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OBTAINMENT OF A REDUCED KINETIC MECHANISM FOR BIODIESEL SURROGATES USING DIRECTED RELATION GRAPH AND SENSITIVITY ANALYSIS

F. C. Minuzzi

F. R. Padilha

A. L. De Bortoli

feminuzzi@hotmail.com

roneipadilha@yahoo.com.br

dbortoli@mat.ufrgs.br

Graduate Program in Applied Mathematics (PPGMAp), Federal University of Rio Grande do Sul

Av. Bento Gonçalves 9500, PO Box 15080, Porto Alegre, Brazil

J. M. Pinho

jean.engmec@gmail.com

Graduate Program in Chemical Engineering, Federal University of Rio Grande do Sul

Street Engenheiro Luiz Englert s/n^{o}- Building 12204, 90040-040, Porto Alegre, Brazil

Abstract. *Combustion plays a significant role for transforming energy, and its better understanding contributes to the reduction of pollutants emission, fuel efficiency and stability. Biodiesel is an alternative to the diesel derived from oil. Since biodiesel composition is too complex to be modeled directly, studies are frequently concentrated in biodiesel surrogates, such as Methyl Butanoate (MB). Efficient numerical simulations of reactive flows, such as combustion, depends on the existence of detailed kinetics mechanisms for fuels. However, detailed mechanisms can have tens or hundreds species and hundreds or thousands reactions, which induces significant stiffness to the system of equations. Consequently, there is the need to develop reduced mechanisms with fewer variables and moderate stiffness, maintaining a good level of* *accuracy of the model. The aim of the present work is to develop reduced mechanisms for MB, applying the Directed Relation Graph (DRG), which is a method that shows the coupling of species through a coefficient based on the reaction rate. Graph search algorithms and some sort of sensitivity analysis are also applied to the skeletal mechanism developed by DRG to further eliminate species and reactions. The advantage of using these methods is the elimination of redundant species and reactions, decreasing the computational cost needed to solve the chemical equations, of about two orders of magnitude for MB, making the numerical simulation of combustion of high chain fuels feasible.*

Keywords: *Combustion, Mechanism Reduction, DRG, Sensitivity Analysis*

1 INTRODUCTION

Combustion is the principal process of energy conversion in the world nowadays. It is employed in piston engines, gas turbines, heating, electrical systems, among others. The debate about using biofuels energy is one of the most important topics nowadays, since fossil fuels are finite and they generate pollutants causing environmental imbalance. Even with the increase in using renewable fuels, such as wind and solar, combustion will remains the principal source of energy conversion for the next years.

However, even for biofuels, two main products cannot be avoided when burning hydrocarbons, namely, CO_2 and H_2O. The latter is not a problem, but the first is. Carbon dioxide is the principal responsible for the global warming and climatic changes that occurred in the past century. The environmental problems caused by combustion need to be taken into account, which makes the main objective of combustion nowadays the conversion of energy spending less fuel as possible, so that the carbon dioxide emission decreases.

Biodiesel is derived from vegetable oils or animal fats via transesterification process and is an alternative fuel to diesel from oil. Currently, soy oil and rapeseed oil represent major sources of biodiesel (Herbinet *et al.*, 2008). Among the advantages of using biodiesel, is obvious the large capacity of lubrication, which enhances the life of engines, the biodegradability, and the possibility of being used in any diesel engine without significant modification (Demirbas, 2009).

The five typical molecules that composes biodiesel are (Herbinet *et al.*, 2008): methyl palmitate $(C_{17}H_{34}O_2)$, methyl stearate $(C_{19}H_{38}O_2)$, methyl oleate $(C_{19}H_{36}O_2)$, methyl linoleate $(C_{19}H_{34}O_2)$ and methyl linolenate $(C_{19}H_{32}O_2)$. Due to the additional atoms of oxygen in the molecules, the atoms of carbon are more oxidized, which reduces the emissions of CO.

Compared to typical diesel surrogate fuels, the carbon chain of biodiesel is longer and more complex, which results in significant differences on the combustion and emission characteristics (An *et al.*, 2014) of them. A complex detailed kinetic mechanism for biodiesel is necessary to describe the process of oxidation, which may have thousands of reactions, increasing considerably the computational cost for its simulation.

The techniques of reduction of chemical mechanisms can be classified in terms of global reduction in the number of reactions, and of refinement of the mechanism (De Bortoli *et al.*, 2015). In this context, Directed Relation Graph (DRG), introduced by Lu and Law (Lu and Law, 2005), is an efficient method for obtaining skeletal mechanisms. It shows the coupling of species through a coefficient based on the reaction rates.

Westbrook *et al.* (2011) developed a detailed kinetic mechanism for the oxidation of biodiesel which has more than 4800 species and about 20000 elementary reactions. Seshadri *et al.* (2009) used DRG to develop a reduced mechanism for methyl decanoate, obtaining a skeletal mechanism of 125 species among 713 reactions. Similarly, Luo *et al.* (2010) derived a skeletal mechanism with 118 species and 837 reactions based on the same mechanism, using an improved version of the DRG method. Since biodiesel composition is too complex to be modeled directly, the studies are concentrated in surrogates, such as Methyl Butanoate (MB), which is a smaller molecule that can reproduce some characteristics of the combustion of biodiesel.

The goal of this work is to simulate the combustion of MB based on a reduced kinetic mechanism. The reduction strategies applied is the Directed Relation Graph (DRG) with graph search algorithms, and some sort of sensitivity analysis is applied to the skeletal mechanism developed by DRG to further eliminate species and reactions. The advantage of using these methods is the elimination of redundant species and reactions, decreasing the computational cost needed to solve the chemical equations, a reduction of about two orders of magnitude for MB.

2 OBTAINMENT OF REDUCED KINETIC MECHANISMS

Chemical kinetic modeling has become an important tool for interpreting and understanding the observed combustion phenomena (Andreis *et al.*, 2013). Computational simulations involving detailed kinetic mechanisms are complicated because of the existence of highly reactive radicals, which induces significant stiffness to the governing equations due to big differences in the time scales of the species (Lu and Law, 2006). Consequently, there exists the need to develop, from these detailed mechanisms, the corresponding reduced mechanisms of fewer variables and moderated stiffness, while maintaining the accuracy and comprehensiveness of the detailed mechanism.

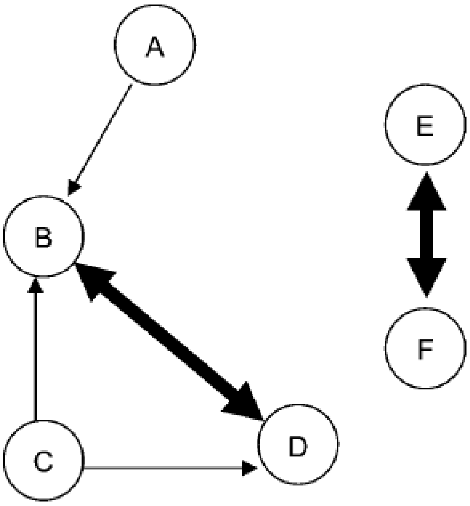

Figure 1: A DRG scheme showing coupling of species (Lu and Law, 2005).

The aim of the DRG (Fig. 1) method is to estimate an index, which indicates that the removal of a species B from the mechanism induces an error on the production of species A. This index, denoted by r_{AB}, can be expressed by

$$r_{AB} = \frac{\sum_{i=1}^{n} |\nu_{A,i}\omega_i\delta_{B,i}|}{\sum_{i=1}^{n} |\nu_{A,i}\omega_i|}, \tag{1}$$

where n is the number of reactions, $\nu_{A,i}$ is the stoichiometric coefficient of species A in the reaction i, ω_i is the rate of reaction i and $\delta_{B,i}$ is given by

$$\delta_{B,i} = \begin{cases} 1, & \text{if the } i^{th} \text{ reaction involves species B;} \\ 0, & \text{otherwise.} \end{cases} \tag{2}$$

The terms in the denominator of Eq. (1) are the contributions of the reactions to the production rate of species A, and the terms of the numerator are those in the denominator that involves the species B.

Defining a threshold value ϵ, and if the coefficient r_{AB} is bigger compared with it $(r_{AB} > \epsilon)$, then the removal of the species B can induce an error in the production of species A, so the species B must be retained in the skeletal mechanism. Usually, the A-species are chosen to be one of the targets, i.e., species that have some desirable chemical features that the reduced mechanism is expected to reproduce (Pepiot-Desjardins and Pitsch, 2008). A different formulation (Løvås, 2012) for the index r_{AB} can be performed using the maximum value instead of summation in Eq. (1).

Species can be coupled direct or indirectly, depending on their index r_{AB}. Suppose A is coupled with B and B is coupled with C, then A is coupled indirectly with C, so it must be retained in the mechanism. The set of species required, either directly or indirectly, by species A are called the dependent set of A. With that argument, if a species A must be retained in the mechanism, so does it dependent set (Lu and Law, 2005).

Figure 1 shows a typical DRG scheme. Note that the dependent set of A is formed by species B and D, since B must be retained to form A and D must be retained to form B. Species C can, thus, be eliminated, as well as species E and F, that are strongly coupled, but are not required by A or its dependent set.

To improve the performance of the DRG method, graph search algorithms, such as the Depth First Search (DFS) can be used for finding all vertices reachable from the starting vertex. Also, some sort of sensitivity analysis is usually required (Vajda *et al.*, 1985), which defines a collection of mathematical methods that can be used to explore the relationships between the values of the input parameters of a mathematical model and its solutions (Turányi and Tomlin, 2014). In chemical systems, sensitivity analysis describes the variation of the concentration of a species at time t_2, when there is a perturbation in the value of parameters at time t_1 $(t_1 < t_2)$. Further theoretical explanations about DFS and sensitivity analysis can be found in Lu and Law (2006) and De Bortoli *et al.* (2015).

The kinetic system of ordinary differential equations defines the relationship between the production rates of a species and rates of the reaction steps (Turányi and Tomlin, 2014). For an isothermal and spatially homogeneous dynamical system, the change of concentrations in time can be obtained by solving the following initial value problem:

$$\frac{d\mathbf{c}}{dt} = \mathbf{f}(\mathbf{c}, \mathbf{k}), \quad \text{with} \quad \mathbf{c}(0) = \mathbf{c}_0, \tag{3}$$

where $\mathbf{c}(t)$ is the vector of concentrations, t is the time, $\mathbf{k}$ is the vector of kinetic parameters that may include rate coefficients, Arrhenius parameters, thermodynamic data, temperature, pressure, etc. The most common variable used as parameter $\mathbf{k}$ is the reaction rate coefficient (Lebedev *et al.*, 2013; Turányi, 1990; Turányi and Tomlin, 2014). The right-hand side of equation (3) can be obtained using

$$f_i(\mathbf{c}, \mathbf{k}) \;=\; \sum_{j=1}^{N_R} \nu_{ij} R_j, \tag{4}$$

where R_j is the rate of reaction, and ν_{ij} is the stoichiometric coefficient of the species i in the reaction j.

After obtaining the derivative with respect to the parameter k_j on both sides of the kinetic system (3), and using the chain rule, results the following system of ordinary differential equa-

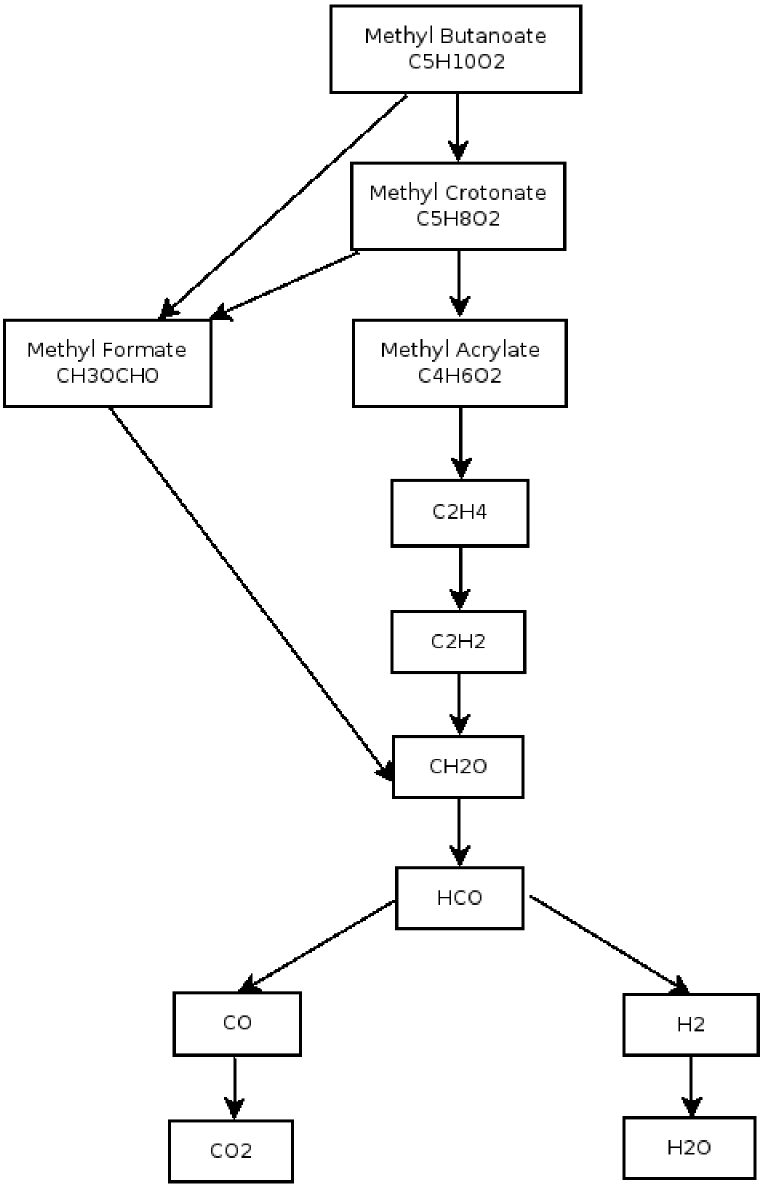

Figure 2: Main path for the oxidation of MB.

tions:

$$\frac{d}{dt}\frac{\partial \mathbf{c}}{\partial k_j} = \frac{\partial \mathbf{f}}{\partial \mathbf{c}}\frac{\partial \mathbf{c}}{\partial k_j} + \frac{\partial \mathbf{f}}{\partial k_j}, \qquad j = 1, 2, \ldots, N_R. \tag{5}$$

with initial condition $\frac{\partial \mathbf{c}}{\partial k_j}(t_0) = 0$. The matrix form of this system is given by

$$\frac{dS}{dt} = JS + F, \tag{6}$$

where $F = \partial \mathbf{f}/\partial k_j$ is the *rate sensitivity matrix*, $S = \partial \mathbf{c}/\partial k_j$ is the *sensitivity matrix* of the system, in which each element $\partial c_i/\partial k_j$ represents the variation of the concentration c_i of species i at time t_2 when there is a perturbation in the parameter k_j at time t_1 (where $t_2 > t_1$), and $J = \partial \mathbf{f}/\partial \mathbf{c}$ is the Jacobian matrix.

A species may be considered redundant if its concentration change has no significant effect on the rate of production of important species. An element of the Jacobian is a measure of such effect. The overall influence of the change of the concentration of species i on the rate of production of a group Ω of important species is given by

$$B_i \;=\; \sum_{n\in\Omega}\left(\frac{\partial \ln f_n}{\partial \ln c_i}\right)^2. \tag{7}$$

The higher the B_i value of an unimportant species, the higher is its direct influence on the group Ω of important species (Whitehouse *et al.*, 2004). Besides, there are necessary species that are linked to the important species through other necessary species. Hence, the group of important species has to be identified by an interaction procedure. The best ranked species based on the B_i values are also considered in the summation, then the B_i values are recalculated and the procedure is repeated again. Redundant species are those which are not included in the summation after the iteration process. The elimination of redundant species from a mechanism has two benefits (Kovács *et al.*, 2007): (i) a smaller mechanism is better interpretable from the chemical point of view; (ii) the simulation with a smaller mechanism requires less computer time.

Table 1: Reactions that involve the major species for MB; units are mol, cm^3, s, K and cal/mol.

	Reaction	A	n	E_a
$R1$	$C_5H_{10}O_2 = CO_2 + nC_3H_7 + CH_3$	$0.500E+17$	0	86800
$R2$	$C_5H_{10}O_2 = CH_2CO + CH_3O + C_2H_5$	$0.500E+17$	0	85200
$R3$	$C_5H_{10}O_2 + H = CH_3OCHO + nC_3H_7$	$0.100E+11$	0	4000
$R4$	$C_5H_{10}O_2 = CH_3OCO + nC_3H_7$	$0.500E+17$	0	89900
$R5$	$C_5H_{10}O_2 + H = C_5H_9O_2 + H_2$	$0.100E+13$	0	7925
$R6$	$C_5H_9O_2 = C_5H_8O_2 + H$	$0.100E+15$	0	42000
$R7$	$C_5H_9O_2 + O_2 = C_5H_8O_2 + HO_2$	$0.250E+10$	0	6000
$R8$	$C_5H_8O_2 + H = C_4H_6O_2 + CH_3$	$0.120E+11$	0	2000
$R9$	$C_5H_8O_2 = CH_3OCHO + pC_3H_4$	$0.100E+15$	0	68000
$R10$	$C_5H_8O_2 + H = C_2H_4 + CH_2CO + CH_3O$	$0.100E+11$	0	2000
$R11$	$C_4H_6O_2 + OH = C_2H_4 + CO_2 + CH_3O$	$0.100E+10$	0	0
$R12$	$C_4H_6O_2 + H = C_2H_4 + CH_3OCO$	$0.200E+11$	0	3000
$R20$	$CH_3OCHO + CH_3O = CH_3OH + CH_2OCHO$	$0.160E+12$	0	7000
$R27$	$CH_2OCHO = CH_3OCO$	$0.260E+12$	0	38200
$R29$	$CH_3OCO + CH_3O_2 = CH_3O + CH_3O_2 + m$	$0.700E+13$	0	-1000
$R33$	$CH_3O + O_2 = CH_2O + HO_2$	$0.550E+11$	0	2420

Fisher et al. (2000) were the first to present a detailed mechanism for MB with 264 species and 1219 reactions. This mechanism was employed to perform the reduction in this work.

After applying the above techniques, a reduced mechanism was determined for MB. The final mechanisms consist in 70 reactions among 30 species. The reactions that involves larger molecules are presented in the Tab. 1, while the main chain for the combustion of MB is presented in the Fig. 2.

3 FLOW EQUATIONS FOR DIFFUSION FLAMES

The major advantage of working with reduced mechanisms is the decrease of computational work for solving the chemical equations, of about two orders of magnitude for MB. When solving diffusion flames is required the solution of equations for pressure, density, species, momentum and energy or temperature (Kuo and Acharya, 2012). These equations are:

$$\frac{\partial(\rho v_j)}{\partial t} + \frac{\partial(\rho v_i v_j)}{\partial x_j} = \frac{\partial p}{\partial x_i} + \frac{\partial \sigma_{ij}}{\partial x_j}, \tag{8}$$

$$\frac{\partial(\rho Z)}{\partial t} + \frac{\partial(\rho v_j Z)}{\partial x_j} = \frac{\partial}{\partial x_j}\left(\rho D \frac{\partial Z}{\partial x_j}\right). \tag{9}$$

Here, t is time, v the velocity, p the pressure, Z the mixture fraction (to obtain the temperature) and D the molecular diffusivity.

The temperature is obtained using the analytical solution of Burke-Schumann, in which:

$$T(Z) = \begin{cases} T_u(Z) + \frac{QY_{F,1}}{c_p v'_F W'_F}, & \text{if } Z \leq Z_{st}; \\ T_u(Z) + \left(\frac{QY_{O_2,2}}{c_p v'_{O_2} W_{O_2}}\right)(1-Z), & \text{if } Z \geq Z_{st} \end{cases} \tag{10}$$

The mass fraction of species is obtained by solving:

$$\frac{\partial(\rho Y_k)}{\partial t} + \frac{\partial(\rho v_j Y_k)}{\partial x_j} = \frac{\partial}{\partial x_j}\left(\rho D_t \frac{\partial Y_k}{\partial x_j}\right) + \dot{W}_k. \tag{11}$$

where, Y_k is the mass fraction of species k and $\dot{W}_k$ is the term that accounts for the consumption or generation of species k, which results from the reaction rate that involves the species k.

The density ρ is obtained using the equation of state for an ideal gas, $\rho = \frac{p}{RT}$, and the pressure gradient comes from the equation (Pitsch and Steiner, 2000):

$$\nabla^2 P = \Delta t \left(\frac{\partial v_i}{\partial x_i} + \frac{\partial \rho}{\partial t}\right). \tag{12}$$

4 VALIDATION AND DISCUSSION

Historically, validations of detailed kinetic models have been done via simulations in homogeneous environments such as shock tubes or rapid compression machines, but simulations of the laminar flame structure have not been very useful as validation tests (Westbrook *et al.*, 2009). In this sense the validation of reduced mechanisms for a laminar flame becomes relevant.

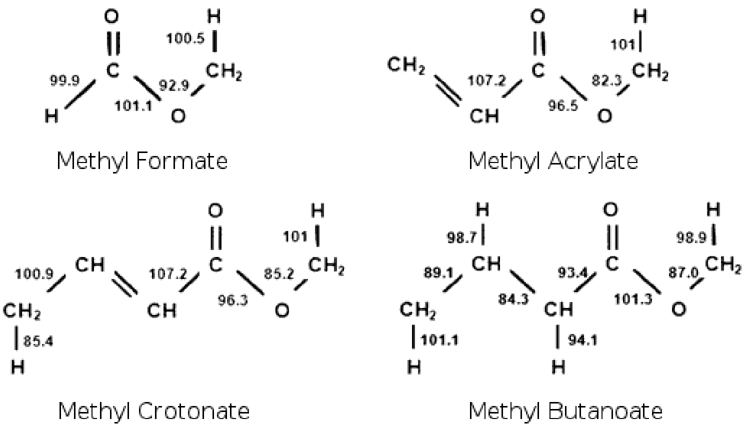

Figure 3: Structures and bond dissociation energies (kcal/mol) of MB, MF, MA and MC (Grana *et al.*, 2012)

The nature of a detailed chemical kinetic mechanism is intrinsically hierarchical (Dooley *et al.*, 2008). Using this affirmation and beginning with species with only a few atoms, for which the reaction mechanism is often relatively simple, can be constructed mechanisms for larger fuel molecules. Grana *et al.* (2012) used a hierarchical approach to obtain a semi-detailed mechanism for MB, based on small esters such as methyl formate (CH_3OCHO), methyl acrylate ($C_4H_6O_2$) and methyl crotonate ($C_5H_8O_2$).

Methyl formate (MF) is mainly converted to methanol and carbon monoxide, being formaldehyde and methane the major intermediate species, while small amounts of ethylene and acetylene are also formed (Grana *et al.*, 2012). Methyl acrylate (MA) and methyl crotonate (MC) are significant intermediates during the decomposition and oxidation of large methyl esters. Figure 3 shows the molecular structure for theses molecules.

In the present work, the hierarchical approach is applied to develop kinetic mechanisms to methyl butanoate. First a reduced mechanism was developed for MF, which latter was extended for MB. Table 1 shows the reaction paths decomposition that includes MF (reactions 3, 20 and 27), MA (reactions 8, 11 and 12) and MC (reactions 8, 9 and 10). Also, intermediate important species, such as nC_3H_7 (reactions 1, 3 and 4), methanol (CH_3OH, reaction 20), formaldehyde (CH_2O, reaction 33) and ethylene (C_2H_4, reactions 10, 11, 12), are presented.

The numerical approach used to validate the reduced mechanism was compared with the experimental data from Niemann *et al.* (2010). A prevaporized fuel configuration was used, where the temperature in the oxidizer stream, T_2, is equal to $298K$, and in the fuel stream is $T_1 = 453K$. The initial values for fuel and oxidizer are, respectively, $Y_{MB,1} = 0.5$ and $Y_{O_2,2} = 0.233$. The problem was solved using a computer code developed in FORTRAN90. The conservation equations were discretized using the second-order centered finite difference method. The mesh used has $161 \times 41 \times 41$ points, and is refined near the injector and along the burner axis. The time step is equal to $\Delta t = 0.0001$s.

Figure 4 shows the comparison of calculated values of mass fractions for H_2O, CO_2 and CO with the experimental data. The mass fractions of the main products of combustion along the burner center line increase as the jet develops, achieving its maximum value in the stoichiometric condition. The results are on good agreement with the experiment.

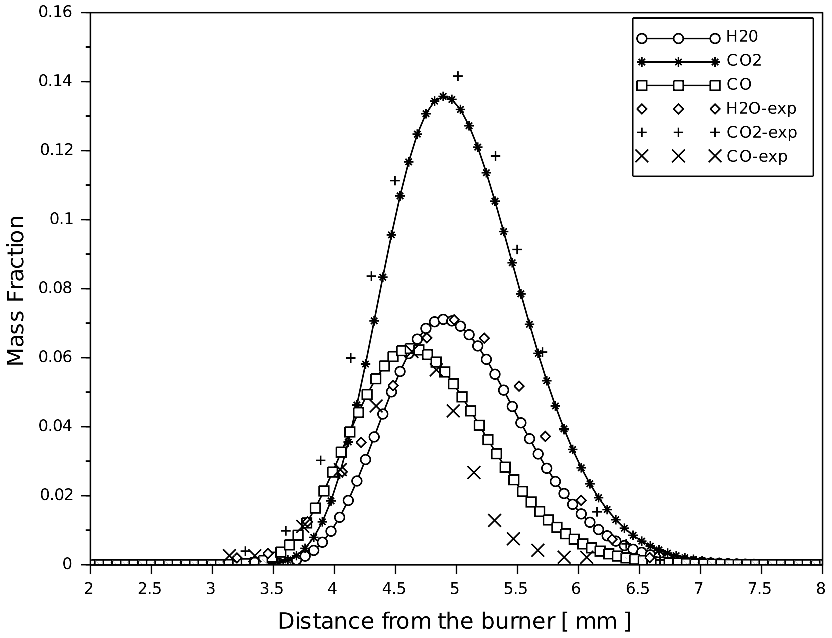

Figure 4: Profiles for H_2O, CO_2 and CO along the mixture fraction space compared with the experimental data.

Figure 5 gives the obtained temperature field, which shows the geometry of the flame, located where the temperature has maximum value. The temperature map shows the potential core near the jet entrance.

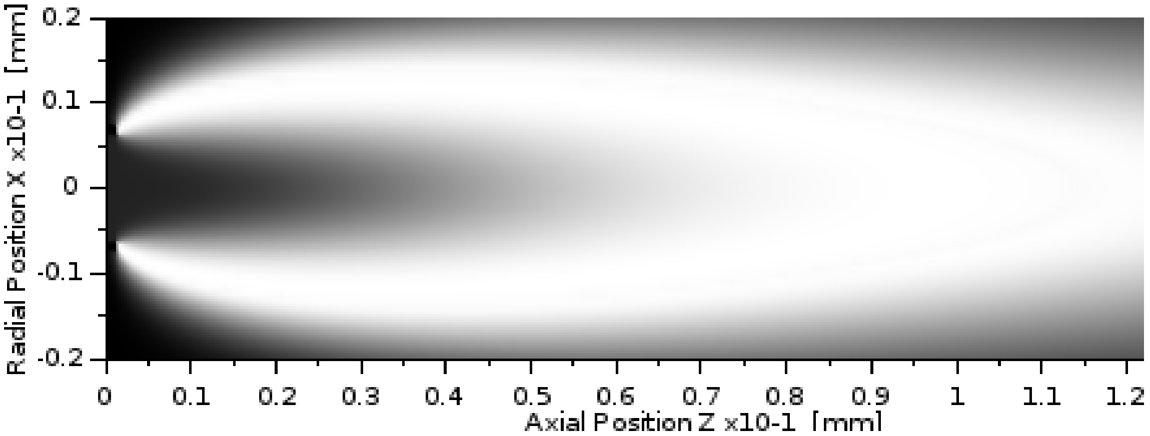

Figure 5: Temperature map for a diffusion flame of MB.

5 CONCLUSIONS

The present work provided a new reduced kinetic mechanism for MB combustion. Starting with a 1219 reactions detailed mechanism, and using the techniques DRG, DFS and sensitivity analysis, a reduced mechanism of 70 reactions among 30 species was developed. The main advantage of the reduced mechanism is the decrease of the computational work needed to solve the differential equations of the chemical system, a decrease of one order of magnitude for MB.

The proposed model allows the analyse of the composition of produced gases, which can help understanding and control the formation of pollutants. Results show that the proposed reduced mechanism, together with the set of flow equations solved, can be used as a good approximation for the simulation of jet diffusion flames of biodiesel, which validates the assumption that MB can be used as a acceptable biodiesel surrogate for jet diffusion flame problems.

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REFERENCES

An, H., Yang, W., Maghbouli, A., Li, J., & Chua, K., 2014. A skeletal mechanism for biodiesel blend surrogates combustion. *Energy Conversion and Management*, vol. 81, pp. 51–59.

Andreis, G. S. L., Vaz, F. A., & De Bortoli, A. L., 2013. Bioethanol combustion based on a reduced kinetic mechanism. *Journal of Mathematical Chemistry*, vol. 51, n. 6, pp. 1584–1598.

De Bortoli, A. L., Andreis, G. S. L., & Pereira, F. N., 2015. *Modeling and Simulation of Reactive Flows*, Elsevier Science Publishing Co Inc.

Demirbas, A., 2009. *Biofuels: Securing the Planet's Future Energy Needs*, Springer London.

Dooley, S., Curran, H. J., Simmie, & J. M., 2008. Autoignition measurements and a validated kinetic model for the biodiesel surrogate, methyl butanoate. *Combustion and Flame*, vol. 153, n. 1-2, pp. 2–32.

Fisher, E. M., Pitz, W. J., Curran, H. J, & Westbrook, C. K., 2000. Detailed chemical kinetic mechanisms for combustion of oxygenated fuels. *Proceedings of the Combustions Institute*, vol. 28, pp. 1579-1586.

Grana, R., Frassoldati, A., Cuoci, A., Faravelli, T., Ranzi, E., 2012. A wide range kinetic modeling study of pyrolysis and oxidation of methyl butanoate and methyl decanoate. Note I: Lumped kinetic model of methyl butanoate and small methyl esters. *Energy*, vol. 43, pp. 124–139.

Herbinet, O., Pitz, W. J., & Westbrook, C. K., 2008. Detailed chemical kinetic oxidation mechanism for a biodiesel surrogate. *Combustion and Flame*, vol. 154, n. 3, pp. 507–528.

Kovács, T., Zsély, I. G., Kramarics, A., & Turányi, T., 2007. Kinetic analysis of mechanisms of complex pyrolytic reactions. *Journal of Analytical and Applied Pyrolysis*, vol. 79, n. 1, pp. 252–258.

Kuo, K. K., & Acharya, R., 2012. *Fundamentals of Turbulent and Multi-Phase Combustion*. John Wiley and Sons.

Lebedev, A., Okun, M., Chorkov, V., Tokar, P., & Strelkova, M., 2013. Systematic procedure for reduction of kinetic mechanisms of complex chemical processes and its software implementation. *Journal of Mathematical Chemistry*, vol. 51, n. 1, pp. 73–107.

Løvås, T., 2012. *Model Reduction Techniques for Chemical Mechanisms*, INTECH Open Access Publisher.

Lu, T., & Law, C. K., 2005. A directed relation graph method for mechanism reduction. *Proceedings of the Combustion Institute*, vol. 30, pp. 1333–1341.

Lu, T., & Law, C. K., 2006. Linear time reduction of large kinetic mechanisms with directed relation graph: n-heptane and iso-octane. *Combustion and Flame*, vol. 144, n. 1, pp 24–36.

Luo, Z., Lu, T., Maciaszek, M., Som, S., & Longman, D., 2010. A reduced mechanism for high-temperature oxidation of biodiesel surrogates. *Energy Fuels*, vol. 24, n. 12, pp. 6283–6293.

Niemann, U., Seiser, R., & Seshadri, K., 2010. Ignition and extinction of low molecular weight esters in nonpremixed flows. *Combustion Theory and Modelling*, vol. 14, n. 6, pp. 875–891.

Pepiot-Desjardins, P., Pitsch, H., 2008. An efficient error-propagation-based reduction method for large chemical kinetic mechanisms. *Combustion and Flame*, vol. 154, n. 1, pp. 67–81.

Pitsch, H., & Steiner, H., 2000. Large eddy simulation of a turbulent piloted methane/air diffusion flame (Sandia flame D). *Physics of Fluids*, vol. 12, n. 10, pp. 2541–2554.

Seshadri, K., Lu, T., Herbinet, O., Humer, S., Niemann, U., Pitz, W., Seiser, R., & Law, C., 2009. Experimental and kinetic modeling study of extinction and ignition of methyl decanoate in laminar non-premixed flows. *Proceedings of the Combustion Institute*, vol. 32, n. 1, pp. 1067–1074.

Turányi, T., 1990. Sensitivity analysis of complex kinetic systems: Tools and applications. *Journal of Mathematical Chemistry*, vol. 5, n. 3, pp. 203–248.

Turányi, T., & Tomlin, A. S., 2014. *Analysis of Kinetic Reaction Mechanisms*, Springer.

Vajda, S., Valko, P., & Turányi, T., 1985. Principal component analysis of kinetic models. *International Journal of Chemical Kinetics*, vol. 17, n. 1, pp. 55–81.

Westbrook, C. K., Naik, C. V., Herbinet, O., Pitz, W. J., Mehl, M., Sarathy, S. M., & Curran, H. J., 2011. Detailed chemical kinetic reaction mechanisms for soy and rapeseed biodiesel fuels. *Combustion and Flame*, vol. 158, pp. 742–755.

Westbrook, C. K., Pitz, W. J., Westmoreland, P. R., Dryer, F.L., Chaos, M., Osswald, P., Kohse-Hinghaus, K., Cool, T. A., Wang, J., Yang, B., Hansen, N., & Kasper, T., 2009. A detailed chemical kinetic reaction mechanism for oxidation of four small alkyl esters in laminar premixed flames. *Proceedings of the Combustion Institute*, vol. 32, n. 1, pp. 221–228.

Whitehouse, L., Tomlin, A., & Pilling, M., 2004. Systematic reduction of complex tropospheric chemical mechanisms. Part I: Sensitivity and time-scale analysis. *Atmospheric Chemistry and Physics*, vol. 4, n. 7, pp. 2025–2056.