOGY

This section describes the approach used for mechanisms reduction in this work. The global description of the detailed kinetics models (base models for this work) is shown in Table 1. For the same fuel (methane in this case), it is observed that one mechanism can find different detailed kinetics models, with different elements, species, and reactions number, in relation to the other one. The third detailed model has, as the main comparative characteristic, a huge difference concerning the species and reaction number in comparison with the methane models. This big kinetics model (Ranzi *et al.*, 2012) allows the chemical kinetics of primary reference fuels (PRF), as well as other gasoline surrogates used for fuel development and formulation.

Table 1. Detailed kinetics models (base-models) used for reduction in this work

	Fuel surrogate		
	Methane	**Methane**	**Multi-Component Mixtures**
Elements	5	6	6
Species	53	58	483
Reactions	325	270	19340
Reference	Smith *et al.* (1999)	UCSDMech (2016)	Ranzi *et al.* (2012)

Multi-Component Mixtures involves all the Primary Reference Fuels (PRF) mixtures compositions

2.1 The low-ranked reaction-rate elementary reaction elimination procedure

The numerical approach used in this work is a simplistic way for detailed kinetics mechanism reduction. The procedure consists in make a ranking of the "reaction rates" along the simulation process (ignition delay time or laminar flame speed) for all elementary reactions involved in the detailed kinetics model. In this work, the ranking was performed over ignition delay time simulations for different thermodynamics conditions (*p, T,* ϕ), attempting to cover as big as possible the initial validation conditions used for the detailed kinetics model. Table 2 shows the thermodynamic spectrum considered in this work to perform the reduction of two well know models for methane (Smith *et al.*, 1999; UCSDMech, 2016)

Table 2. Numerical and experimental conditions used for mechanism reduction for methane / air mixtures

	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

From Table 2 can be observed that not all the available experimental conditions were used as "target" for mechanisms reduction, even with the chosen kinetics model being "small" ones, the numerical procedure became time expensive if all the experimental conditions are adopted as the target for the reduction. For both the kinetics models used as base-model for methane reduction (Smith *et al.*, 1999; UCSDMech, 2016), reduction process simulation under conditions described on Table 2 spent nine days working on full-time running in a HP - Workstation Intel Xeon E5420 CPU @ 2.50 GHz.

Table 3 shows the numerical and experimental conditions used for mechanism reduction for PRF / air mixtures. The PRF adopted is a binary mixture of i-octane and n-heptane. So the nomenclature PRF0 correspond to 100% *n*-heptane and PRF100 to 100% *i*-octane, of this form, a mixture PRF60 correspond to a mixture of 40% *n*-heptane and 60% *i*-octane.

From Table 3 can be observed that not all the available experimental conditions were used as "target" for mechanisms reduction, as explained for the methane reduction process. The numerical procedure became time expensive if all the experimental conditions are adopted as the target for reduction. For the multicomponent mixtures detailed kinetics model

Table 3. Numerical and experimental conditions used for mechanism reduction for PRF / air mixtures

	Temperature [K]	**Pressure** [atm]	ϕ [-]
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)	∼1100 to ∼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

(Ranzi *et al.*, 2012), the reduction process simulation under conditions described on Table 3 spent 42 days working on full-time running in a HP - Workstation Intel Xeon E5420 CPU @ 2.50 GHz.

2.2 Numerical Assessment: An In-House Computational Tool

In this work, all the numerical procedures were programmed in Python 3.8.9 using the Cantera-PYTHON 2.5.1 interface. Python scripts were developed in order to follow the logical steps and process presented in Figure 2. Cantera[1] is an open-source suite of tools for problems involving chemical kinetics, thermodynamics, and transport processes, (Goodwin *et al.*, 2021). Its functions can automate the chemical kinetics simulation process.

The Python script native to CANTERA was adapted according to the purposes of this work. The calculated ignition delay times were obtained by simulating the chemical evolution of a reactive system in a homogeneous, adiabatic, and constant volume reactor. The laminar flame speed calculations are performed simulating a free propagating laminar adiabatic flat flame. Both the models are numerically implemented in the Cantera suite tools.

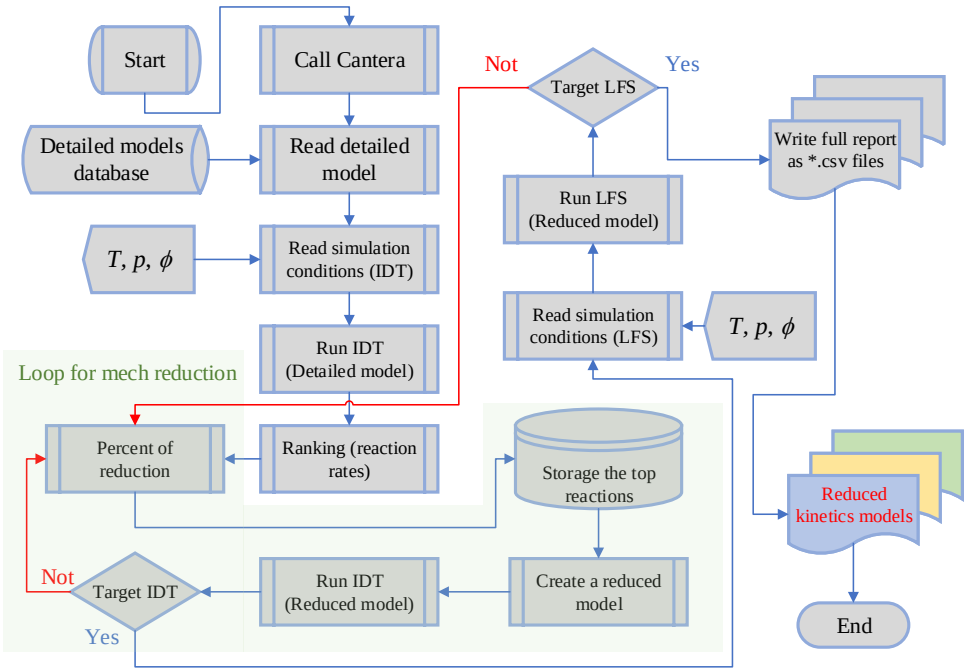

Figure 2. Flowchart implemented in Python, using Cantera interface, for detailed kinetics models reduction.

The flowchart describes, simplistically, all the programming behind the python scripts used in this work for detailed kinetics model reduction. It is noticed that the process involves two "filters", defined by the thresholds for IDT difference and LFS difference among the detailed mechanism and reduced models. The reduced model will be created according to the percentage of elementary reactions chosen in the ranking process related to reaction rate (top reactions of the mechanism). The "reduced" model will have the same number of reactions that the detailed one if all the reactions are chosen. On the other hand, if the percentage is 60%, the reduced model pursues sixty percent of the elementary reactions of the detailed model. The final percentage of reactions in the reduced model must be observed because it is not an input in the reduction routine. This final percentage is a result of the calculations performed in the mechanism reduction loop, as a consequence of IDT and LFS thresholds defined by the user.

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

3. RESULTS AND DISCUSSION

Table 4 shows the main comparative characteristics of the reduced kinetics models compared to their respective base models. In addition to the reduction, a threshold of 4% was set on the difference of the LFS numerical prediction, comparing the results obtained with the detailed mechanism and the reduced one, calculating this difference based on Equation 1. This percentage limit on the difference for the LFS prediction returns a maximum difference of IDT prediction of 2% among both the models. From Table 4 can be observed that different percentages of reduction were obtained, for both the models, among the predefined maximum difference percentage for numerical predictions of LFS and IDT.

$$Diff.\% = \left| \frac{LFS_{Detailed} - LFS_{Reduced}}{LFS_{Detailed}} \right| \cdot 100 \tag{1}$$

Table 4. Reduced kinetics models obtained in this work compared to the base-models

	Methane				**PRF Mixtures**	
	GRIMech 3.0	**Reduced**	**San Diego 2016**	**Reduced**	**POLIMI**	**Reduced**
Elements	5	5	6	6	6	4
Species	53	46	58	42	483	338
Reactions	325	188	278	164	19340	7155
Reduced to (%)	—	57(%)	—	60(%)	—	36(%)
Reference	Smith *et al.* (1999)	This work	UCSDMech (2016)	This work	Ranzi *et al.* (2012)	This work

Reduced to (%): percentage of the initial elementary reactions in the base model

3.1 Reduced kinetics models for Methane

Figure 3 shows the performance of the kinetics models (detailed and reduced) for laminar flame speed. Following the trend, each "pair" detailed/reduced model prediction is similar because of the threshold defined along the reduction process. Although it can be observed that the San Diego 2016 model shows a more expressive variation when the mixture becomes richer ($\phi \geq 1.1$) when compared with the experimental results, on the other hand, this is not observed in the results with GRIMech 3.0 model, where presented resembling results for detailed and reduction models for laminar flame speed analyses. Up to the stoichiometry, both models present a good agreement with the experimental results, presenting small variations between them.

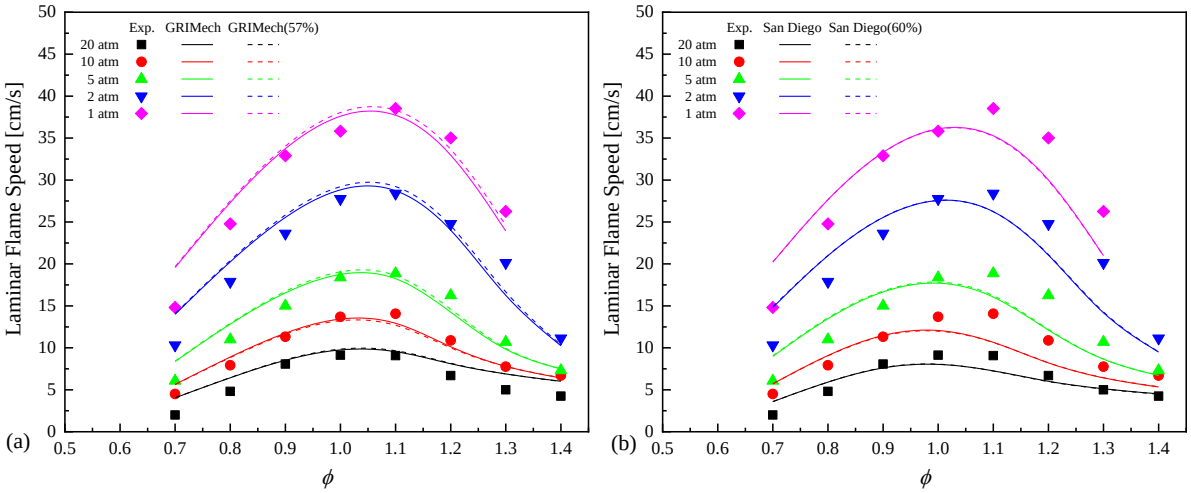

Figure 3. Laminar flame speed predictions for methane / air mixtures. Experimental data from Hu *et al.* (2015). (a) GRIMech (Smith *et al.*, 1999) continuous lines, GRIMech reduced in this work (57% of elementary reactions) dot lines. (b) San Diego Mech (UCSDMech, 2016) continuous line, San Diego Mech reduced in this work (60% of elementary reactions) dot lines

Figure 4 shows the numerical predictions from both, detailed and reduced models in terms of ignition delay times. Both the models were then compared under the same experimental conditions from Hu *et al.* (2015). It should be necessary to advise that the focus of this work is on the detailed kinetics model reduction instead of the experimental validation of that kinetics model. Of this form, the reader can observe that the GRIMech 3.0 better predicts the IDT experimental results for pressure around 1.0 atm, stoichiometric and rich methane/air mixtures when compared to the San Diego 2016 model.

The trend inverts when observed the results for the pressure of 5 atm (and above) and with lean methane/air mixtures. Both the reduced models follow the numerical predictions of the base-model ones, with errors (IDT and LFS difference predictions) among the thresholds defined along the reduction process. The accuracy trend of reduced models through this method in relation to experimental results is as follows: the better the accurate prediction of the detailed model, the better the prediction accuracy of reduced models.

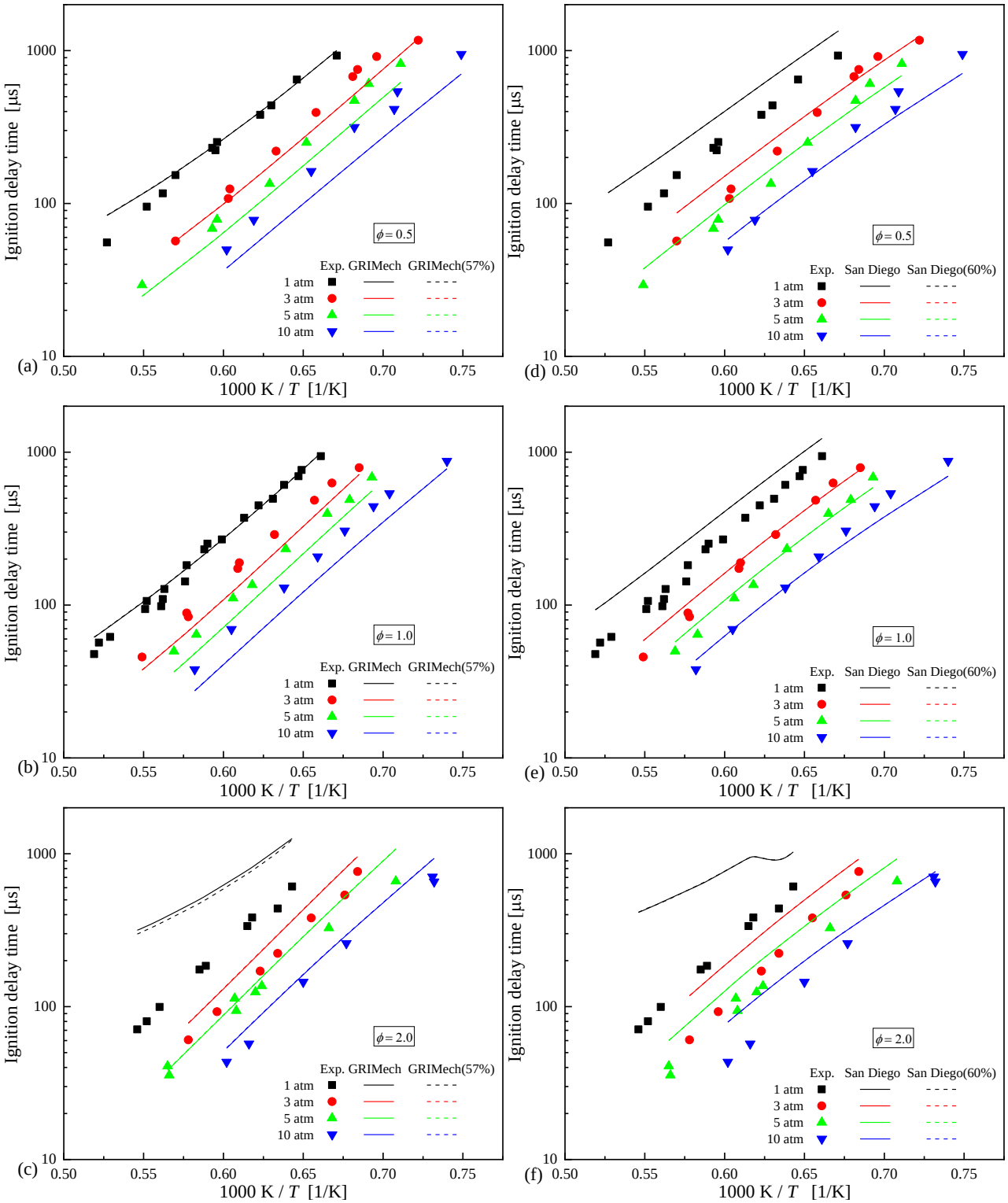

Figure 4. Ignition delay time predictions for methane / air mixtures. Experimental data from Hu *et al.* (2015). (a),(b) and (c) GRIMech (Smith *et al.*, 1999) continuous lines, GRIMech reduced in this work (57% of elementary reactions) dot lines. (d), (e) and (f) San Diego Mech (UCSDMech, 2016) continuous line, San Diego Mech reduced in this work (60% of elementary reactions) dot lines

3.2 Reduced kinetics model for Primary Reference Fuels mixtures

Using systematic reduction by tracking the maximum reaction rates for each reaction to determine which reactions are the most important, the detailed kinetics model with 483 species among 19340 elementary reactions (Ranzi *et al.*, 2012) was reduced to 338 species and 7155 elementary reactions, with 0.01% of maximum difference for IDT prediction and 0.19% of maximum difference for LFS predictions using PRF90 as fuel surrogate.

Figure 5 shows the numerical predictions from both the kinetics models as well as the experimental data available at the literature (Table 3).

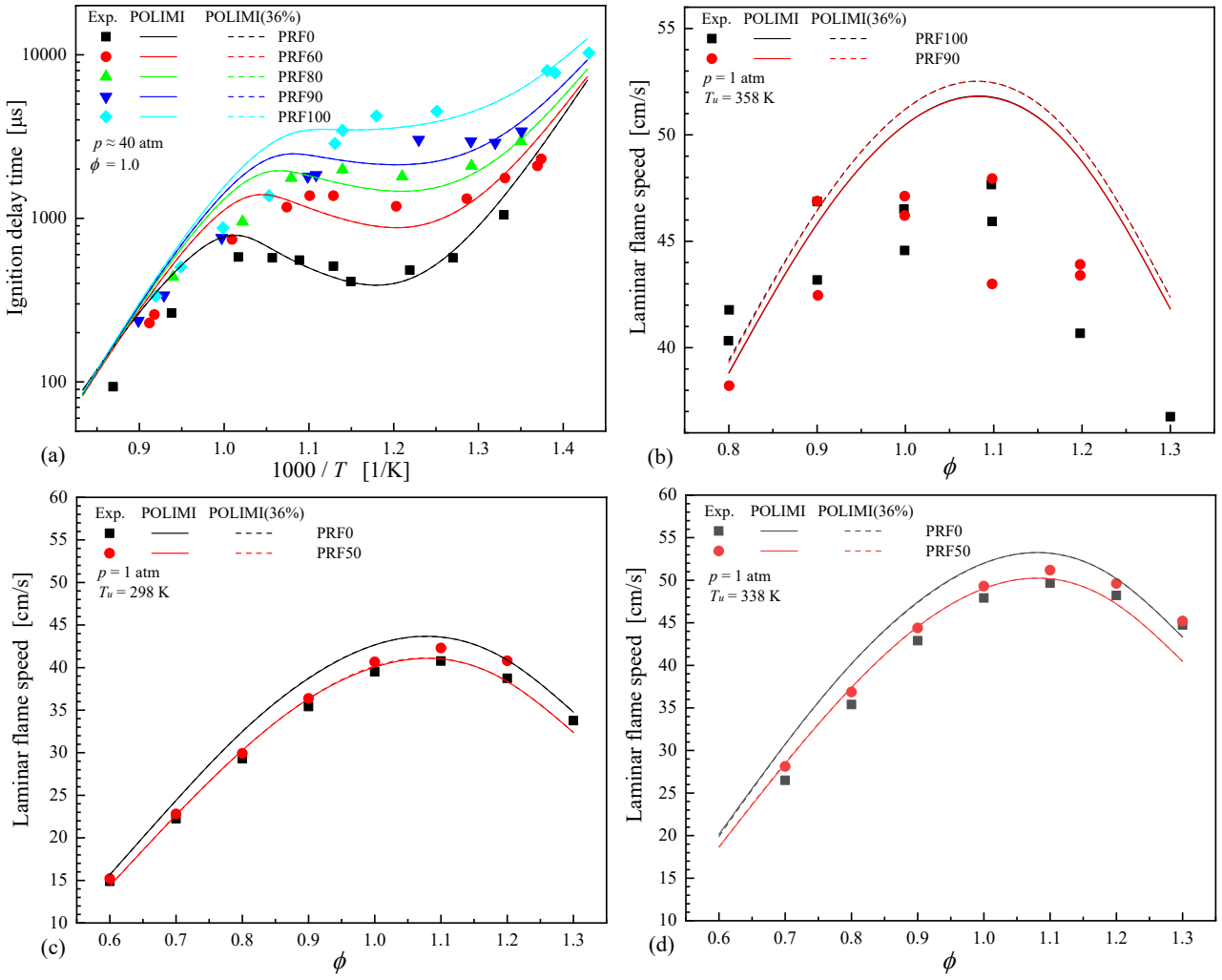

Figure 5. Ignition delay time and Laminar flame speed predictions from both, the detailed and reduced kinetics models for PRF mixtures. (a) Experimental data from Fieweger *et al.* (1997). (b) Experimental data from Bradley *et al.* (1998), (c) and (d) Experimental data from van Lipzig *et al.* (2011)

In Figure 5(a) can be observed that the detailed kinetics model from Ranzi *et al.* (2012) is able to capture the typical NTC behavior of PRF mixtures, being increased with the *n*-heptane proportion in the mixture. The reduced model (36% of the reactions of the base model) also reproduces the observed NTC behavior in both the detailed base model and from the experimental data. This is a very important aspect in the reduced model because the reduction strategy used in this work was set to obtain the reduced model from a PRF90 mixture, containing just 10% vol.% of *n*-heptane.

Another important point to raise is the reasonable accuracy of the detailed and reduced model for LFS predictions of PFR mixtures with high *n*-heptane content (Figures 5(c) and (d)) when compared to the LFS predictions of PRF mixtures with high content of *i*-octane (Figures 5(b)).

4. CONCLUSION

In this work, three detailed chemical kinetics models for methane and primary reference fuels were reduced in terms of species and reactions number, using a systematic reduction procedure based on the ranking reaction rates. A numerical tool based on Python scripts native to the Cantera toolkit was developed, leading into account ignition delay time and laminar flame speed predictions obtained by simulations, along with the reduction of mechanisms based on the reaction rate-ranking process.

Based on the results, it was possible to identify that laminar flame speed simulations are more sensitive to the ranking process when compared to ignition delay time simulations, it means, the elimination of a small set of elementary reactions with low-rank reaction rates in the indirect-injection (IDI) simulations may not have a strong effect in the IDT prediction, however, will have in the LFS prediction. Although, it can be observed that the bigger effect in LFS prediction will result in a little variation in the IDT prediction. The reduction methodology used in this work returned reduced kinetics models capable of numerically reproduce the predictions of the detailed base models. It is also observed that the accuracy of the obtained reduced model will be strongly dependent on the base model accuracy.

5. ACKNOWLEDGEMENTS

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