

NUMERICAL STUDY OF DIESEL-BIODIESEL BLENDS IN 1D FREELY PROPAGATING PREMIXED FLAMES

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Abstract. Diesel is a complex real fuel, which is derived from conventional petroleum sources, and is composed of hundreds of compounds. These characteristics indicate the difficulty of using this fuel for numerical studies. In order to avoid these difficulties, simplified synthetic fuels, called "surrogate fuels" are used. On the other hand, biodiesel is a complex mixture of methyl esters with different chain lengths and degrees of unsaturation and can be used in pure form or may be blended with diesel without major modifications in diesel engines. However, changing the fuel in diesel engines induces changes in combustion behavior, which can impact pollutants emission. Therefore, a better understanding of diesel-biodiesel blend combustion is needed. This paper presents numerical studies of diesel-biodiesel blends combustion in a 1D freely propagating gaseous premixed flame configuration. We have developed and validated a new chemical scheme by carefully combining two schemes available in the literature: one for diesel and one for biodiesel. This guarantees reproducing the principal features of both fuels combustion characteristics. The new combined scheme, consists of 235 species and 1113 elementary reactions. Laminar flame velocities were obtained as a function of equivalence ratio for different diesel-biodiesel blends. And the new combined model was validated comparing flame velocities of pure diesel and pure biodiesel using the combined model and the original models.

Keywords: Diesel, Biodiesel, Kinetic modeling, Numerical Simulation, Premixed flame

1. INTRODUCTION

Diesel is a complex real fuel, which is derived from conventional petroleum sources, and is composed of hundreds of compounds. Although the composition of petroleum-based diesel fuel is highly variable, there are some trends (Farrell *et al* 2007): The carbon numbers of the components range from approximately $C_{10} - C_{22}$. An average carbon number is 14 or 15.

These characteristics indicate the difficulty of using diesel for experimental studies associated with numerical simulations. In effect, due to its complex and varying composition, the number of possible reaction pathways in a chemical reaction mechanism increases drastically. Development of models that represent all these components is prohibitive because the model would be too large for current computational resources.

In order to avoid these difficulties, simplified synthetic fuels, called "surrogate fuels", with shorter chain lengths and known physical chemical properties are chosen to carry combustion studies. The term surrogate refers to a simpler representation of a real complex fuel.

The purpose of using surrogates is to simplify the combustion mechanism by using a single fuel molecule or a blend of relatively small molecules to represent the real fuel. Numerically, the use of surrogate fuels reduces significantly the number of possible chemical reactions in the kinetic scheme, while still representing the main properties of the real fuel.

On the other hand, biodiesel is a complex mixture of methyl esters with different chain lengths and degrees of unsaturation and can be used in pure form or may be blended with diesel without major modifications in diesel engines. In Paraguay, the percentage of diesel vehicles is about 80% of the fleet, and currently 100% of diesel fuel is imported and

only B1 (1% biodiesel) is used. Therefore, the potential in the development of such alternative fuel is enormous.

However, changing the fuel in diesel engines induces changes in combustion behavior, which can impact pollutants emission. Indeed, the use of biodiesel in diesel engines decreases emissions of pollutants such as carbon monoxide, unburned hydrocarbons, and particulate matter, although a slight increase in emissions of nitrogen oxides is observed in some cases (Agarwal *et al* 2007 and Zheng *et al* 2008). Therefore, a better understanding of diesel-biodiesel blend combustion is suitable.

Chemical kinetic mechanisms for hydrocarbon fuels have been the focus of intense research for several decades. However, there is surprisingly little information on the combustion properties and pathways of common liquid fuels. This is due in part to the difficulty in representing real fuels containing hundreds of components with a wide variation in composition by surrogate fuels for the purpose of chemical kinetic modelling. Nevertheless, due to the increasing number of researchers working in the development of either kinetic modelling or experimental database of this fuel, this field has experienced a significant amount of recent developments.

This paper presents numerical studies of diesel-biodiesel blends combustion in a 1D freely propagating gaseous premixed flame configuration. We have developed and validated a new chemical scheme by carefully combining the schemes proposed by Andrae *et al* 2011 (diesel) and Zhayou Luo *et al* 2012 (biodiesel). This guarantees reproducing the principal features of both fuels combustion characteristics. The new combined scheme, consists of 235 species and 1113 elementary reactions.

The kinetic modelling for diesel-biodiesel blend oxidation in a 1D freely propagating gaseous premixed flame was performed using the 1D-PREMIXED code within the REGATH package developed at EM2C laboratory (N. Darabiha *et al* 1993, Candel *et al* 2011 and Franzelli *et al* 2013), that takes into account the detailed kinetic and transport phenomena (heat and mass transfer) through a numerical predictive 1D code.

Laminar flame velocities were obtained as a function of equivalence ratio for different diesel-biodiesel blends. And the new combined model was validated comparing flame velocities of pure diesel and pure biodiesel using the combined model and the original models.

2. DIESEL AND BIODIESEL CHEMICAL STRUCTURE

Diesel is a complex combination of hydrocarbons produced by the distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of $C_{10} - C_{20}$.

The composition varies widely, depending on the crude oils used, the refinery processes available, the overall balance of product demand, and the product specifications. The typical composition of diesel shows approximately, by volume, 66% of saturated hydrocarbons, 30% aromatics (benzene derivatives) and 4% olefins (unsaturated hydrocarbons).

Due to the complex chemical structure of diesel, simplified synthetic fuels, called surrogate fuels, with shorter chain lengths are chosen to carry numerical combustion studies.

There has been much recent progress in the area of surrogate fuels for diesel. In the last few years, experiments and modeling have been performed on higher molecular weight components of relevance to diesel fuel. Chemical kinetic models have been developed for all the n-alkanes up to 16 carbon atoms. Also, there has been experimental and modeling work on lower molecular weight surrogate components such as n-decane and n-dodecane that are most relevant to jet fuel surrogates, but are also relevant to diesel surrogates where simulation of the full boiling point range is desired (W. Pitz *et al* 2011).

According to a recent paper (Hernandez *et al* 2014), a mixture of toluene and n-heptane was the best diesel surrogate in comparison to other species surrogates. Luo *et al* 2012 have shown that the ignition delay and smoke emission of TRF20 (80% n-heptane/20% toluene in volume) were closer to that of diesel fuel as compared with the pure n-heptane and TRF30 (70% n-heptane/30% toluene in volume) fuel.

Following these works, in this paper TRF20 (80% n-heptane/20% toluene in volume) have been chosen as a surrogate of the commercial diesel. Chemical structures of these surrogates are presented in Figure 1.

Biodiesel is a complex mixture of methyl esters with different chain lengths and degrees of unsaturation.

Rapeseed-derived biodiesel (most produced around the world) concentrations and mole fractions has been estimated (D. Alviso *et al* 2015) and is presented in Table 1. In comparison to the literature values (Herbinet *et al* 2008), it corresponds to the classical composition of biodiesel obtained from this oil.

The chemical structure of each methyl ester is presented in Figure 2. The structures of these components show considerable similarities in these chemical species, each with a methyl ester attached to a large hydrocarbon chain. Main differences are:

- the length of the hydrocarbon chain; 15 atoms of carbon for methyl palmitate and 17 for the other methyl esters,
- the number of double bonds in the hydrocarbon chain; no double bond for methyl palmitate and methyl stearate, one double bond for methyl oleate, two for methyl linoleate and three for methyl linolenate.

Due to the complex chemical structure of biodiesel, surrogate fuels are also chosen to carry numerical combustion

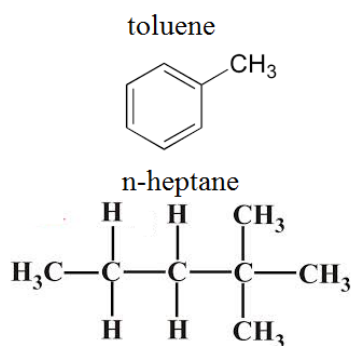


Figure 1. Diesel surrogates chemical structures

Rapeseed biodiesel composition		
Methyl ester	CC (ppm)	Mole fraction
Palmitate	417	4.73
Stearate	157	1.78
Oleate	5660	64.21
Linoleate	1866	21.16
Linolenate	715	8.11

Table 1. Composition of rapeseed-derived biodiesel.

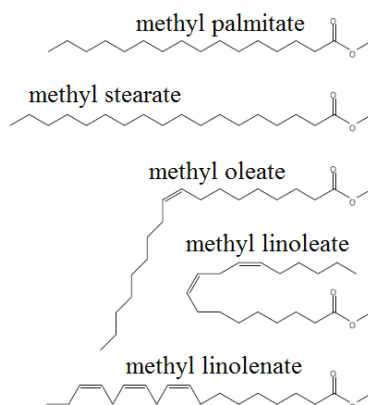


Figure 2. Structures of the main components of rapeseed-derived biodiesel

studies.

In this sense, Seshadri *et al* 2009 proposed methyl decanoate $C_{11}H_{22}O_2$ (MD) as a possible surrogate. The chemical structure of methyl decanoate MD is presented in Figure 3.

More recently, Z. Luo *et al* 2012 proposed a tri-component biodiesel surrogate, which consists of methyl decanoate $C_{11}H_{22}O_2$ (MD), methyl 9-decenoate $C_{11}H_{20}O_2$ (MD9D) and n-heptane C_7H_{16} (chemical structures presented in Figure 3). Methyl-9-decenoate was chosen because the double bond is at the same position as the one in methyl oleate and at the same location as the first double bond in methyl linoleate and in methyl linolenate (Figure 2).

In this work, methyl decanoate $C_{11}H_{22}O_2$ (MD) and methyl 9-decenoate $C_{11}H_{20}O_2$ (MD9D) were the surrogates chosen to represent biodiesel combustion. Methyl palmitate and stearate (without double bonds) will be represented by MD. And methyl oleate, linoleate and linolenate (with one or more double bonds) will be represented by MD9D.

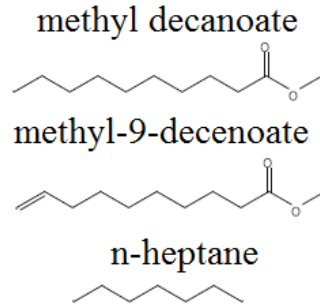


Figure 3. Biodiesel surrogates chemical structure

3. LAMINAR FLAME VELOCITY

The laminar burning velocity is a physicochemical property dependent on the temperature, pressure, and mixture composition (fuel type, equivalence ratio, and amount of diluents). As a result, the laminar burning velocity provides invaluable information on the combustion properties and the underlying oxidation chemistry of the given fuel. It is also an important parameter in the design of engines, burners and other equipment where combustion is involved. Several experimental setups can be used to measure the laminar burning velocity of fuels: flat flame burners, combustion chambers, counterflow burners, etc. (Ranzi *et al* 1998)

It is found that a detailed knowledge of laminar premixed flames will provide insights into such properties as heat release rate, flammability limits, propagation rates, quenching and emissions characteristics. It is also common to use measured burning velocities to validate chemical kinetic schemes. Although the majority of fuel is probably burnt in turbulent combustion, data on laminar burning velocities are still needed as input to many turbulent combustion models. Also, in internal combustion engines the initial combustion is laminar, so again there is a need for the laminar burning velocity (Takashi *et al*).

In this study, laminar flame velocities as a function of the equivalence ratio have been estimated in the case of pure diesel, pure biodiesel, and different blends of these two fuels using the 1D-PREMIXED code within the REGATH package.

4. FREELY PROPAGATING PREMIXED FLAMES GOVERNING EQUATIONS

We consider a steady, isobaric, quasi-one-dimensional flame propagation configuration. A diesel-biodiesel/air mixture is injected from one side, and a premixed flame propagates freely towards fresh gases with the corresponding laminar flame velocity. In order to get a stabilized flame (instead of a propagating flame) one must inject fresh gases with a velocity equal to the laminar flame velocity.

Gaseous phase are described by the following balance equations (mass, energy and species, respectively). It must be noted that there is one species conservation equation for each species present in the numerical model (N_{sp}).

$$\frac{\partial \rho_g v_g}{\partial z} = 0, \quad (1)$$

$$\rho_g v_g c_{p_g} \frac{\partial T_g}{\partial z} = \frac{\partial}{\partial z} \left(\lambda_g \frac{\partial T_g}{\partial z} \right) - \sum_{k=1}^K h_k W_k \Omega_k - \left(\sum_{k=1}^K \rho_g Y_k V_{kz} c_{p_{gk}} \right) \frac{\partial T_g}{\partial z}, \quad (2)$$

$$\rho_g v_g \frac{\partial Y_k}{\partial z} = - \frac{\partial}{\partial z} (\rho_g Y_k V_{kz}) + W_k \Omega_k, \quad k = 1, \dots, N_{sp} \quad (3)$$

The solutions have the form: gas density $\rho_g = \rho_g(z)$, gas axial velocity $v_g = v_g(z)$, gas temperature $T_g = T_g(z)$ and species mass fractions $Y_k = Y_k(z)$, $k = 1, \dots, N_{sp}$ (N_{sp} is the number of species).

In these equations $c_{p_{gk}}$ and c_{p_g} are the heat capacity at local constant pressure of species k and of the mixture respectively. h_k , W_k , Ω_k are the specific enthalpy, the molar weight and the molar chemical production rate of the k^{th} species respectively, and V_{kz} is the diffusion velocity of the k^{th} species in the axial direction.

The above system of equations is completed by the ideal gas equation.

4.1 Kinetic modeling

As explained in Section 2, TRF20 (80% n-heptane/20% toluene in volume) have been chosen as a surrogate of the commercial diesel. The mechanism due to Andrae *et al* 2011 consisting of 150 species and 759 reactions was chosen to represent diesel chemistry. This model consists of a semi-detailed description of toluene oxidation and skeletal mechanisms of iso-octane and n-heptane.

On the other hand, methyl decanoate $C_{11}H_{22}O_2$ (MD) and methyl 9-decenoate $C_{11}H_{20}O_2$ (MD9D) were the surrogates chosen to represent biodiesel combustion. The mechanism due to Zhayou Luo *et al* 2012 with 115 species and 460 reactions for a tri-component biodiesel surrogate: methyl decanoate (MD), methyl 9-decenoate (MD9D) and n-heptane, was chosen to represent biodiesel chemistry.

In order to be able to simulate a diesel-biodiesel/air flame, species representing these two fuels must be present in a single model. The kinetic model proposed here is designed from the original diesel oxidation framework of Andrae *et al* 2011. This latter chemical scheme is used as a starting base model. Then additional species found in kinetic scheme of Zhayou Luo *et al* 2012 (biodiesel) and the corresponding reactions are added. For the common species (which are 30), reactions present in Zhayou Luo *et al* 2012 model and not present in Andrae *et al* 2011 model are also added. For the common reactions (which are 106), Arrhenius constants of Andrae *et al* 2011 model are chosen, due to the fact that diesel is usually the majority component in the blend. Thus, the new combined scheme, consists of 235 species and 1113 elementary reactions. This guarantees reproducing the principal features of both fuels combustion characteristics.

4.2 Numerical conditions

The set of equations for the gaseous phase is then replaced by a fully coupled set of discrete relations. The solution of this system is then based on a global adaptive nonlinear method using Newton iterations (N. Darabiha *et al* 1993). The grid is adapted to first and second order derivatives of all variables and the smallest grid size is $5 \mu m$.

The kinetic modeling for diesel-biodiesel blends oxidation in the 1D freely propagating flame was performed using the 1D-PREMIXED code within the REGATH package (N. Darabiha *et al* 1993, Candel *et al* 2011 and Franzelli *et al* 2013) with detailed thermochemical and transport properties developed at EM2C laboratory. The inputs to each simulation include a chemical kinetic reaction mechanism, a dataset of thermochemical properties and a dataset of transport properties.

Diesel-biodiesel/air freely propagating premixed flames operating condition have been chosen, considering the equivalence ratio (ϕ): from $\phi = 0.6$ to $\phi = 1.4$. The mixture stream is kept at an initial temperature of 300 K. The pressure is equal to one atmosphere.

5. RESULTS AND DISCUSSION

As the laminar burning velocity provides invaluable information on the combustion properties (see Section 3), we have first used the kinetic scheme proposed by Andrae *et al* 2011 and Zhayou Luo *et al* 2012 to simulate 1-D freely propagating pure diesel and pure biodiesel (respectively) premixed flames using 1D-PREMIXED code within the REGATH package.

Flame velocities estimated as a function of equivalence ratio are presented in Figure 4, for pure diesel (Andrae, continuous line) and pure biodiesel (Zhayou, discontinuous line), where one can see that the maximum flame velocity for pure diesel is obtained for an equivalence ratio of 1.1, whereas that of biodiesel is obtained for an equivalence ratio of 1.2

Then, we have used the combined kinetic scheme to simulate 1-D freely propagating flames. In order to validate the developed model proposed in this study, we have first compared the flame velocities of pure diesel using the combined model and that of Andrae *et al* 2011. Flame velocities estimated as a function of equivalence ratio are presented in Figure 5. Results using Andrae *et al* 2011 model are presented in continuous line, whereas those of the combined model are presented in discontinuous line. This figure shows that for equivalence ratios higher than 1, the combined model reproduces very well the results of Andrae *et al* 2011, whereas for equivalence ratios lower than 1, there is a slight difference between the two models (about 10 %).

Finally, we have compared the flame velocities of pure biodiesel using the combined model and that of Zhayou Luo *et al* 2012. Flame velocities estimated as a function of equivalence ratio are presented in Figure 6. Results using Zhayou Luo *et al* 2012 model are presented in continuous line, whereas those of the combined model are presented in discontinuous line. This figure shows that for equivalence ratios lower than 1, the combined model reproduces fairly well the results of

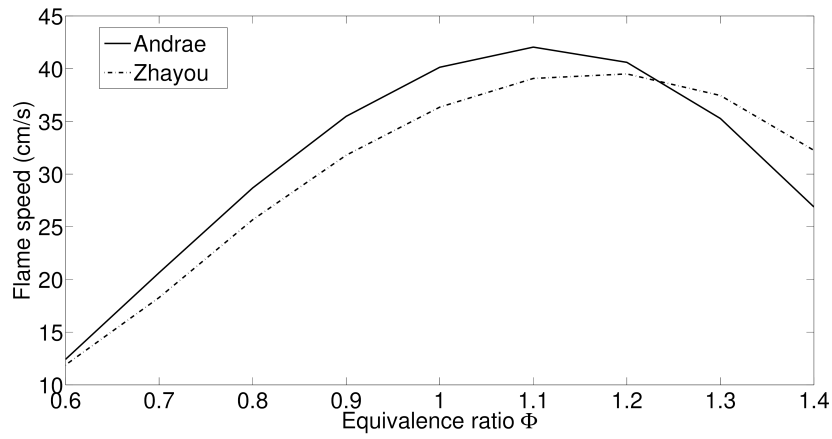


Figure 4. Diesel (Andrae) and biodiesel (Zhayou) flame velocity as a function of equivalence ratio

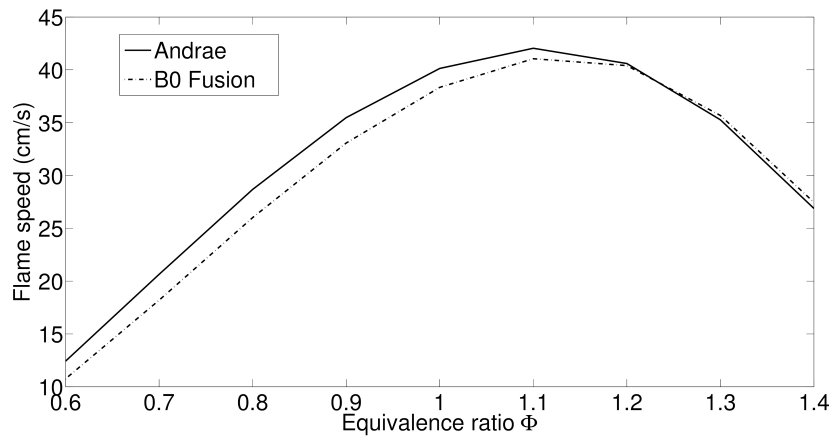


Figure 5. Pure diesel flame velocity as a function of equivalence ratio using the combined model (discontinuous line) and Andrae model (continuous line)

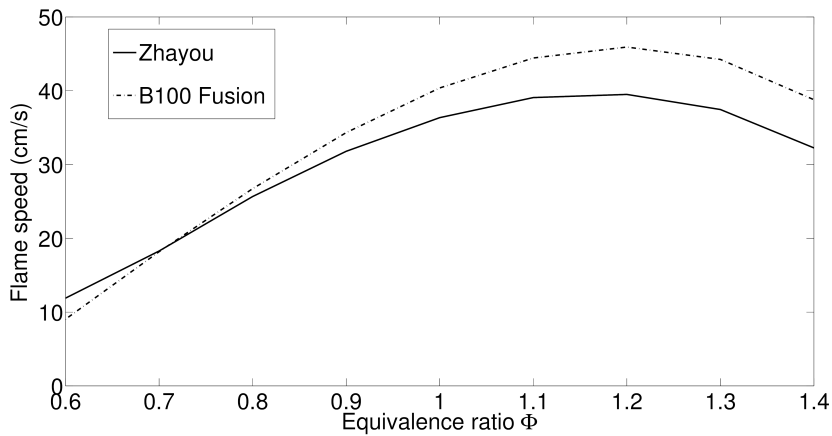


Figure 6. Pure biodiesel flame velocity as a function of equivalence ratio using the combined model (discontinuous line) and Zhayou Luo model (continuous line)

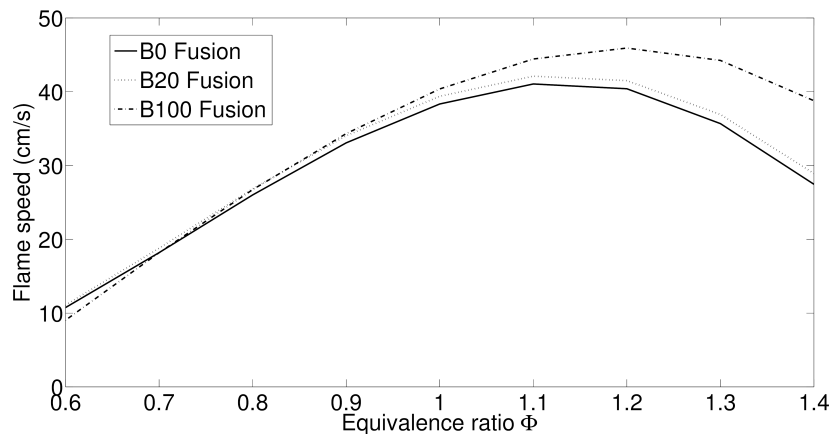


Figure 7. Diesel-biodiesel blend flame velocity as a function of equivalence ratio using the combined model

Zhayou Luo *et al* 2012, whereas for equivalence ratios higher than 1, there is a more pronounced difference between the two models, which might be due to the fact that during the kinetic modeling, for all common reactions between the two models (which are 106), Arrhenius constants of Andrae *et al* 2011 model were chosen, since diesel is usually the majority component in the blend.

Diesel-biodiesel blends flame velocities as a function of equivalence ratio using the combined model are presented in Figure 7. The blend correspond in volume to: B20 (80% diesel, 20% biodiesel). B20 is the most common blend used around the world. Agarwal and Das 2001 found out that B20 is the optimum biodiesel blend giving maximum increase in thermal efficiency, lowest brake-specific energy consumption (BSEC) and advantage in terms of lower emissions.

In Figure 7 one can see that the influence of adding biodiesel is not negligible, concerning the blend flame velocity. In fact, for equivalence ratios higher than 1, B20 flame velocities curve is located in average, at 20% from B0, and 80% from B100, whereas for equivalence ratios lower than 1, flame velocities of B0 and B100 are very similar, and consequently B20 flame velocities are very near from B0 and B100 flame velocities.

6. CONCLUSIONS

This paper has presented numerical studies of diesel-biodiesel blends combustion in a 1D freely propagating gaseous premixed flame configuration.

A new chemical scheme was developed and validated by carefully combining the schemes proposed by Andrae *et al* 2011 (diesel) and Z. Luo *et al* 2012 (biodiesel). This guarantees reproducing the principal features of both fuels combustion characteristics. The new combined scheme, consists of 235 species and 1113 elementary reactions.

We have first used the kinetic scheme proposed by Andrae *et al* 2011 and Zhayou Luo *et al* 2012 to simulate 1-D freely propagating pure diesel and pure biodiesel (respectively) premixed flames.

Then, in order to validate the developed model proposed in this study, we have compared the flame velocities of pure diesel using the combined model and that of Andrae *et al* 2011, and the flame velocities of pure biodiesel using the combined model and that of Zhayou Luo *et al* 2012. For pure diesel, it was shown that for equivalence ratios higher than 1, the combined model reproduces very well the results of Andrae *et al* 2011, whereas for equivalence ratios lower than 1, there is a slight difference between the two models (about 10 %). On the other hand, for pure biodiesel it was shown that for equivalence ratios lower than 1, the combined model reproduces fairly well the results of Zhayou Luo *et al* 2012, whereas for equivalence ratios higher than 1, there is a more pronounced difference between the two models, which might be due to the fact that during the kinetic modeling, for all common reactions between the two models (which are 106), Arrhenius constants of Andrae *et al* 2011 model were chosen, since diesel is usually the majority component in the blend.

Diesel-biodiesel blends (B20: 80% diesel, 20% biodiesel) flame velocities using the combined model were presented, where it was shown that the influence of adding biodiesel is not negligible, concerning the blend flame velocity. In fact, for equivalence ratios higher than 1, B20 flame velocities curve is located in average, at 20% from B0, and 80% from B100, whereas for equivalence ratios lower than 1, flame velocities of B0 and B100 are very similar, and consequently B20 flame velocities are very near from B0 and B100 flame velocities.

These results are promising in order to continue research works in modeling kinetic schemes for diesel-biodiesel blends.

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