

Application of reduced mechanism by DRGEP-CSP approach to the numerical simulation of biogas diluted with the H₂-CO₂ couple

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Abstract. A numerical simulation was used to investigate an approach of reduction of the chemical kinetics coupled with two methods: Computational Singular Perturbation (CSP) and Directed Relation Graph with Propagation Error (DRGEP), in order to simulate the laminar premixed Biogas diluted by the H₂-CO₂. In this reduction approach, DRGEP allowed the identification of important species, elementary reactions involving unimportant species were eliminated from the detailed mechanism. To have a skeletal mechanism containing a minimum number of elementary reactions, the CSP method was used. The skeletal mechanism reduced by the DRGEP-CSP approach was opted for the simulation of biogas diluted by the H₂-CO₂ couple, given its high fidelity with the detailed mechanism. This reduction approach was applied to the laminar premixed flame biogas with the effect of varying the proportion of H₂ and CO₂. It emerges from the results that this reduction approach has a wide field of application in the study of the numerical combustion of biogas. It also appears that, the dilution of the biogas by H₂-CO₂ couple has a significant influence on the laminar flame speed and temperature over a wide range of aeration factors. **Keywords:** Computational Singular Perturbation, Directed Relation Graph with Propagation Error, Biogas, Laminar Flame Speed, Chemkin II, Reduced Mechanism

1 Introduction

One of the greatest dilemmas of this century is the issue of energy resources. Fossil fuels are a valued energy source. However, it is difficult to reconcile their operations with the requirements of sustainable development. The current challenge is the need to find an alternative to energy dependence on fossil fuels: renewable energies. Biogas is a satisfactory alternative to gaseous biofuel, which can be produced from several resources and organic wastes by anaerobic digestion, such as cow sludge, pig slurry, agro-food waste and household waste [1,2]. The production of biogas plays a considerable role, its combustion is not 100% clean, however, it does not contribute enough to global warming [3]. One of the motivations for the study of combustion is that the subject itself is intellectually stimulating due to the coupling between physics and chemistry: chemical thermodynamics and modelling with engineering practice. The detailed chemical kinetic models necessary for the proper representation of physical and chemical phenomena are increasingly precise, and therefore inevitably contain more and more species and chemical reactions.

we can cite among others: GRI.3.0 for methane, the most generally used for the simulation of natural gas and biogas, it contains 53 species and 325 reversible reactions [4]. Despite the rise in power of computers, the numerical simulation of physical phenomena involving a detailed chemical kinetic mechanism leads to a long calculation time. To resolve this problem, several researchers have developed techniques for reducing detailed mechanisms in order to save memory space and computing time while retaining all the information of the detailed mechanism. We can cite among others the Computational Singular Perturbation (CSP) method introduced by Lam and Goussis [5], recently [6,7] was applied by Awakem et al. to the simulation of a turbulent diffusion flame of flame-A and the validation of the ignition delay table. The Directed Relation Graph with Error Propagation (DRGEP) [8]. This work makes it possible to evaluate an approach for reducing chemical kinetics based on two approaches (DRGEP-CSP and CSP-DRGEP).

2 Methodologies

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2.1.1 Chemical composition of biogas

In this study, the chemical composition of the biogas used is that of Wei et al. [8], with the volume percentages of CH₄ and CO₂ is given in table 1. The added dihydrogen is defined by the following

$$\text{relationship, } \alpha_{H_2} = \frac{V_{H_2}}{(V_{CH_4} + V_{CO_2})} \quad (1)$$

where V_{H_2} , V_{CH_4} and V_{CO_2} are mole fractions of hydrogen, methane and carbon dioxide, respectively. Eq.1 makes it possible to obtain the final biogas-dihydrogen composition.

Table 1: chemical composition of biogas [9]

BG80		BG60		BG40	
CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂
80%	20%	60%	40%	40%	60%

To better analyze the effects of the H₂ and CO₂ pair, the content of these species was set at the same percentages, with $\alpha_{H_2} = 20\%$, 40% and 60% .

The choice of this biogas-hydrogen composition was motivated by the desire to study the coupling effects of H₂ and CO₂, dilution, thermal and chemical effects of H₂ and CO₂, the effect of these two species.

2.2 Different techniques for reducing chemical kinetics

2.2.1 Modelling of the Directed Relation Graph with Propagation Error method

In this study, the DRGEP method was modelled as a first reduction step with the objective of selecting fast species as much as possible. This approach is modelled by Equations 5 and 6.

$$r_{AB} = \frac{|P_{AB} - D_{AB}|}{\max(P_A - D_A)} \quad (5)$$

$$= \frac{|\sum_{i=1}^N S_{A,i} q_i \delta_B^i|}{\max(\sum_{i=1}^N \max(S_{A,i} q_i, 0), \sum_{i=1}^N \max(-S_{A,i} q_i, 0))} \quad (6)$$

Where $\delta_B^i = \begin{cases} 1, & \text{if } i\text{th elementary reaction contains specie } B \\ 0, & \text{otherwise} \end{cases}$

$$(7)$$

$$q_i = q_{f,i} - q_{b,i} \quad (8)$$

r_{AB} is the relative error which implies species A for a probable elimination of species B, the subscript i indicates the ith elementary reaction; $S_{A,i}$ is the net stoichiometric coefficient of species A in the ith reaction; q_i , $q_{f,i}$ and $q_{b,i}$ are net, forward, and inverse reaction rates of the ith reaction, respectively. P_A and D_A are the total rate of production and destruction of species A, respectively; P_{AB} and D_{AB} the rate of production and destruction of species A, respectively, due to the existence of species B. species A is considered important if r_{AB} is greater than the precision requested by the user according to of the fidelity of the skeletal mechanism to the detail requested. This precision is between 0 and 1. The number of important and necessary species is

inversely proportional to the relative error set by the user.

2.2.2 Modeling of the Computational Singular perturbation method

This method has already been developed and applied in recent work by Awakem et al. [6, 7]. Awakem et al. applied this method to the reduction of Yang and Pope's mechanism [10] which contains 16 species and 41 to 22 elementary reactions.

In this subsection, a brief description of the CSP approach based on the analysis of groups of reactions on the evolution of each chemical species and the degree of participation of each elementary reaction is made.

The mathematical modeling of a chemical kinetic mechanism is represented by the following equations

$$\frac{dy}{dt} = g(y) \quad (9)$$

And $\frac{dg}{dt} = Jg$, with $J = \frac{dg}{dy}$

$$(10)$$

Where y is the concentration vector of chemical species and J is the Jacobian matrix of Eq. 9. The rates of the reaction groups are assessed by Eq. 11.

$$f^i = B^i g = \sum_{r=1}^R B_r^i F^r, i=1, \dots, N \quad (11)$$

with $B_r^i = B^i S_r$ $i=1, \dots, N$; where B^i is the ith row vector of the inverse matrix of A; S_r , F^r and R are the stoichiometric coefficient, the rate of the rth reaction and the total reaction number, respectively. The first values of f^i which tend towards zero are said rapid reactions groups to be eliminated from the detailed mechanism. The participation index of reaction groups is assessed by Eq. 12.

$$K_j^i = \frac{|A_j^i f^i|}{\sum_{k=1}^N |A_k^i f^k|} \quad i=1, \dots, N \quad (12)$$

The value of K_j^i is between 0 and 1, a reaction group is important when

K_j^i tends towards 1, otherwise fast. The degree of participation of an elementary reaction is evaluated by Eq. 13.

$$I_r^i = \frac{|C_r^i f^i|}{\sum_{k=1}^N |C_k^i f^k|} \quad i = 1, \dots, N, r = 1, \dots, R \quad (13)$$

3 Results and discussion

This section presents the results of this work in two steps: on one hand, the results of the two reduction approaches (CSP-DRGEP and DRGEP-CSP) implemented in this study and on the other, hand the application of the reduced mechanism to the numerical simulation of biogas with dilution of the H₂-CO₂.

3.1 Results and discussion of the two reduction approaches DRGEP-CSP and CSP-DRGEP

This subsection presents the results of the two reduction approaches implemented in this work. The DRGEP method is best suited to obtain a minimum number of species while the CSP method based on the analysis of reaction groups and the participation index of elementary reactions is more suitable for obtaining a minimum number of elementary reactions. Good fidelity with the detailed mechanism is observed, as shown by the temperature profiles of the various skeletal mechanisms obtained, Fig. 1. Both approaches have a very good agreement with the detailed mechanism, with the same percentage reduction in species (54%). However, the CSP-DRGEP approach has a slightly higher percentage reduction in reaction 91% compared to the DRGEP-CSP approach, which is at a reduction percentage of 81%.

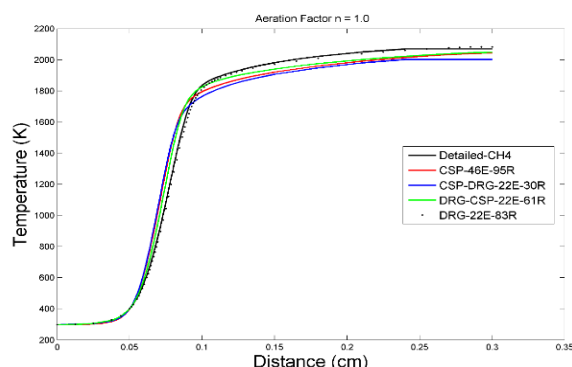


Figure 1 : Comparison of the temperature profiles of the detailed (Detailed-CH4) and reduced mechanism.

For the rest, we opted for the skeletal mechanism obtained by the DRGEP-CSP approach (22 species and 61 reactions) for the simulation of a laminar premixed flame biogas with variation of CO_2 and H_2 . The choice is motivated by careful consideration of laminar premixed flame speed and the formation of CO/NO_x during combustion of biogas diluted by the $\text{H}_2\text{-CO}_2$ couple.

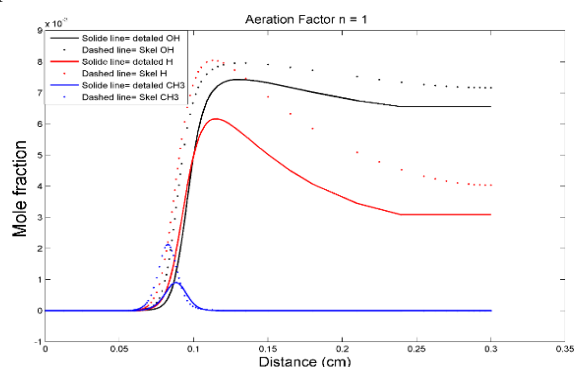


Figure 2: Comparison of profiles of key intermediate species between reduced (DRGEP-CSP, 22 species and 61 reactions) and detailed mechanism.

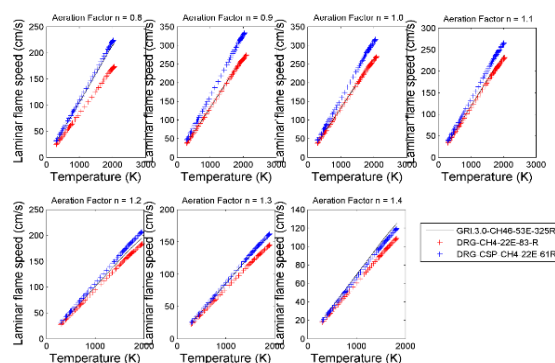


Figure 3: comparison of the laminar flame speed between the detailed and reduced mechanism

Fig. 2 presents the mole fractions profiles of key intermediate species, the results are similar to the work of Yulin Chen and Jyh-Yuan Chen [36], with the aeration factor $n = 1.4$. A large decay of peaks exists between the reduced and detailed mechanism. To better qualify the relationship between the main radicals (H , OH and CH_3) and the laminar flame speed, the work was carried out with air aeration factors from 0.8 to 1.4 with the step of 0.1. Laminar flame speed results are presented as a function of temperature. Despite a large difference in the level of radical peaks (Fig. 2), the results confirm a good prediction of laminar flame speed of reduced compared to the detailed mechanisms. A good laminar flame speed match is observed in the low temperature region (298 - 600 K at constant pressure, 1atm), over a wide range of air aeration factors, from 0.8 to 1. The degree of fidelity becomes more and more considerable with the air aeration factors ($n > 1$), Fig. 3. It appears from this that the laminar flame speed of the reduced mechanism (DRGEP-CH4-22 sp-83 re) by the DRGEP method is in good agreement with the detailed mechanism over the whole range of the air aeration factor. However, there is a considerable difference between the reduced mechanism (DRGE-CSP-CH4-22 sp-61 re) and the detailed one, for all $n \leq 1$. This is explained by the fact that for all $n \leq 1$, combustion is incomplete and there is production of the CO radical, as shown in equations 2 and 4, but during the second reduction step of the DRGEP-CSP approach, the reactions ($\text{O} + \text{CH}_2 (\text{S}) \rightleftharpoons \text{H}_2 + \text{CO} (\text{R8})$, $\text{O} + \text{HCO} \rightleftharpoons \text{OH} + \text{CO} (\text{R13})$, $\text{H} + \text{HCO} \rightleftharpoons \text{H}_2 + \text{CO} (\text{R55})$ and $\text{CH}_2 (\text{S}) + \text{CO}_2 \rightleftharpoons \text{CO} + \text{CH}_2\text{O} (\text{R153})$) have been identified as rapid reactions and eliminated by the CSP method, these reactions involve the CO radical which has a non-negligible production rate for $n \leq 1$. Several previous studies [11] have added the radical species CH_2O , OH and CO to better conserve the ignition delay at low temperature, because in the NTC region, it is difficult to obtain a precise large-scale reduction without these additional species-related pathways. These species are selected as necessary species by the two reduction approaches presented in the methodological part.

3.2 Results and discussion of the simulation of a laminar flame biogas diluted by the H₂-CO₂ couple.

In this subsection the mechanism reduced by the DRGEP-CSP approach is used to carry out a study on the laminar premixed flame biogas diluted by the H₂-CO₂ couple, with a look at the emission and the formation of CO/NO_x, the thermal and chemical effect and the laminar premixed flame speed.

The temperature and the mole fractions of the majority species of the detailed (GRI.30) and reduced mechanisms (DRGEP-CSP-22 species, 61 reactions) of methane are compared to biogas diluted with the H₂-CO₂ pair. These results are illustrated by figure 4, a perfect agreement is observed between the detailed and reduced mechanisms according to the four compositions of the diluted biogas studied.

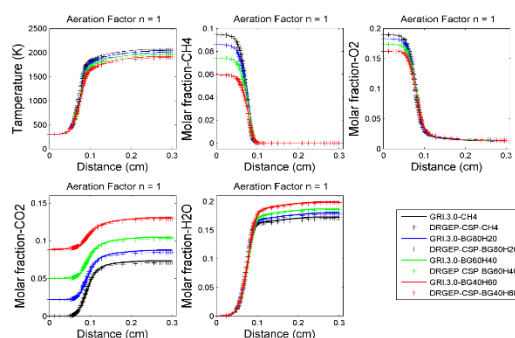


Figure 4: Comparison of temperature and majority species between the detailed and reduced mechanism of several biogas diluted with hydrogen, air aeration factor $n = 1$, Pressure 1 atm.

It is observed that by increasing the proportion of the H₂-CO₂ couple, the peak of temperature of the biogas mixture gradually decreases. This explains the dominant role played by CO₂ over H₂ to attenuate the rate of heat released during combustion, since dihydrogen has a lower calorific value much greater than that of methane, it contributes much more to the increase the temperature. By setting the content of H₂ and CO₂ at the same percentage, we can easily understand the chemical effect of CO₂ and H₂ in the initial mixture of biogas. This increase in the rate of heat released exhibits noticeable effects on flame structure and laminar flame speed. In addition, the effects of dilution of biogas by the H₂-CO₂ couple play a very important role in the decrease of the speed of the laminar premixed flame Biogas and the rate of heat release, as shown in figures 5 and 6 for the evolution of the temperature and figures 7 and 8 for the evolution of the laminar flame speed as a function of the temperature (298-600 K) over a wide range of air aeration factor ($n = 0.8$ to 1.4 with a step of 0.1).

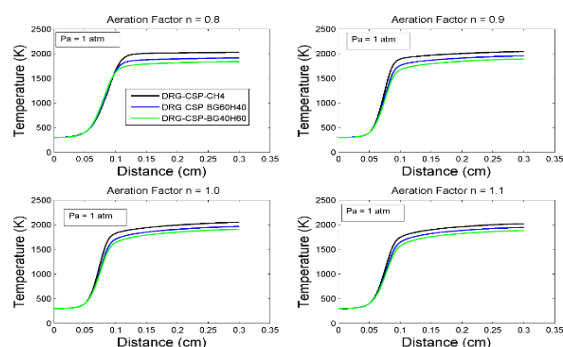


Figure 5: Temperature comparison between methane (100% in CH₄) and several diluted biogas, air aeration factors $n = 0.8, 0.9, 1; 1.1$; Pressure 1 atm.

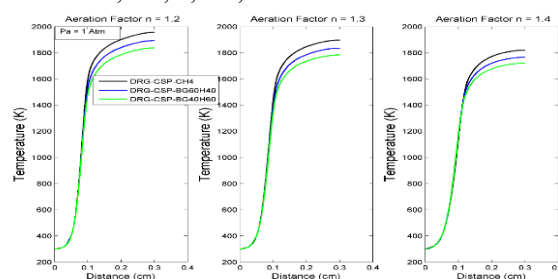


Figure 6: Temperature comparison between methane (100% CH₄) and several diluted biogas, air aeration factors $n = 1.2$ and $1.3, 1.4$; Pressure 1 atm.

It is observed that the dilution of the biogas by the H₂-CO₂ couple has thermal effects and on the structure of the flame, and are considerably increased with their increased proportions, while the chemical species H₂ and CO₂ exert more obvious influences on the laminar premixed flame speed, in a rich or lean fuel mixture. Overall, it is known that the dilution effects of biogas by the H₂-CO₂ couple have a significant influence on the laminar flame speed with the increased proportions of H₂ and CO₂. The variation of the laminar flame speed is normalized by the sum of the absolute values of the variations of the laminar flame speed caused by different effects at the same conditions, which clearly shows the relative importance of the dilution of the biogas by the H₂-CO₂ couple. The results of the temperature profiles obtained are shown in Figures 5 and 6, with the increase in the contents of H₂ and CO₂, the contribution of the chemical effect of CO₂ decreases, while that of the chemical effect H₂ increases the heat release rate in rich and fuel lean condition. About these figures, the temperature peaks are inversely proportional to the content of the H₂-CO₂ pair over the entire air aeration factor range ($n = 0.8$ to 1.4 with the step of 0.1). Since, these two chemical species have the same percentages by volume in the initial mixture of biogas, we can say that the effect of CO₂ is more dominant on the release of heat. In addition, the thermal effects of the H₂-CO₂ couple both become complex in varying the laminar premixed flame speed. It should be noted that in certain range of air aeration factors ($n = 0.9, 1, 1.1, 1.2$ and 1.3) that the laminar flame speed is inversely proportional to the increase in the H₂-CO₂ couple and the opposite is observed with the aeration factors ($n = 0.8$ and 1.4), as shown in figures 7 and 8. A particular attention allows us to observe a progressive approximation of the different curves between $n = 0.9$ and 1.3 , then

permutation of part and other. This variation of positions reflects the complexity of the effect of the H_2 - CO_2 couple on the evolution of the laminar flame speed.

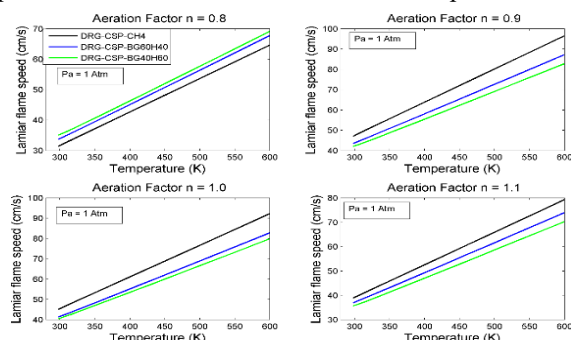


Figure 7: Comparison of the laminar flame speed between methane (100% CH_4) and several diluted biogas, air aeration factors $n = 0.8, 0.9, 1, 1.1$; Pressure 1 atm.

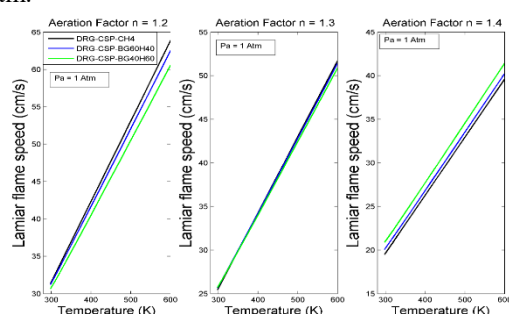


Figure 8: Comparison of the laminar flame speed between methane (100% CH_4) and several diluted, air aeration factors $n = 1.2, 1.3$ and 1.4 ; Pressure 1 atm.

4 Conclusion

This work made it possible to develop an approach to reduce chemical kinetics mechanism based on two reduction methods, DRGEP and CSP. In this study, DRGEP made it possible to identify all unimportant species, the skeletal mechanism is obtained by eliminating the elementary reactions involving these species. The CSP method based on the analysis of the importance of the reaction groups and the degree of participation of the elementary reactions made it possible to identify the fast reactions. The skeletal mechanism is obtained by suppressing these less important reactions. It emerges from this work that the DRGEP method is better suited to obtain a skeletal mechanism with a minimum number of chemical species and a low relative error with the detailed mechanism, while the CSP method presented in this work reduces the number of elementary reactions, but with a relative error greater than that of the DRGEP method. The combination of the two methods made it possible to obtain skeletal mechanisms with a minimum number of chemical species and elementary reactions (22 species, 30 and 61 reactions). A very good agreement of temperature profiles, majority chemical species and laminar flame speed was observed between the reduced mechanisms and the detailed mechanism. The reduced mechanism (22 species and 61 reactions) was used to carry out a study on a laminar premixed

flame biogas diluted by the H_2 - CO_2 couple. A good agreement between the detailed and reduced mechanism is also observed on several biogas diluted with the H_2 - CO_2 couple and over a wide range of air aeration factor, showing that the reduced mechanism developed in this work can allow to simulate a laminar premixed flame. It emerges from this work that the rate of heat released is inversely proportional to the percentage content of the H_2 - CO_2 couple, which would mean that the effect of CO_2 is more dominant than that of H_2 , since the two play antagonistic roles. We also note a significant influence of the effect of dilution of the biogas by the H_2 - CO_2 couple on the structure of the flame and on the variation of the laminar premixed flame speed depending on the initial mixture.

Nomenclature

C_r	vector of reduced stoichiometric coefficient
D_A	total rate of destruction of species A
D_{AB}	rate of destruction of species A due to the existence of species B
f^i	rates of the i^{th} reaction group
g	global rate of reaction
I_{error}	relative error
I_r^i	degree of participation of r^{th} elementary reaction
J	Jacobian matrix
K_j^i	participation index of the i^{th} reaction groups
P_A	total rate of production of species A
P_{AB}	rate of production of species A due to the existence of species B
$q_{b,i}$	inverse reaction rates of the i^{th} reaction
q_i	net reaction rates of the i^{th} reaction
$q_{f,i}$	forward reaction rates of the i^{th} reaction
$Q(M)$	projection matrix on the fast subspace
r_{AB}	relative error which implies species A for a probable elimination of species B
$S_{A,i}$	net stoichiometric coefficient of species A in the i^{th} reaction

Abbreviations

CFD	Computational Fluid Dynamics
CSP	Computational Singular Perturbation
DRGEP	Directed Relation Graph with Propagation Error

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