

## Reduced Kinetic Model of Biodiesel Fuel Combustion

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In times where the attention on alternative energy sources is continuously increasing, the study of biofuels is taking a primary role, as a possible replacement, or integration, of traditional transportation fuels. Among them, biodiesel fuels are typically a complex mixture of large fatty acids, obtained through transesterification of soybean and rapeseed oils with methanol. In this background, the pyrolysis and combustion kinetics of methyl esters is essential for a proper understanding of the combustion behavior and pollutant formation from biodiesel fuels. From a modeling point of view, when studying the combustion of large methyl esters a reliable kinetic mechanism is required. Nevertheless, the main problems of these molecules lie in their length and lack of symmetry in their structure, which results in the huge size of the related detailed kinetic mechanisms (thousands of species) with a consequent significant computational load, even when dealing with 0D and 1D models. In order to maintain the applicability of the kinetic mechanism also in multidimensional models, it should be useful somehow to reduce its dimensions. For this reason, a reduced kinetic scheme for methyl esters was developed and is presented in this work. It is the result of the coupling of two different techniques: (i) an upstream lumping of species and reactions, through which several species are grouped into a single pseudo-species according to proper rules; (ii) a successive further reduction of the kinetic mechanism through a novel technique, based on the analysis of the reacting system in the desired range of operating conditions. The reduced mechanism was validated through comparison with experimental data in a wide range of conditions using shock tube, laminar flame speeds and ideal reactors. A satisfactory agreement with both experimental data and the original scheme was observed. Additionally, thanks to its limited dimensions, the kinetic model could be applied on more complex, multidimensional models. As an instance, its performances on a multi-zone model of an HCCI (*Homogeneous Charge Compression Ignition*) engine are assessed: the obtained results show the great advantages of this mechanism, which can then be used in place of the original one without losing in accuracy, but with considerable savings in computational times.

### 1. Introduction

The introduction of biodiesel fuels in a market currently dominated by fossil sources is one of the current research paths towards a higher exploitation of renewable energies. Indeed, they are obtained from the transesterification of vegetable oils or animal fats with methanol, which results in fatty acid methyl esters (FAME) with physicochemical properties very similar to traditional diesel fuels (Lin et al., 2011).

From a chemical point of view, the transesterification process produces five major methyl esters: methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl linolenate. In the last decade, the deep experimental and modeling effort around them was crucial in understanding their kinetics of pyrolysis and oxidation, as well as in defining the reaction classes involved. In spite of this, when a detailed kinetic mechanism for methyl esters is built up, the geometrical asymmetry of the molecules becomes a serious disadvantage. The final number of species may reach the order of some thousands (Herbinet et al., 2008, Westbrook et al., 2011), thus restricting its field of applicability to the simplest 0D and 1D simulations.

When a smaller mechanism for methyl esters is needed, e.g. for CFD applications, two strategies can be adopted (Lu and Law, 2009): chemical lumping and skeletal reduction. In this case, these techniques are of fundamental importance: indeed, the number of radicals and isomers increases with the size (and

asymmetry) of the molecule. Similarly (and consequently), intermediate species and possible reaction paths grow more than linearly, too.

Through chemical lumping the original species are grouped into a smaller number of pseudo-compounds. Among the others, this methodology was developed by Ranzi et al. (1995) with positive outcomes on the size of the kinetic mechanism, without a significant loss in the accuracy of the final output. As already discussed in Saggese et al. (2013), the kinetic description of heavy methyl esters oxidation simply requires the extension of the overall kinetic mechanism with 60 lumped species and 2,000 reactions. On the other hand, skeletal reduction strategies aim at individuating and eliminating unimportant species and reaction paths from a detailed mechanism.

In this work, a downstream reduction of the mechanism, carried out through the analysis of reacting fluxes in ideal reactors (RFA) is coupled to a lumped approach to the kinetic model of methyl esters. The following sections describe in more detail the adopted procedure and successive validation: after the description of the lumped model (Section 2), the reduction step is explained in Section 3. The obtained mechanism is finally validated in Section 4, where a representative example of a multidimensional application of methyl-esters mechanism is given. Finally, conclusions are drawn in the last section.

## 2. Lumped kinetic scheme of biodiesel fuels

A first reduction of the detailed kinetic mechanism was carried out according to the chemical lumping procedures described by Ranzi et al. (2001). Through this approach, species are organized into lumps according to their chemical structure and reactivity. Indeed, if radicals larger than  $C_4$  are concerned, they quickly evolve into their primary decomposition and isomerization products at high temperatures; therefore, they can be directly replaced with them. This steady state approximation allows to drastically reduce the number of involved species: decomposition paths are taken into account by simply writing the continuity equations on heavy radicals, and then deducing the apparent reaction stoichiometry. On the other hand, at low temperatures the large radicals follow similar branching paths, and consequently the isomers and radicals are grouped into lumped species as previously explained. This strategy is then combined to a “vertical” lumping: the fact that adjacent species with a consecutive number of carbon atoms have similar physicochemical properties, allows to split them between the two closest references according to the lever rule. For instance the pyrolysis and oxidation of the methyl ester of myristic acid ( $C_{15}H_{30}O_2$ ) is obtained with a molar mixture 1:2 of methyl-decanoate ( $C_{11}H_{22}O_2$ ) and methyl-palmitate ( $C_{17}H_{34}O_2$ ). Doing so, the number of stable species and intermediate compounds can be further reduced.

The procedures just outlined were originally conceived for n-alkanes (Ranzi et al., 2005). Though, they can be easily extended to methyl esters, as the reaction classes involving the related radicals are the same. Additional details about the development of the lumped model for methyl esters can be found in Grana et al. (2012) and Saggese et al. (2013). The final, lumped model for methyl esters is made up of 393 species and 11,951 reactions.

### 2.1 Validation

In order to complement the validation carried out in the previously mentioned works, a new set of experimental data is here analysed. In fact, the ignition delay times of methyl oleate and methyl linoleate were measured behind reflected shock waves, using an aerosol shock tube by Campbell et al. (2013).

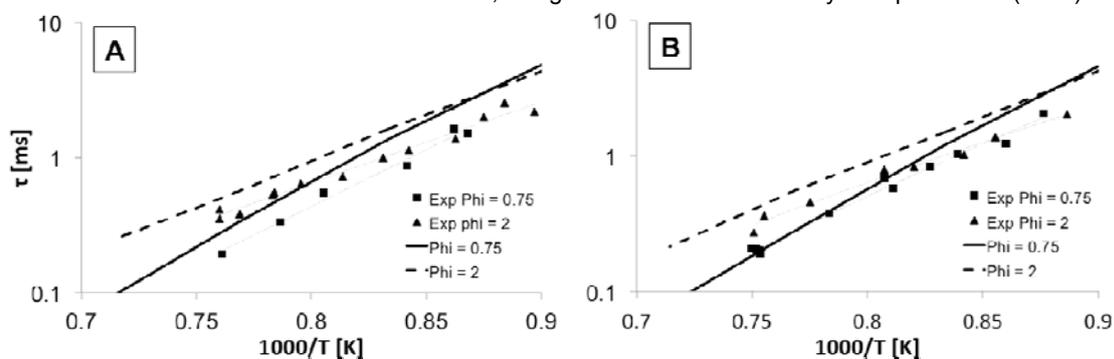


Figure 1. Methyl oleate (Panel A) and methyl linoleate (Panel B) ignition delay times at 7 atm. Effect of the equivalence ratio  $\Phi = 0.75 - 2$  (Campbell et al., 2013). Comparisons of experimental data (symbols and dotted lines) and model predictions (solid and dashed lines)

Reflected shock conditions covered temperatures from 1,100 to 1,400 K, pressures of 3.5 and 7.0 atm, and equivalence ratios from 0.6 to 2.4. Figure 1 shows the comparison of the experimental and model predicted ignition delay times for methyl oleate and methyl linoleate ignition at 7 atm and two different equivalence ratios ( $\Phi = 0.75$  and  $\Phi = 2$ ). At high temperatures and mainly for methyl oleate, the model underpredicts the reactivity but captures the experimental trends with equivalence ratios. Moreover, the decrease in activation energy as equivalence ratio increases is correctly predicted, while the value of activation energy is slightly overpredicted. The crossover of the ignition delays for both the species is correctly predicted at  $\sim 1,150$  K. According to the sensitivity analysis, the important reactions are not fuel specific, but they mainly belong to the  $C_0$ - $C_4$  mechanism.

### 3. Reduced kinetics of methyl esters

The lumped kinetic mechanism for methyl esters is made up of  $\sim 400$  species and 12,000 reactions, which is still an excessive size for multidimensional applications. Therefore, a reduction technique must be applied downstream. As pointed out by Lu and Law (2009), modern reduction techniques are targeted at an automatic elimination of those species and reactions, which are classified as unimportant according to one or more parameters. They can be based on the elimination of unimportant reactions, and species accordingly, or vice versa. Actually, most of reduction methods are focused on the individuation of unimportant species, which is a more complex task because of the frequent couplings among them. In the present work, reduction is carried out through a recently introduced methodology, based on the analysis of reacting fluxes in ideal reactors. In the following, the fundamentals of the reduction procedure are briefly summarized. Then, the obtained mechanism is analysed and finally validated.

#### 3.1 Reacting Flux Analysis (RFA)

The reduction methodology is based on the analysis of the behavior of the original mechanism in ideal, isothermal plug flow reactors. In particular, the importance of each species is evaluated according to the production and consumption rate history throughout the whole reactor.

For each reactor, the absolute formation rate of each  $i$ -th species is evaluated as:

$$R_i = \sum_{j=1}^{NR} |v_{i,j} \omega_j| \quad (1)$$

where  $NR$  is the number of reactions,  $v_{i,j}$  is the stoichiometric coefficient of the  $i$ -th species in the  $j$ -th reaction,  $\omega_j$  is the net reaction rate of the  $j$ -th reaction. The total flux of each species in each reactor is evaluated as:

$$F = \int_0^{t_f} R_i dt \quad (2)$$

where  $t_f$  is the residence time of each reactor. The flux values of each reactor are normalized with respect to the local maximum value, in order to give the same importance to all of them. Afterwards, the fluxes of all the reactors are summed up and sorted in descending order. According to the desired size of the mechanism, the first  $n$  species are kept in the skeletal model, and consequently the reactions are kept if and only if all the reactants and products belong to the set of important species. Inert species like  $N_2$  are forcibly added upstream, even if their fluxes are null.

The operating range where the mechanism is aimed at working is described in Table 1, in terms of temperature, pressure and equivalence ratio. The initial conditions of the basket of sample reactors is obtained by combining the previously defined parameters. Following the reference composition of common biodiesel fuels in terms of fatty acids reported in Lin et al. (2011), the inlet composition was taken as the molar average of soybean, rapeseed and palm oil. The Polimi lumped model for methyl esters was reduced to a mechanism of 174 species and 3181 reactions, by setting a 10% maximum error on the ignition delay times.

Table 1. Operating conditions used to generate the skeletal mechanism for methyl esters

	Range
Temperature	600 – 1,700 K
Pressure	1 – 40 atm
Equivalence ratio	0.5 – 2

### 3.2 Reduced Kinetic Scheme

The reduced mechanism of biofuels shows the prevailing presence of 104 radicals. Its dimensions are significantly larger than the ones obtained when reducing the kinetic model of n-dodecane (Stagni et al., 2013). Figure 2 shows that the required species largely belongs to the core kinetics C<sub>0</sub>-C<sub>4</sub>. These 77 species are of course in common also with the reduced kinetics of n-dodecane. Moreover, together with the 60 specific species required to characterize the biofuels and their primary propagation products, several C<sub>5</sub>-C<sub>10</sub> species belonging to the nC<sub>12</sub>H<sub>26</sub> mechanism are also required.

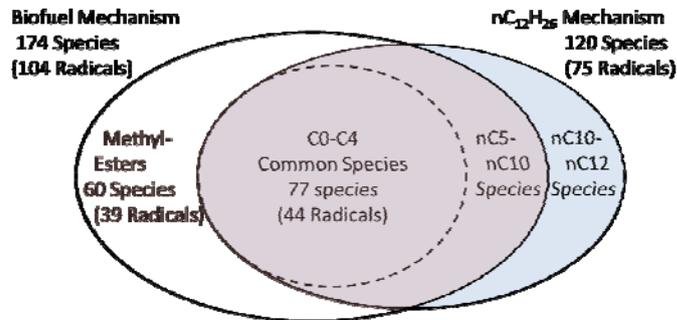


Figure 2. Species involved in the reduced oxidation mechanisms of Biofuels and n-dodecane

### 4. Validation and applications

The reduced mechanism was validated on the whole operating space of temperature, pressure and equivalence ratio. Figure 3 shows the maps of the relative deviations on ignition delay at 3 different pressures. Apparently, the most critical conditions are observed at low pressure. Anyway, the maximum observed error is about 9.5 %, which satisfies the defined criterion.

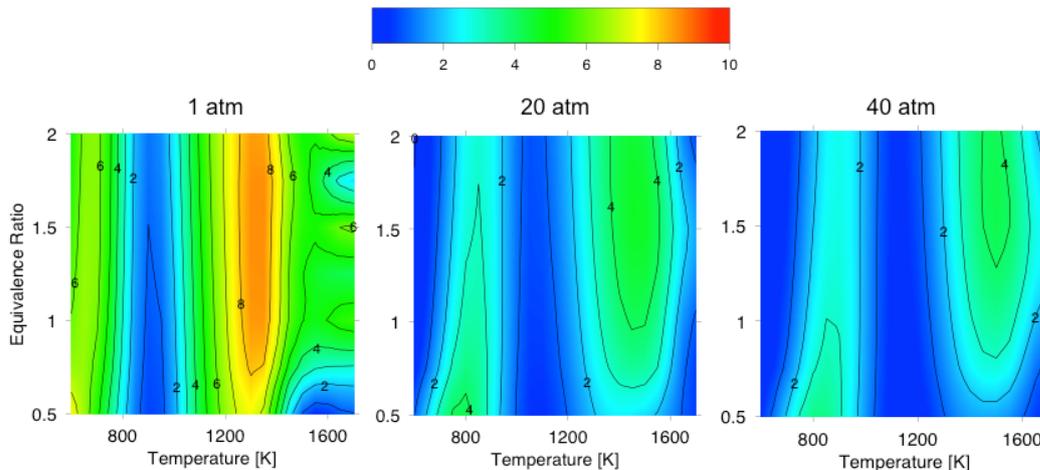


Figure 3. Maps of error [%] of the reduced mechanism on the ignition delay with respect to the detailed one at 1, 20 and 40 atm

Figure 4 compares the behavior of detailed and reduced model in predicting the formation of several species in a jet stirred reactor (Dagaut and Sahasrabudhe, 2007), at two different operating conditions. The agreement between them is evident for all the investigated species, and confirms the ability of the reduced mechanism to reproduce the trends of the detailed model, even with a starting composition (rapeseed) different from the one used for the reduction (average of the most representative biofuels). Similarly, Figure 5 shows the comparisons of experimental, detailed and reduced kinetic models for premixed laminar flame speeds. As a useful case study, the performance of detailed and reduced model in a HCCI engine is analyzed (Szybist et al., 2007). The absence of a spark ignition emphasizes the role of

the chemistry. Therefore, the auto-ignition can be described only through detailed kinetic schemes, able to consider both the low and high temperature mechanisms.

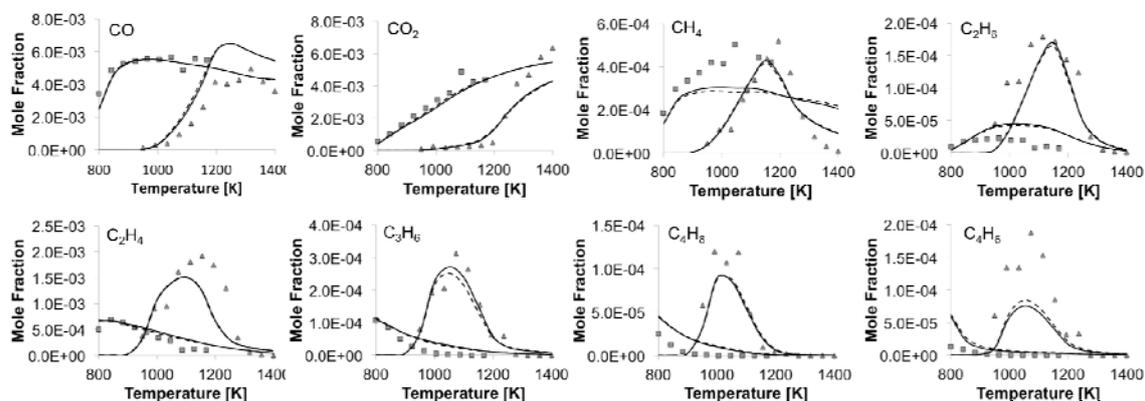


Figure 4. Comparison between detailed (continuous lines) and reduced (dashed lines) model predictions of rapeseed methyl ester in a jet stirred reactor (Dagaut and Sahasrabudhe, 2007). Experimental data at 1 atm and 0.07 s (squares) and 10 atm and 1 s (triangles), respectively

The approach used to describe the system is based on a quasi-dimensional multi-zone model developed by Bissoli et al. (2013): the reacting volume inside the cylinder is discretized into 10 zones, each of which is treated as an ideal reactor with a time-variable volume, able to exchange mass and heat through diffusive fluxes, both laminar and turbulent.

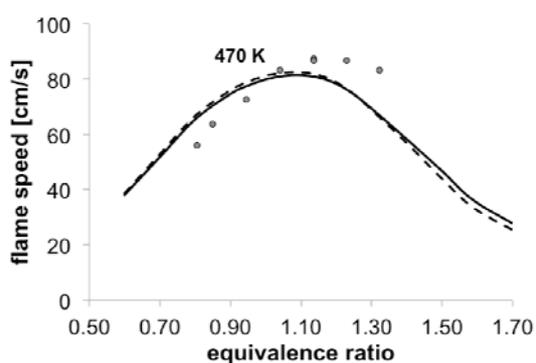


Figure 5. Premixed laminar flame speed of palm methyl esters/air mixture at 470 K, 1 atm. Continuous line: detailed model. Dashed line: reduced model. Symbols: Experimental data (Chong and Hochgreb, 2011)

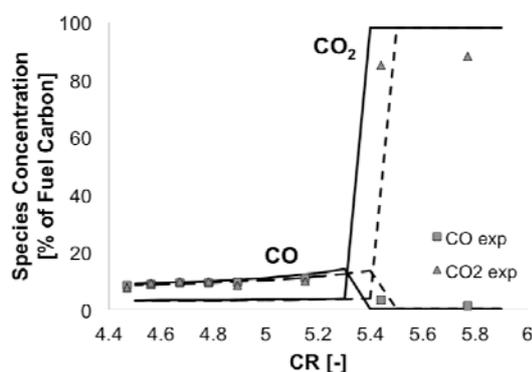


Figure 6. Comparison between experimental data and model predictions for methyl decanoate oxidation in a HCCI for different Compression Ratios (CR). Continuous lines: detailed model. Dashed lines: reduced model. Symbols: Experimental data (Szybist et al., 2007)

Figure 6 shows the comparison between experimental data and simulation results for the combustion of methyl-decanoate in terms of CO and CO<sub>2</sub> measured at the exhaust for different compression ratios (CR). In order to obtain a stable solution several cycles must be performed for each CR, since the model describes also the perturbation effects on the charge fed at the beginning of a new cycle by the burned gasses remained trapped in the cylinder. These two aspects contribute to increase the computational effort for the simulation of a single point. The CO and CO<sub>2</sub> profiles show that the use of the reduced scheme does not involve significant differences in the description of the reactivity in the system. In fact, the low temperature ignition is basically the same, as well as the ignition point (delayed only of 0.1 CR). On the other hand, the advantage in terms of simulation time is significant, since the reduced mechanism allows to reduce the simulation time of 12 times: an average time of 20 min instead of 255 min.

## 5. Conclusions

A skeletal kinetic model for the oxidation of heavy methyl esters at low and high temperature was obtained by reducing the lumped model of Saggese et al. (2013). A novel reduction method was adopted, based on the analysis of reacting fluxes within ideal plug flow reactors. The final scheme is made up of 174 species, more than 15 times smaller than the reference detailed model of biodiesel fuels (Westbrook et al., 2011). The reduced mechanism was first validated in ideal reactors, showing that it is able to evaluate the ignition delay times and species formation in JSRs with an accuracy similar to the original model. Then, the reduced model proved effective in more complex systems, as the laminar flame speed and the multi-zone model of a HCCI engine. Indeed, in CFD applications, a limited number of species is crucial for achieving results in reasonable times. Of course, the procedure discussed here is not specific for methyl esters, but is applicable to all complex fuel mixtures, such as the conventional transportation fuels and surrogates. In these cases, the coupling between lumping and reduction techniques seems a very convenient way to carry out the related simulations with the desired accuracy on the kinetic part of the model.

## References

- Bissoli, M., Cuoci, A., Frassoldati, A., Faravelli, C., Ranzi, E., Lucchini, T., D'errico, G. & Contino, F. 2013. Detailed Kinetic Analysis of HCCI Combustion Using a New Multi-Zone Model and CFD Simulations. *SAE Int. J. Engines*, 6, 1594-1609.
- Campbell, M. F., Davidson, D. F., Hanson, R. K. & Westbrook, C. K. 2013. Ignition delay times of methyl oleate and methyl linoleate behind reflected shock waves. *Proceedings of the Combustion Institute*, 34, 419-425.
- Chong, C. T. & Hochgreb, S. 2011. Measurements of laminar flame speeds of liquid fuels: Jet-A1, diesel, palm methyl esters and blends using particle imaging velocimetry (PIV). *Proceedings of the Combustion Institute*, 33, 979-986.
- Dagaut, P. & Sahasrabudhe, M. 2007. Rapeseed oil methyl ester oxidation over extended ranges of pressure, temperature, and equivalence ratio: Experimental and modeling kinetic study. *Proceedings of the Combustion Institute*, 31, 2955-2961.
- Grana, R., Frassoldati, A., Saggese, C., Faravelli, T. & Ranzi, E. 2012. A wide range kinetic modeling study of pyrolysis and oxidation of methyl butanoate and methyl decanoate - Note II: Lumped kinetic model of decomposition and combustion of methyl esters up to methyl decanoate. *Combustion and Flame*, 159, 2280-2294.
- Herbinet, O., Pitz, W. J. & Westbrook, C. K. 2008. Detailed chemical kinetic oxidation mechanism for a biodiesel surrogate. *Combustion and Flame*, 154, 507-528.
- Lin, L., Cunshan, Z., Vittayapadung, S., Xiangqian, S. & Mingdong, D. 2011. Opportunities and challenges for biodiesel fuel. *Applied Energy*, 88, 1020-1031.
- Lu, T. F. & Law, C. K. 2009. Toward accommodating realistic fuel chemistry in large-scale computations. *Progress in Energy and Combustion Science*, 35, 192-215.
- Ranzi, E., Dente, M., Goldaniga, A., Bozzano, G. & Faravelli, T. 2001. Lumping procedures in detailed kinetic modeling of gasification, pyrolysis, partial oxidation and combustion of hydrocarbon mixtures. *Progress in Energy and Combustion Science*, 27, 99-139.
- Ranzi, E., Faravelli, T., Gaffuri, P. & Sogaro, A. 1995. Low-Temperature Combustion - Automatic-Generation of Primary Oxidation Reactions and Lumping Procedures. *Combustion and Flame*, 102, 179-192.
- Ranzi, E., Frassoldati, A., Granata, S. & Faravelli, T. 2005. Wide-range kinetic modeling study of the pyrolysis, partial oxidation, and combustion of heavy n-alkanes. *Industrial & Engineering Chemistry Research*, 44, 5170-5183.
- Saggese, C., Frassoldati, A., Cuoci, A., Faravelli, T. & Ranzi, E. 2013. A lumped approach to the kinetic modeling of pyrolysis and combustion of biodiesel fuels. *Proceedings of the Combustion Institute*, 34, 427-434.
- Stagni, A., Cuoci, A., Frassoldati, A., Faravelli, T. & Ranzi, E. 2013. Lumping and Reduction of Detailed Kinetic Schemes: an Effective Coupling. *Industrial & Engineering Chemistry Research*, in press.
- Szybist, J. P., Boehman, A. L., Haworth, D. C. & Koga, H. 2007. Premixed ignition behavior of alternative diesel fuel-relevant compounds in a motored engine experiment. *Combustion and Flame*, 149, 112-128.
- 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*, 158, 742-755.