COBEM 2021 26th International Congress of Mechanical Engineering
ABCM Associação Brasileira de Engenharia e Ciências Mecânicas
November 22-26, 2021, Virtual Congress, Brazil

COB-2021-0494
AUTOMATIC REDUCTION FOR CHEMICAL KINETICS MECHANISM THROUGH LAMINAR FLAME SPEED SENSITIVITY ANALYSIS USING CANTERA

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Abstract. *Due to the tightening of the emission laws, new studies and developments to improve combustion efficiency must be carried out. As a result of the complexity and high cost of implementing scientific experiments, many studies in a simulation are being developed. However, for a realistic approach to simulation, an equally realistic approach is needed. Detailed chemical kinetics mechanisms are developed to supply this demand, but its use entails a substantial computational cost for 2D and 3D simulations, making its use impossible. To reduce the computational costs, a reduction of chemical kinetics mechanisms is employed with the slightest compromise in the model's accuracy. This paper aims to present an automatic algorithm for reducing the chemical kinetics mechanism by analyzing each chemical reaction's flame speed sensitivity. The algorithm automatically selects the most sensitive reactions through a threshold of a difference between the original and the reduced mechanism. Its performance will be compared to traditional methods. For comparison, the reduced mechanisms' accuracy and the total simulation time were considered.*

Keywords: *Automatic Mechanism Reduction, Chemical Kinetics, Cantera, Laminar Flame Speed, Sensitivity Analysis.*

1. INTRODUCTION

Fossil fuels are still the most significant source of energy for transport vehicles, both freight and passengers. New research in the development of fuels is being carried out to improve combustion efficiency and reduce the emission of pollutants to minimize the environmental impacts generated by burning. Due to the complexity and high cost of developing scientific experiments on the combustion process, computational simulations of the combustion process are increasingly being used.

For a realistic simulation, an equally realistic approach to the chemical and physical laws that govern the combustion process is needed and a detailed characterization of the physical and chemical characteristics of the gases present in the process. Detailed chemical kinetic mechanisms are developed to meet this need. Chemical kinetic mechanisms are computational tools that describe the transformation of reactants into products at a molecular level through elementary chemical reactions during the combustion process.

Because the time required for a combustion process simulation varies almost cubically with the number of species present in the chemical kinetic mechanism, the more detailed the simulation, the higher the computational cost to perform the simulation, but detailed mechanisms tend to contain all processes physicists and chemicals involved in the combustion process within a general and a broader spectrum of use, which may not be necessary for some simulations. Thus, to reduce the computational cost, the chemical kinetic mechanisms can be reduced to meet the desired contour characteristics better, eliminating chemical reactions that have little influence, reducing the computational cost without significantly changing the model's accuracy.

In fuel research and development, flame speed is one of the main characteristics analyzed. Its analysis is essential in the development of burners and combustion chambers. To estimate the flame velocity through computer simulations, we use a numerical solution of the conservation equations for a premixed adiabatic flat laminar flame using computational tools such as CANTERA Software developed by Goodwin *et al.* (2021).

2. METHODOLOGY

For this study, an algorithm was developed that, by analyzing the sensitivity of chemical reactions on laminar flame speed, generates an ordered list from the most influential to the least influential reaction. Given a tolerance determined by the user, the algorithm automatically generates a mechanism with the lowest amount of reactions to reach the error tolerance in the value of the laminar flame speed. The primary use of this method is to automatically generate the most appropriate mechanism for the boundary and tolerance conditions determined by the user.

Sensitivity analysis is an analysis method used to verify the influence of a given parameter on changing the final results. The sensitivity analysis used in the development of this algorithm uses chemical reactions as a parameter and verifies the change in the simulated flame speed. The model used is widely used and well known as normalized sensitivity of flame speeds concerning the reaction rate constant and defined as shown in Eq. (1):

$$S_i = \frac{k_i}{S_u}\frac{dS_u}{dk_i} \quad (1)$$

Where $\boldsymbol{S_i}$ represents normalized sensitivity, $\boldsymbol{k_i}$ represents a constant rate of reaction and $\boldsymbol{S_u}$ represents flame speed.
For the analysis, two detailed chemical kinetics mechanisms were used, the GRI-Mech 3.0 presented by Frenklach *et al.* (2021) containing 53 species and 325 reactions and the mechanism presented by Marinov (1999) containing 57 species and 383 reactions. Tolerances of 0.1%, 1%, 5% and 10% were used. For the tolerance check, the ratio between the flame speed using the reduced mechanism and the flame speed with the detailed mechanism was calculated. A spectrum equivalence ratio of 0.5 to 1.5 was used.

To analyze the simulation data, the temperature profile curves, the fuel molar fraction curve and the CO and CO2 chemical species curves were considered to analyze the differences found between the simulation with the detailed mechanism and the reduced mechanism. In addition, the simulation time for each equivalence ratio and total time for all of them in sequence will also be analyzed.

2.1 GRI-Mech 3.0

GRI-Mech 3.0 was developed by the University of California, Berkeley and is an optimized mechanism for the combustion of natural gas containing NO formation and reburn chemistry and presented by Frenklach *et al.* (2021). The detailed mechanism contains 53 species and 325 reactions. Table 1 shows the number of species, and table 2 shows the amount of reactions present in the reduced mechanisms for each studied equivalence ratio.

Table 1. Number of species presents in the reduced mechanisms

	Equivalent Ratio										
Mechanism	**0.5**	**0.6**	**0.7**	**0.8**	**0.9**	**1.0**	**1.1**	**1.2**	**1.3**	**1.4**	**1.5**
Reduced 0.1%	41	31	32	31	31	52	52	52	39	52	52
Reduced 1%	24	31	26	24	28	52	31	33	39	38	37
Reduced 5%	24	26	26	24	28	30	31	33	39	38	32
Reduced 10%	24	25	23	24	28	29	31	33	39	38	31

Table 2. Number of reactions presents in the reduced mechanism

	Equivalent Ratio										
Mechanism	**0.5**	**0.6**	**0.7**	**0.8**	**0.9**	**1.0**	**1.1**	**1.2**	**1.3**	**1.4**	**1.5**
Reduced 0.1%	198	108	134	136	135	294	289	319	141	316	283
Reduced 1%	55	105	68	55	72	294	107	104	141	137	137
Reduced 5%	55	65	68	55	72	87	107	104	141	137	84
Reduced 10%	55	59	50	55	72	78	107	104	141	137	70

Table 3 presents the time required for flame velocity simulation for both the detailed and reduced models. The table also shows the total time for calculating all equivalence ratios in sequence.

Table 3. Time needed to run the simulation

	Equivalent Ratio											
Mechanism	**0.5**	**0.6**	**0.7**	**0.8**	**0.9**	**1.0**	**1.1**	**1.2**	**1.3**	**1.4**	**1.5**	**Total Time**
GRI-Mech 3.0, s	36	16	15	9	16	17	13	8	8	4	7	157
Reduced 0.1%, s	20	4	4	2	4	15	12	7	3	4	6	97
Reduced 1%, s	16	3	2	1	3	15	4	2	3	2	3	70
Reduced 5%, s	15	2	2	1	3	4	4	2	3	2	4	57
Reduced 10%, s	16	2	2	1	4	3	4	2	3	2	2	54

We can see how fewer chemical reactions mean less time for simulation by analyzing the three tables in sequence. If we look at the number of reactions, even with different tolerance conditions, the same amount of reactions was presented, but it still presented a significant reduction in the total time to run the simulation when looking at the total simulation time. For example, with a 10% tolerance on the flame speed value, it took approximately only 1/3 of the time to fully simulate the problem.

Image 2 presents the temperature profile curves, mole fraction curve for fuel (CH4), CO and CO2 for stoichiometric combustion.

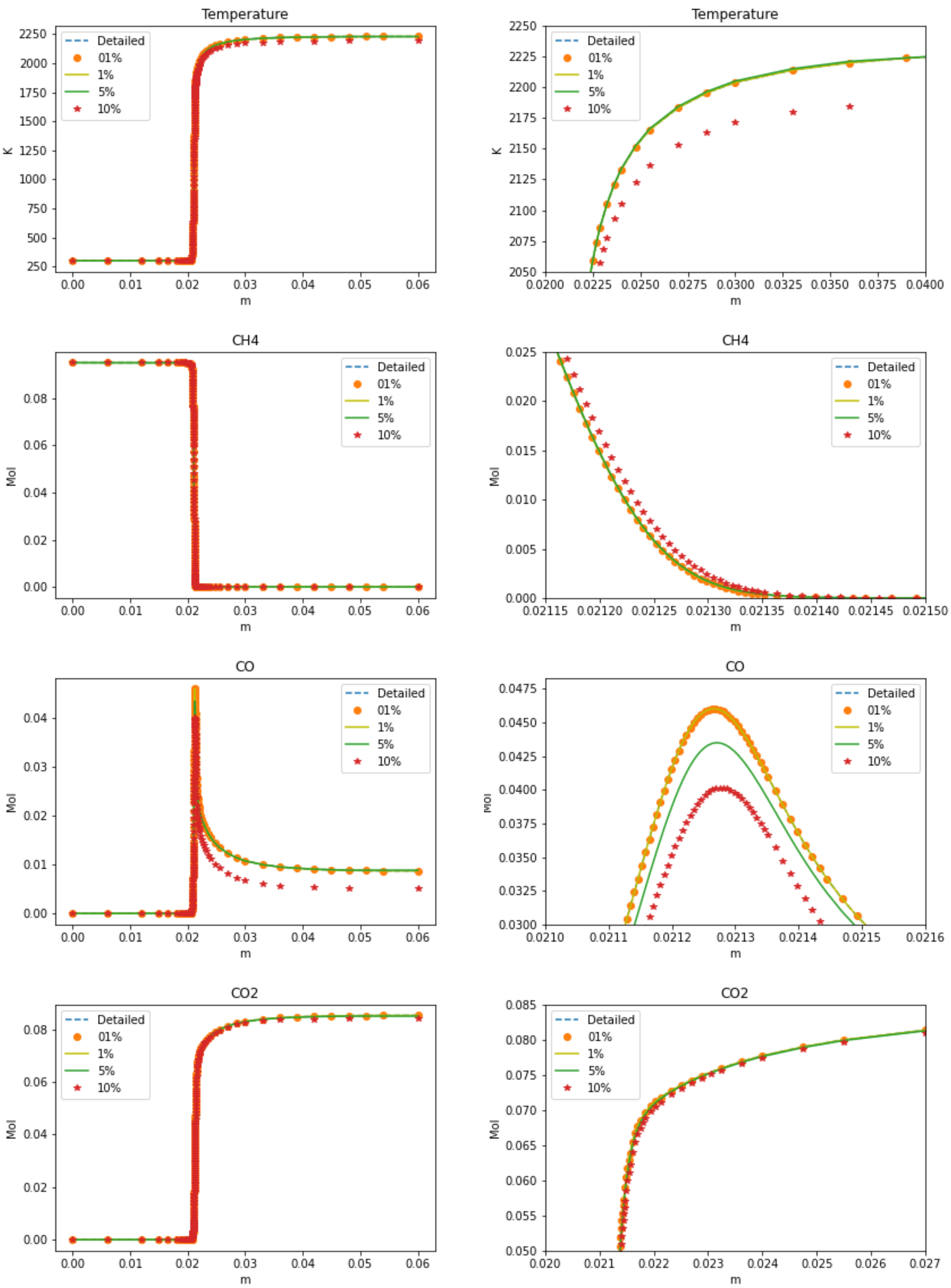


Figure 1. Graphics for stoichiometric combustion. On the right the complete process, on the left, a zoom for better comparison.

When verifying the curves, we can conclude that for the formation of CO2, even the model with 10% tolerance managed to simulate the response well, being very close to the detailed response. As for the formation of CO, there was a significant distance between the detailed model and the model with a 10% tolerance. For CO, the model with 5% was also at a significant distance from the detailed model. For CH4 consumption, the model with 10% showed a slight change in the temperature profile curve, and the model with 10% also showed a significant change in the curve. The 0.1% and 1% models did not show significant changes in the curves.

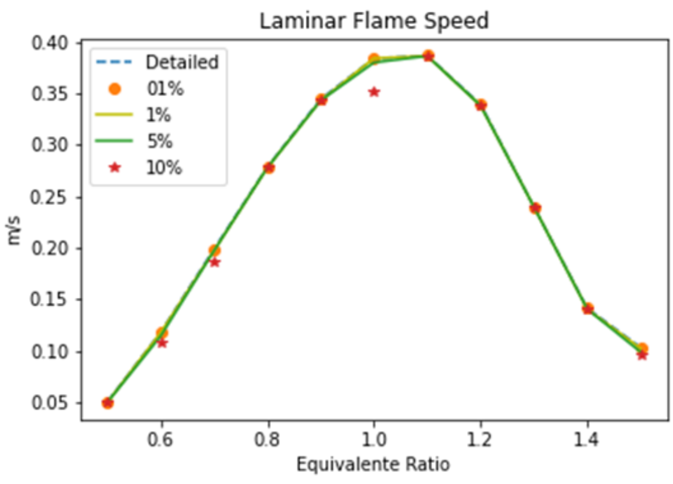


Figure 2. Flame velocity graph for stoichiometric combustion.

When verifying the flame velocity curve in image 3, we verified a slight alteration for the mechanism with 10% tolerance in 3 cases, and the other 7 cases did not present significant alteration.

2.2 A mechanism for Ethanol Produced by Marinov

Another mechanism studied was presented by Marinov (1999), where the ethanol combustion process is characterized. The detailed engine has 57 species and 383 reactions. Table 4 shows the number of species, and table 5 shows the number of reactions present in the reduced mechanisms for each equivalence ratio studied.

Table 4. Number of species presents in the reduced mechanisms

	Equivalent Ratio										
Mechanism	**0.5**	**0.6**	**0.7**	**0.8**	**0.9**	**1.0**	**1.1**	**1.2**	**1.3**	**1.4**	**1.5**
Reduced 0.1%	57	56	56	56	56	56	56	52	56	56	56
Reduced 1%	56	56	56	54	56	49	56	52	50	56	56
Reduced 5%	56	52	53	53	56	49	56	49	49	56	56
Reduced 10%	56	52	53	53	56	49	52	46	49	56	56

Table 5. Number of reactions presents in the reduced mechanism

	Equivalent Ratio										
Mechanism	**0.5**	**0.6**	**0.7**	**0.8**	**0.9**	**1.0**	**1.1**	**1.2**	**1.3**	**1.4**	**1.5**
Reduced 0.1%	368	365	327	339	339	343	359	265	372	352	372
Reduced 1%	359	298	306	276	306	214	359	266	200	352	372
Reduced 5%	315	248	269	266	306	214	359	189	182	352	372
Reduced 10%	315	248	269	266	306	214	257	150	169	352	372

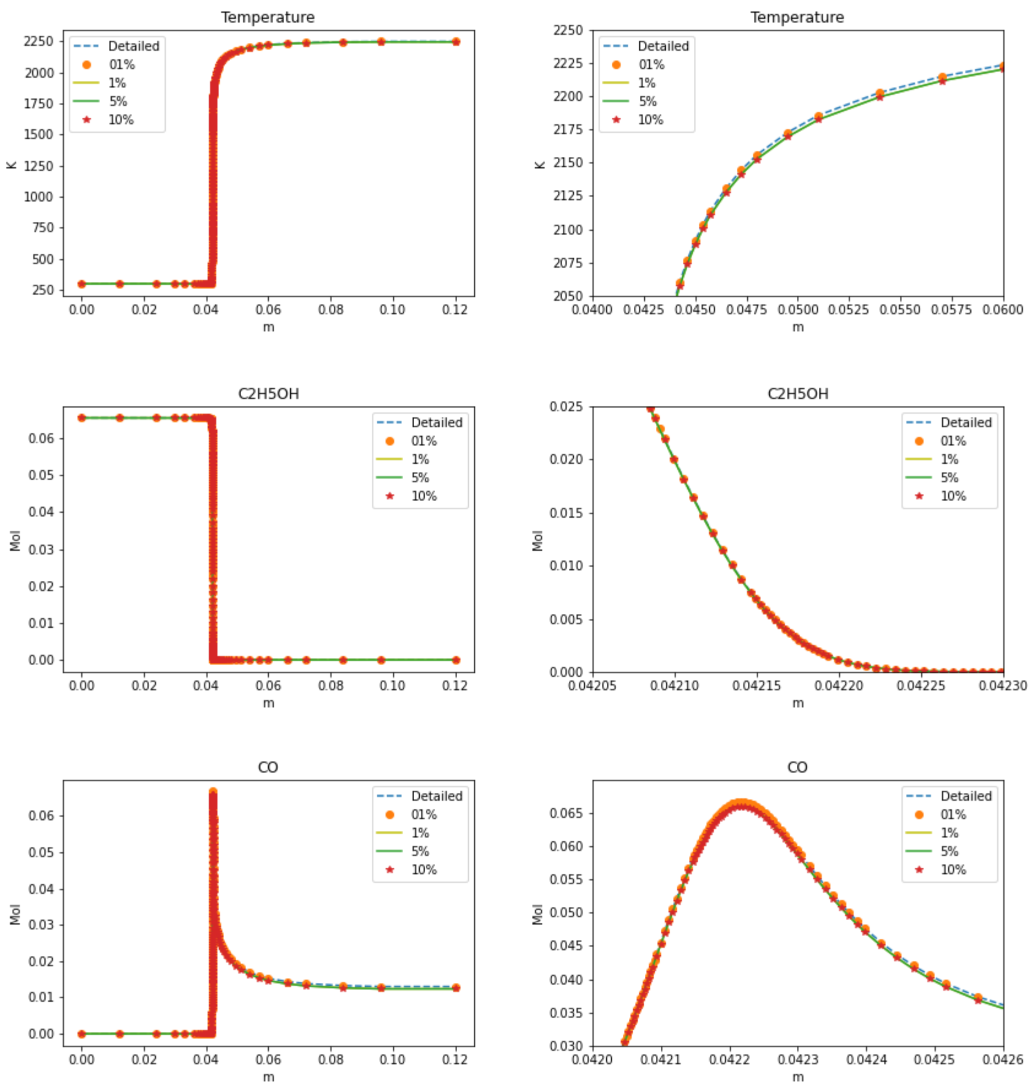
Table 6 presents the time required for flame velocity simulation for both the detailed and reduced models. The table also shows the total time for calculating all equivalence ratios in sequence.

Table 6. Time needed to run the simulation

	Equivalent Ratio										
Mechanism	**0.5**	**0.6**	**0.7**	**0.8**	**0.9**	**1.0**	**1.1**	**1.2**	**1.3**	**1.4**	**1.5**	**Total Time**
Marinov, s	23	21	22	23	21	70	17	12	11	10	9	245
Reduced 0.1%, s	23	19	17	19	18	60	16	8	11	9	8	226
Reduced 1%, s	19	15	17	16	16	38	17	8	6	9	8	186
Reduced 5%, s	19	12	14	14	16	38	16	5	5	9	8	174
Reduced 10%, s	20	12	15	14	16	38	13	4	5	9	8	171

When analyzing the tables, we verified the same behaviour in the GRI-Mech 3.0 study. Again, fewer reactions mean less simulation time, even with equal amounts of reactions in some cases, the final time was even lower. Nevertheless, this time, the difference in total time was not so expressive. For example, with 10% tolerance, it took approximately 2/3 of the time to simulate the problem entirely.

Image 4 presents the temperature profile curves, mole fraction curve for fuel (C2H5OH), CO and CO2 for stoichiometric combustion.



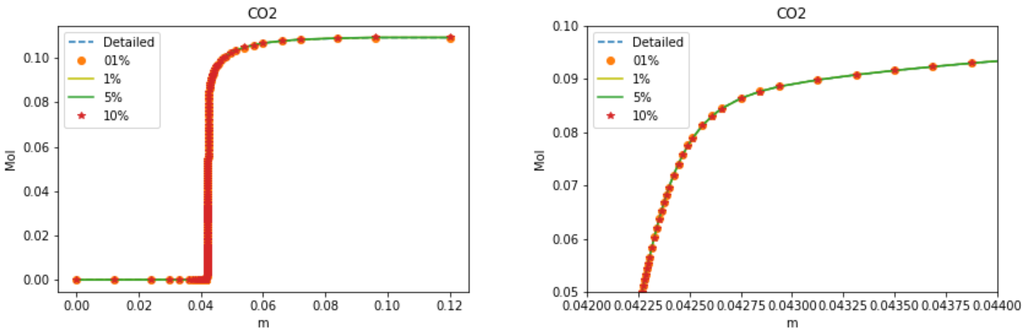


Figure 3. Graphics for stoichiometric combustion. On the right the complete process, on the left, a zoom for better comparison.

Contrary to what was seen in the analysis of the GRI-Mech 3.0, for the mechanism proposed by Marinov, in all conditions, no significant changes were found in the molar fraction curves. Moreover, the slight difference seen in the fuel profile curve is relatively tiny, where 1%, 5% and 10% are grouped and slightly shifted downwards.

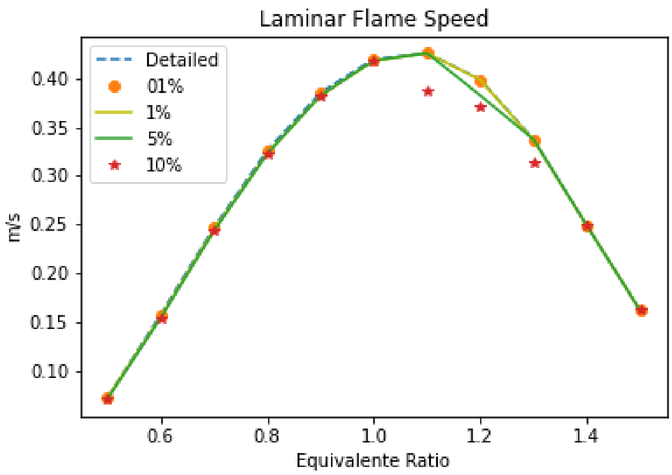


Figure 4. Flame velocity graph for stoichiometric combustion

When verifying the flame velocity curve, in image 5, we verified a slight alteration for the mechanism with 10% tolerance in 3 cases, but in the other 7 cases, it did not present significant alteration. For 5% tolerance, there is also a change, but in only 1 case (equivalence ratio equal to 1.2).

3. CONCLUSION

After analyzing the answers and the simulation time, it was verified that the proposed algorithm presents an excellent result for obtaining reduced mechanisms automatically. For the GRI-Mech 3.0 study, the algorithm found a solution that needed approximately 1/3 of the time required for the detailed mechanism in the fastest case, maintaining a fair value in the changes in the temperature profile and the analyzed molar fraction curves. On the other hand, in the analysis of the mechanism proposed by Marinov, the algorithm found a solution that needed approximately 2/3 of the time needed for the detailed mechanism in the fastest case, but this time without showing significant changes in the temperature profile and molar fraction curves. The difference between the two cases is due to the greater specificity of the mechanism produced by Marinov for the combustion of Ethanol. Because it is more optimized, its reduction does not become as expressive. However, its accuracy even reduced is excellent, and the time variation may not be expressive when calculated for more minor cases, but in larger cases, such as 2D or 3D cases, the computational cost difference is undeniable.

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5. RESPONSIBILITY NOTICE

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