ANALYSIS OF DIFFUSION FLAMES OF METHYL BUTANOATE

J.M. PINHO, jean.pinho@ifsc.edu.br [1]
F.R.R. PADILHA, roneipadilha@yahoo.com.br[2]
F.C. MINUZZI, feminuzzi@hotmail.com[2]
A.L. DE BORTOLI, dbortoli@mat.ufrgs.br[1,2]

[1]Federal University of Rio Grande do Sul, Graduate Program in Chemical Engineering, Street Engenheiro Luiz Englert S / no - Building 12204 , Porto Alegre, 90040-040, Brazil
[2]Federal University of Rio Grande do Sul, Graduate Program in Applied Mathematics, Street Bento Gonçalves 9500 – Building 43111, Porto Alegre, 91509900, Brazil

Abstract: *The replacement of fossil fuels by biofuels intensifies day by day. The Biodiesel is a complex mixture of Fatty Acid Methyl Esters (FAMES) and is the main candidate to replace petroleum diesel. Methyl Butanoate (MB) is a small chain methyl ester selected as a biodiesel surrogate. This work makes an analysis of the temperature and geometry of laminar diffusion flames of MB for a configuration frequently used in the industry. The chemistry is evaluated based on a reduced kinetic mechanism obtained using the techniques DRG, DFS and Sensitivity Analysis. The main chain of the reduced kinetic mechanism is presented. For the flow are solved the equations of motion, mixture fraction, to obtain the temperature, and mass fraction of species. Obtained results show good agreement with experimental data available in the literature for jet diffusion flames of biodiesel surrogates.*

Keywords: *Diffusion Flame, Reduced Kinetic Mechanism, Methyl Butanoate, Biodiesel Surrogates, Numerical Simulation*

1. INTRODUCTION

The growing global demand for energy, coupled with the environmental, economic and political issues have encouraged the search for energy sources that may replace fossil fuels. Taking also into account the environmental disequilibrium that is occurring, it is clear that conducting research into environmentally clean energy is a necessity to the preservation of the planet and the species that live in it. In this scenario the study of oxygenated fuels, such as biodiesel to reduce emissions of CO, NOx, particulate matter and hydrocarbons in engine emissions, gain importance.

Biodiesel is a complex mixture of fatty acid methyl esters (FAME) with various chain lengths and degrees of unsaturation, derived from vegetable oil or animal fat (Sarathy *et al.*, 2011). It is an alternative fuel to petrodiesel. The biodiesel term refers to the equivalent liquid fuel to diesel processed from biomass. Vegetable oils can be transformed into methyl esters by transesterification process in the presence of a catalyst (Demirbas, 2003).

The diesel from biomass is typically comprised of significant amounts of unsaturated methyl esters Methyl Oleate ($C_{19}H_{36}O_2$), methyl linoleate ($C_{17}H_{32}O_2$) and Methyl linolenate ($C_{17}H_{34}O_2$) and minor amounts of saturated compounds Methyl Palmitate ($C_{17}H_{34}O_2$) and Methyl Stearate ($C_{19}H_{38}O_2$) (Herbinet *et al.*, 2008; Grana *et al.*, 2012). Table 1 shows the average composition of biodiesel derived from soybean oil and rapeseed oil.

Table 1: **Average compositions of biodiesel derived from soybean and rapeseed oil (Adapted from Golovitchev and Yang (2009))**

Chemical Species	from soybean oil	from rapeseed oil
Methyl Palmitate $C_{17}H_{34}O_2$	6 – 10 %	4.3 %
Methyl Linoleate $C_{17}H_{34}O_2$	50 – 60 %	1.3 %
Methyl Linolenate $C_{17}H_{32}O_2$	5 – 11 %	59.9 %
Methyl Stearate $C_{19}H_{38}O_2$	2 – 5 %	2.1 %
Methyl Oleate $C_{19}H_{36}O_2$	20 – 30 %	13,2 %

Molecules that constitute the biodiesel are large, so the kinetic mechanisms for describing its oxidation are large and complex. Westbrook *et al.* (2011) developed a detailed kinetic mechanism for the oxidation of components of Tab. 1, which has more than 4,800 chemical species and approximately 20,000 elementary reactions.

Models of detailed chemistry are used to predict the characteristics of an engine as autoignition, delay time of ignition and emissions. However, direct implementation of detailed kinetic chemistry is far from being used in practice (Egüz *et al.*, 2013). According to Bykov *et al.* (2013), for the simulation of combustion problems in complex geometries are needed models with compact chemical kinetics. On the other hand, such model must accurately describe the thermodynamic and hydrodynamic effects of chemicals reactions and all thermochemical states in the field.

Biodiesel composition is very complex, so the efforts have been directed to the development of mechanisms for biodiesel surrogates, which are simpler molecules that can produce the primary characteristics of combustion of biodiesel.

The research was initially focused at smaller molecules, such as Methyl Formate (MF -$C_2H_4O_2$) and Methyl Butanoate (MB - $C_5H_{10}O_2$)(Sarathy *et al.*, 2011).

Experiments suggest that differences in the physical and chemical properties of fuels lead to different spray characteristics such as droplet size, penetration of spray and flame temperature, for example. Simulating the influence of different characteristics of different fuels in combustion is a challenge that requires the evaluation of the sensitivity of CFD tools for the simulation of physical and chemical properties of fuels Yasin *et al.* (2014).

The majority of fundamental studies have focused on a few stand-alone biodiesel surrogates with $5 \leq C_n \leq 11$, where n is the carbon number. Studies of small alkyl esters, with $C_n \leq 5$, are also relatively scarce, although they are of great relevance as they can aid in the systematic development and validation of the kinetic models of their larger counterparts.

Methyl Butanoate was chosen as biodiesel surrogate because it is the lower alkyl ester to represent FAMES comprising biodiesel. The choice is due to the fact that MB contains much of the essential chemical structure of its long-chain counterparts,i.e., the methyl ester termination and a shorter, but similar alkyl chain, and because detailed reaction mechanisms which describe MB are of manageable size. Another fact that confirms the choice of MB are the results of Diévart *et al.* (2013); it was observed that MB and larger methyl esters have similar overall reactivity.

This work has two main objectives. The first is the development of a reduced kinetic mechanism for the MB, and the second objective is the development of a model for the simulation of coflow diffusion flames.

2. OBTAINMENT OF THE REDUCED MECHANISM FOR METHYL BUTANOATE

Simulations of reactive flows demand high computational cost, even for simple models. When the kinetic equations are solved in addition to conservation equations for complex flow models, the computational time may become excessive Vaz and De Bortoli (2014).

Fisher *et al.* (2000) were the first to present a detailed model for the combustion of MB with 264 species and 1219 elementary reactions. This mechanism was taken as the basis for obtaining the proposed reduced mechanism.

Metcalfe *et al.* (2007) conducted experimental studies in a shock tube reactor for oxidation of Ethyl Propanoate (EP) and Methyl Butanoate (MB). Based on experimental results they proposed a detailed kinetic mechanism to describe the oxidation of EP and MB. One important observation is that neither the model nor the experiments exhibited a pronounced negative temperature coefficient (NTC).

Dooley *et al.* (2008) developed a reaction mechanism for MB using shock tube and rapid compression machine experimental data for mechanism validation. In this study, they extended the range of the previously published detailed chemical kinetic mechanism of Metcalfe *et al.* (2007) in order to enhance knowledge of the oxidation and soot reduction processes of biodiesel fuels. Their results show that methyl butanoate does not exhibit NTC behavior, as has been reported for long-chain methyl esters typical of biodiesel constituents. Therefore, MB is not an ideal surrogate molecule for a detailed study of biodiesel combustion. However, it can serve as a starting point for the detailed study of larger methyl esters.

Hakka *et al.* (2010) made an experimental investigation for the oxidation of MB and EB. Using these experimental data and the software EXGAS they developed a detailed model for the oxidation of the MB with 203 species and 1317 elementary reactions.

Systematic reduction of kinetic mechanisms has been studied by several authors in the last three decades. Lu and Law (2009) and De Bortoli *et al.* (2015) perform an interesting review of various techniques of mechanisms reduction that can be used. Frequently, Directed Relation Graph (DRG), Depth First Search (DFS) and Sensitivity Analysis are applied.

Brakora *et al.* (2009) developed and validated a reduced kinetic model for multidimendional simulation of internal combustion engines. The authors used as initial model the mechanism proposed by Fisher et al. (2000). The reduction was carried out using the DFS technique, ignition sensitivity analysis and optimization of reaction rates at constant volume conditions. As a result, they obtained a kinetic model of 41 species and 150 reactions, able to describe with good agreement the behavior of the full mechanism.

Lin *et al.* (2016) reduced the detailed mechanism proposed by Dooley *et al.* (2008). The reduction was carried out using a combination of methods, including DFS, and analyzing molar concentration peaks. As a result they obtained a model with 38 species and 170 reactions.

To obtain a reduced mechanism for MB are used n this work the techniques Directed Relation Graph (DRG), Depth First Search (DFS) and Sensitivity Analysis. Directed relation graph (DRG), introduced by Lu and Law (2005), is an efficient method for obtaining skeletal mechanisms. The aim of the method is to resolve the coupling of species, estimating 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, noted as 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 reaction 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 in the numerator are those in the denominator that involve species B.

Defining a threshold value ϵ, and if the value of r_{AB} is bigger compared to it $(r_{AB} > \epsilon)$, then the removal of species B can induce an error in the production of species A, so that species B must be retained in the skeletal mechanism. Usually, the A-species is 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).

Figure 1 shows a typical DRG scheme. Note that the dependent set of species 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.

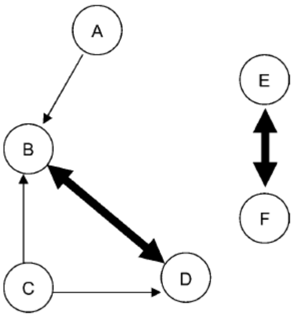

Figure 1: A DRG scheme.

When one estimates the coefficient r_{AB} between species A and B, the DRG considers all species from the detailed mechanism. Nevertheless, considering the A-species as targets, the results of DRG are improved. Figure 2 shows the relation between the number of species and the threshold value ϵ. In DRG, all species have the same importance level, possible leading to the presence of non-essential reactions, and species that have its coefficients r_{AB} smaller than the threshold. To circumvent this drawback, important intermediate species can be considered as targets, so the reduction becomes more efficient.

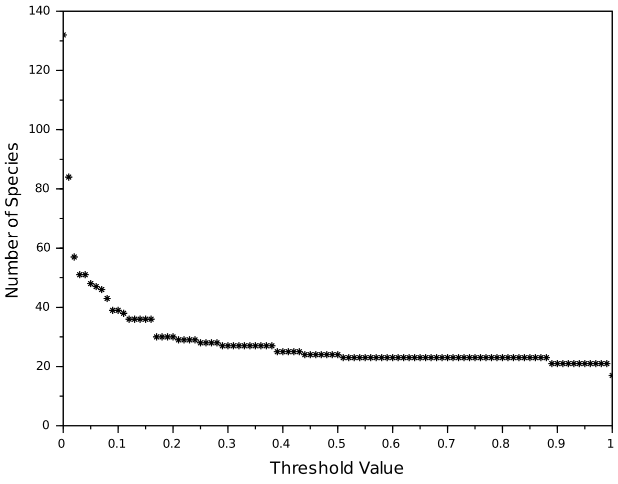

Figure 2: Relation between the number of species and the threshold value ϵ

To improve the performance the method, graph search algorithms, such as Depth First Search (DFS), can be used to find all the vertices reachable from the starting vertex. The DFS initiates at a root node (such as the target species) and explores the graph edges connecting other nodes. The first node found is added to a list, then the search moves to this node and the process is repeated. The search continues deeper down the graph pathway until all connecting nodes have been explored (Niemeyer and Sung, 2011). The search is performed separately using each target species as a root node. In many cases, it is sufficient to begin with only one species, such as the fuel.

The term sensitivity analysis 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). Sensitivity analysis can be used for mechanism reduction, help us to better understand the chemical processes and to identify those pathways that determine key model outputs or production distributions.

After applying the above techniques, a reduced mechanism for Methyl Butanoate was developed. The mechanism obtained consists of 43 species and 73 elementary reactions. The reactions involving the major species are presented in the Tab. 2 and the path for the consumption of principal species is presented in the Fig. 3.

Table 2: **Reactions involving the main species of MB**

	Reactions	A	n	E_A
$R1$	$C_5H_{10}O_2 = CO_2 + nC_3H_7 + CH_3$	$5.0E16$	0	86800
$R2$	$C_5H_{10}O_2 = CH_2CO + CH_3O + C_2H_5$	$5.0E16$	0	85200
$R3$	$C_5H_{10}O_2 = CH_3OCO + nC_3H_7$	$5.0E16$	0	89900
$R4$	$C_5H_{10}O_2 + H = CH_3OCHO + nC_3H_7$	$1.0E10$	0	4000
$R5$	$C_5H_{10}O_2 + H = C_5H_9O_2 + H_2$	$1.0E12$	0	7925
$R6$	$C_5H_9O_2 = C_5H_8O_2 + H$	$1.0E14$	0	42000
$R7$	$C_5H_9O_2 = C_2H_4 + CH_3O + CH_2CO$	$1.0E14$	0	33000
$R8$	$C_5H_8O_2 = C_3H_5 + CO_2 + CH_3$	$5.0E16$	0	82000
$R9$	$C_5H_8O_2 = C_3H_5 + CH_3OCO$	$3.50E15$	0	84439
$R10$	$C_5H_8O_2 + OH = CH_3CHO + CH_2CH_3O$	$1.0E10$	0	0
$R11$	$C_5H_8O_2 + H = C_4H_6O_2 + CH_3$	$1.2E10$	0	2000
$R12$	$C_5H_8O_2 = C_2H_4 + CH_2CO + CH_3O$	$1.E111$	0	2000
$R13$	$C_4H_6O_2 = C_2H_3 + CH_3 + CO_2$	$2.0E16$	0	85000
$R14$	$C_4H_6O_2 + OH = C_2H_4 + CO_2 + CH_3O$	$1.0E10$	0	0
$R15$	$C_4H_6O_2 + OH = CH_2O + CH_2CO + CH_3O$	$1.0E10$	0	0
$R16$	$C_4H_6O_2 + H = C_2H_3CHO + CH_3O$	$2.0E10$	0	3000
$R17$	$nC_3H_7 = H + C_3H_6$	$2.67E15$	-0.64	36820

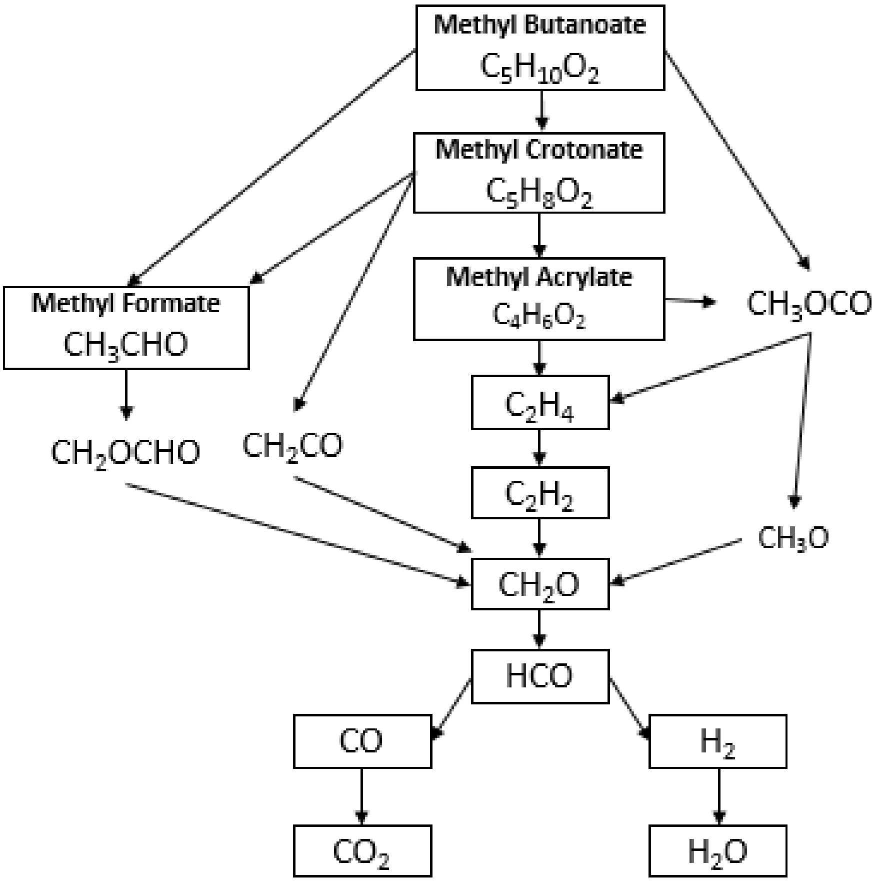

Figure 3: Principal path for MB combustion.

3. FLOW EQUATIONS FOR DIFFUSION FLAMES

When solving diffusion flames is required the solution of equations for pressure, density, species, momentum and energy or temperature (Kuo and Acharya, 2012). In this work was solved the equations:

$$\frac{\partial(\rho v_j)}{\partial t} + \frac{\partial(\rho v_i v_j)}{\partial x_j} = \frac{\partial p}{\partial x_i} + \frac{\partial \sigma_{ij}}{\partial x_j}, \tag{3}$$

$$\frac{\partial(\rho Z)}{\partial t} + \frac{\partial(\rho v_j Z)}{\partial x_j} = \frac{\partial}{\partial x_j}\left(\rho D \frac{\partial Z}{\partial x_j}\right). \tag{4}$$

Here, t is time, v the velocity, p the pressure, Z the mixture fraction (to obtain the temperature) and D the molecular diffusivity. For a jet diffusion flame, the mixture fraction is defined by

$$Z = \frac{\dot{m}_1}{\dot{m}_1 + \dot{m}_2}, \tag{5}$$

where $\dot{m}_1$ is the fuel stream and $\dot{m}_2$ is the oxidant stream. The equivalent ratio Φ is related to the mixture fraction Z by

$$\Phi = \left(\frac{Z}{1-Z}\right)\left(\frac{1-Z_{st}}{Z_{st}}\right), \tag{6}$$

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

$$T(Z) = \begin{cases} T_u(Z) + \frac{QY_{F,1}}{c_p v'_F W'_F}, & \text{if } Z \leq Z_{st}; \\ T_u(Z) + \left(\frac{QY_{O_2,2}}{c_p v'_{O_2} W_{O_2}}\right)(1-Z), & \text{if } Z \geq Z_{st} \end{cases} \tag{7}$$

The mass fraction of species is obtained by solving:

$$\frac{\partial(\rho Y_k)}{\partial t} + \frac{\partial(\rho v_j Y_k)}{\partial x_j} = \frac{\partial}{\partial x_j}\left(\rho D \frac{\partial Y_k}{\partial x_j}\right) + \dot{W}_k. \tag{8}$$

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 involve species k.

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

$$\nabla^2 P = \Delta t \left(\frac{\partial v_i}{\partial x_i} + \frac{\partial \rho}{\partial t}\right). \tag{9}$$

4. NUMERICAL PROCEDURE AND OBTAINED RESULTS

The validation of the model was done using both simulation and experiment published in the work of Kholghy *et al.* (2015). They present numerical and experimental results for a laminar coflow diffusion flame for a biodiesel surrogate composed by mixing 50% of n-decane and 50% of methyl-octanoate (molar), named B100, to represent methyl-oleate (MO - $C_{19}H_{36}O_2$).

The surrogate used in this work is the MB. To approximate the energy flux in our model with the energy flux of the experiment, and the numerical model of Kholghy *et al.* (2015), were considered 4 molecules of MB per molecule of MO, setting what was called here as MB-surrogate. The Tab. 3 shows the relation of C, H and O for MB-surrogate, B-100 surrogate (Kholghy *et al.*, 2015) and Methyl Oleate.

Table 3: **Comparison of atomic contents of MB-surrogate, B100-surrogate (Kholghy *et al.*, 2015) and Methyl Oleate**

Component	C	H	O
MB-surrogate	20	40	8
B100-surrogate	19	40	2
Methyl Oleate	19	36	2

The reactive flow configuration can be visualized in Fig. 4. The inlet conditions are similar to the conditions used by Kholghy *et al.* (2015). The fuel stream has velocity of 0.4365 m/s, 700 K for temperature and molar fraction of 0.952 for Nitrogen and 0.048 for fuel. In the air stream velocity has the value of 0.2092 m/s, 400 K for the temperature and molar fraction of 0.745 for nitrogen and 0.255 for oxygen. The inner and outer diameters of fuel injector are 10.9 and 12.7 mm, respectively, and the inner diameter of burner is 90.0 mm. The fuel was injected vaporized.

The problem was solved using a computer code developed in FORTRAN90. The conservation equations were discretized using the second-order centered finite difference scheme. The mesh used has $161 \times 41 \times 41$ points, and is refined

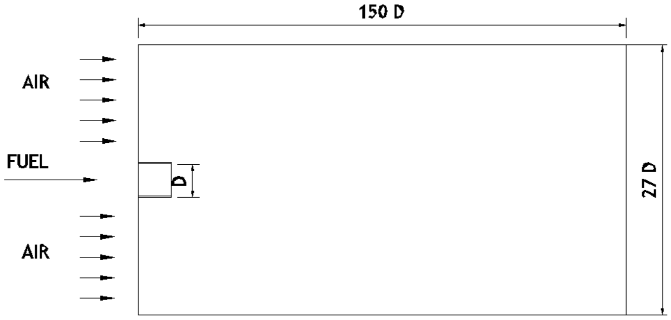

Figure 4: Geometry of the domain for jet diffusion flame.

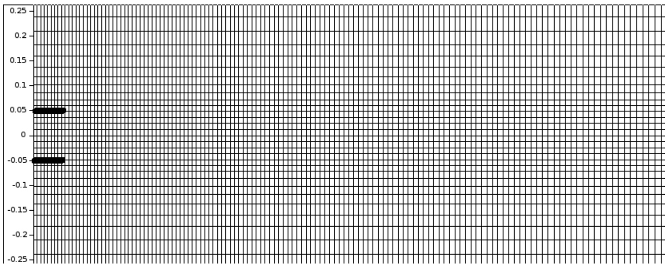

Figure 5: Mesh detail for jet diffusion flame.

near the injector and along the burner axis. A section of the mesh near the injector is presented in the Fig. 5; such mesh is refined by an exponential function. The time step is equal to $1.0E - 5$ seconds.

Obtained results show that the maximum temperature calculated is 1890 (see Fig. 7) versus 1900 and 1950 K by experiment and numerical model solved by Kholghy *et al.* (2015). The value obtained for the length of the flame is 88 mm versus 80 and 72 mm observed by experiment and numerical model of Kholghy *et al.* (2015), respectively. The

Temperature was obtained from the mixture fraction, whose stoichiometric value is .245. Figure 6 shows the axial behavior of mixture fraction.

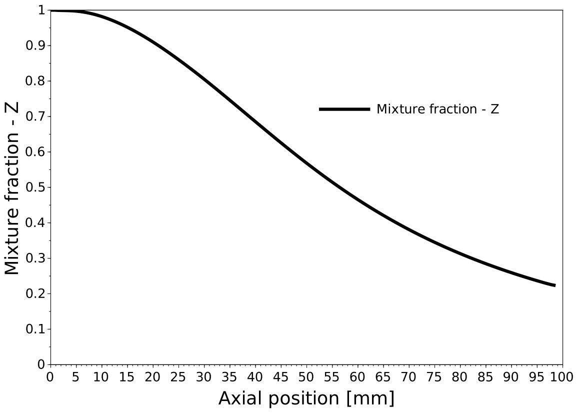

Figure 6: Axial behavior of the mixture fraction.

Figures 7 and 8 show the comparison of the calculated radial values of temperature with experimental and numerical values of Kholghy *et al.* (2015) at two burner positions; 50 and 80 mm from the burner inlet. For a section in the axial position of 50 mm, is observed good agreement among the results obtained and the experiment. Few deviations can be noted for positions far from the jet centerline. Moreover, for a section in the axial position 80 mm, near tip of the flame, the temperature distribution agrees with the experiment along of radius.

Finally, the Fig.9 shows 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, which is responsible for promoting the oxidation reactions distant from the nozzle. This behavior is in agreement with data found in the literature (Rajaratnam, 1976).

5. CONCLUSIONS

To enable a simulation for biodiesel flame, a reduced kinetic mechanism for the biodiesel MB surrogate was proposed. After applying the DRG, DFS and Sensivity Analysis, a mechanism of 264 species and 1219 elementary reactions, a

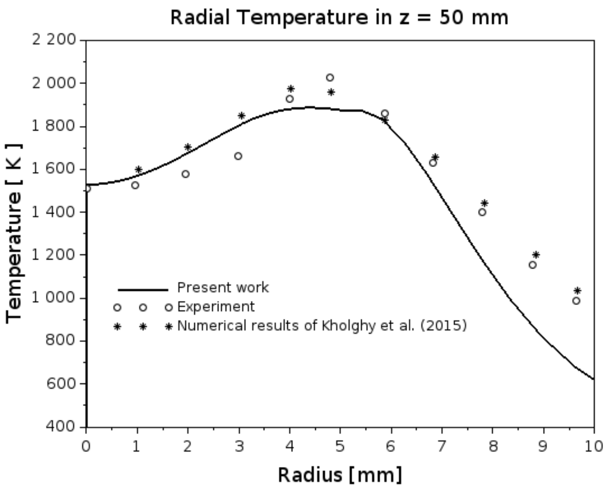

Figure 7: Comparison of radial temperature profile at $z = 50\ mm$.

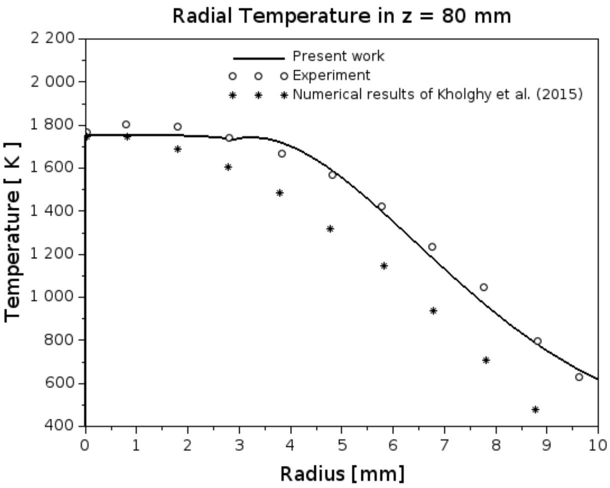

Figure 8: Comparison of radial temperature profile at $z = 80\ mm$.

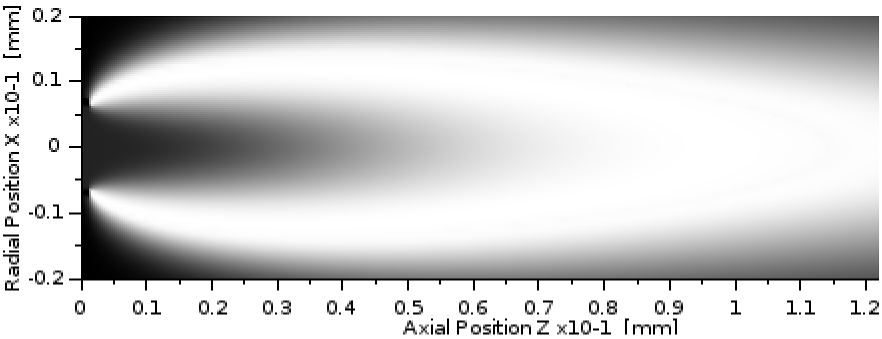

Figure 9: Temperature map for diffusion flame of MB.

reduced mechanism with 43 species and 73 elementary reactions was obtained. The mechanism developed is used to calculate the source terms for the Eq. 8 of chemical species.

The Figs. 7, 8 and 9 indicate two interesting facts. The first is that the reduced mechanism proposed, with the set of flow equations solved can be applied as an approximation for the simulation of diffusion flames of biodiesel; the second is that, in kinetic terms, the MB-surrogate proposed here can be used as a biodiesel surrogate for jet flame problems.

It is clear that this work is simple to be taken for making definitive conclusions. The results were obtained for a specific situation, according to the settings of the experiment carried out. The fact that Kholghy *et al.* (2015) has injected the fuel in the gas phase has contributed to eliminate the effects of viscosity and droplet size of Methyl Oleate jet. The viscosity and droplet size may probably have significant influence on the length and temperature distribution of the flame.

It is common sense that there are significant differences between the kinetics of oxidation of MO and MB. However the obtained results show that these kinetic differences can be absorbed by the time scales that dominate the reactive flow. In this particular case, a laminar jet diffusion flame, the characteristic time is the molecular diffusion time scale.

The proposed model can also be employed for the determination of the composition of the combustion products. In a future work will be performed analyses about the composition of the produced gases. Such analyse can help understanding and control the formation of pollutants.

Besides, it is worth pointing out that there are few experimental studies for biodiesel flames in the available literature. This difficulty becomes greater when the search is for works involving specific molecules that make up the biodiesel structure, as Methyl Butanoate, Methyl Decanoate and Methyl Oleate.

6. REFERENCES

Brakora, J.L., Ra, Y., Reitz, R.D., McFarlane, J. and Daw, C.S., 2009. "Development and validation of a reduced reaction mechanism for biodiesel-fueled engine simulations". *SAE International Journal of Fuels and Lubricants*, Vol. 1, No. 1, pp. 675–702.

Bykov, V., Neagos, A. and Maas, U., 2013. "On transient behavior of non-premixed counter-flow diffusion flames within the REDIM based model reduction concept". *Proceedings of the Combustion Institute*, Vol. 34, No. 1, pp. 197–203.

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

Demirbas, A., 2003. "Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey". *Energy Conversion and Management*, Vol. 44, No. 13, pp. 2093–2109.

Diévart, P., Won, S.H., Gong, J., Dooley, S. and Ju, Y., 2013. "A comparative study of the chemical kinetic characteristics of small methyl esters in diffusion flame extinction". *Proceedings of the Combustion Institute*, Vol. 34, No. 1, pp. 821–829.

Dooley, S., Curran, H.J. and Simmie, J.M., 2008. "Autoignition measurements and a validated kinetic model for the biodiesel surrogate, methyl butanoate". *Combustion and Flame*, Vol. 153, No. 1, pp. 2–32.

Egüz, U., Ayyapureddi, S., Bekdemir, C., Somers, B. and de Goey, P., 2013. "Manifold resolution study of the FGM method for an igniting diesel spray". *Fuel*, Vol. 113, pp. 228–238.

Fisher, E.M., Pitz, W.J., Curran, H.J. and Westbrook, C.K., 2000. "Detailed chemical kinetic mechanisms for combustion of oxygenated fuels". *Proceedings of the Combustion Institute*, Vol. 28, No. 2, pp. 1579–1586.

Golovitchev, V.I. and Yang, J., 2009. "Construction of combustion models for rapeseed methyl ester bio-diesel fuel for internal combustion engine applications". *Biotechnology Advances*, Vol. 27, No. 5, pp. 641–655.

Grana, R., Frassoldati, A., Cuoci, A., Faravelli, T. and 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, No. 1, pp. 124–139.

Hakka, M.H., Bennadji, H., Biet, J., Yahyaoui, M., Sirjean, B., Warth, V., Coniglio, L., Herbinet, O., Glaude, P.A., Billaud, F. *et al.*, 2010. "Oxidation of methyl and ethyl butanoates". *International Journal of Chemical Kinetics*, Vol. 42, No. 4, pp. 226–252.

Herbinet, O., Pitz, W.J. and Westbrook, C.K., 2008. "Detailed chemical kinetic oxidation mechanism for a biodiesel surrogate". *Combustion and Flame*, Vol. 154, No. 3, pp. 507–528.

Kholghy, M.R., Weingarten, J. and Thomson, M.J., 2015. "A study of the effects of the ester moiety on soot formation and species concentrations in a laminar coflow diffusion flame of a surrogate for B100 biodiesel". *Proceedings of the Combustion Institute*, Vol. 35, No. 1, pp. 905–912.

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

Lin, K.C., Tao, H., Kao, F.H. and Chiu, C.T., 2016. "A minimized skeletal mechanism for methyl butanoate oxidation and its application to the prediction of C3-C4 products in non-premixed flames: A base model of biodiesel fuels". *Energy & Fuels*.

Lu, T. and Law, C.K., 2005. "A directed relation graph method for mechanism reduction". *Proceedings of the Combustion Institute*, Vol. 30, No. 1, pp. 1333–1341.

Lu, T. and Law, C.K., 2009. "Toward accommodating realistic fuel chemistry in large-scale computations". *Progress in Energy and Combustion Science*, Vol. 35, No. 2, pp. 192–215.

Metcalfe, W.K., Dooley, S., Curran, H.J., Simmie, J.M., El-Nahas, A.M. and Navarro, M.V., 2007. "Experimental and modeling study of C5H10O2 ethyl and methyl esters". *The Journal of Physical Chemistry A*, Vol. 111, No. 19, pp. 4001–4014.

Niemeyer, K.E. and Sung, C., 2011. "On the importance of graph search algorithms for DRGEP-based mechanism reduction methods". *Combustion and Flame*, Vol. 158, No. 1, pp. 1439–1443.

Pepiot-Desjardins, P. and Pitsch, H., 2008. "An efficient error-propagation-based reduction method for large chemical kinetic mechanisms". *Combustion and Flame*, Vol. 154, No. 1, pp. 67–81.

Pitsch, H. and Steiner, H., 2000. "Large-eddy simulation of a turbulent piloted methane/air diffusion flame (Sandia flame D)". *Physics of Fluids (1994-present)*, Vol. 12, No. 10, pp. 2541–2554.

Rajaratnam, N., 1976. *Turbulent jets*, Vol. 5. Elsevier.

Sarathy, S., Thomson, M., Pitz, W. and Lu, T., 2011. "An experimental and kinetic modeling study of methyl decanoate combustion". *Proceedings of the Combustion Institute*, Vol. 33, No. 1, pp. 399–405.

Turányi, T. and Tomlin, A.S., 2014. *Analysis of kinetic reaction mechanisms*. Springer.

Vaz, F.A. and De Bortoli, A., 2014. "A new reduced kinetic mechanism for turbulent jet diffusion flames of bioethanol".

Applied Mathematics and Computation, Vol. 247, pp. 918–929.

Westbrook, C.K., Naik, C.V., Herbinet, O., Pitz, W.J., Mehl, M., Sarathy, S.M. and Curran, H.J., 2011. “Detailed chemical kinetic reaction mechanisms for soy and rapeseed biodiesel fuels”. *Combustion and Flame*, Vol. 158, No. 4, pp. 742–755.

Yasin, M.M., Cant, R., Chong, C. and Hochgreb, S., 2014. “Discrete multicomponent model for biodiesel spray combustion simulation”. *Fuel*, Vol. 126, pp. 44–54.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.