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CHEMICAL KINETICS MODELS FOR BIODIESEL COMBUSTION - A REVIEW

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Abstract.
Diesel oil is the base fuel for road transport. It can be partially displaced by biodiesel. Computational models reduce experimental costs and allow faster optimization of fuels and motors. Therefore, a detailed comprehension of the combustion process is vital to advance combustion technology. The objective of this paper is to present and compare chemical kinetics models for the oxidation of large methyl-ester molecules, such as methyl butanoate and methyl decanoate, and their use in chemical surrogates for biodiesel. Both measurements and modeling are addressed, including the cost of simulation with detailed mechanisms and the impact of the reduction of the chemical kinetics mechanisms.

Keywords: *Oxidation of methyl esters, detailed chemical kinetics model, reduced chemical kinetics model, biodiesel combustion.*

1. INTRODUCTION

Diesel is the most used fuel in Brazilian transports. Brazilian highway diesel has a mandatory percentage of biodiesel that started at 2 % (by volume) in 2008 (Empresa de Pesquisa Energética, 2018) and reached 10 % in 2019 (Agencia Nacional de Petroleo Gas Natual e Biocombustiveis, 2019). Present regulations provide for this proportion to reach 15 % by 2023 (DOU, 08/11/2019). There are several possible raw materials that can be used to produce biodiesel. Their feasibility depends on their physical-chemical characteristics, and also economic, ecological and social sustainability aspects (Nogueira, 2011).

The increase in the use of biodiesel implies a need to increase the depth and coverage of studies of this fuel if high levels of thermal efficiency and reduced aggression to the environment and public health are to be guaranteed. Understanding the chemical kinetics of combustion is fundamental to develop new fuels and motors (Merker *et al.*, 2005). A chemical kinetics model unveils combustion's ideal conditions and how to avoid the formation of undesired species. Developing a new chemical kinetics model is challenging because even the combustion of relatively small species involves tenths of species and hundreds of reactions. As an example, the detailed chemical modeling of the oxidation of methane, the simplest model for a hydrocarbon fuel, involves 53 species and 325 reactions, as modeled by the GRIMech mechanism in its 3.0 version (Smith *et al.*; Law, 2006). Biodiesel is mainly composed of long-chain methyl esters (Graboski and McCormick, 1998), which makes its computational modeling even more challenging (Westbrook *et al.*, 2011a).

The objective of the present work is to review the chemical kinetics models for biodiesel combustion available in the literature, including a review of the background of this development and methodologies, a comparison and analysis of different models available, and concluding with a discussion of difficulties and future prospects.

This article is divided in five sections. First, a non-extensive review of the main aspects of chemical kinetics modeling is presented. Then, the evolution of the kinetics modeling of biodiesel is presented, with emphasis in the developments for methyl butanoate, the initial prototype of biodiesel surrogate, the modeling of larger methyl esters with up to 19 carbon atoms and surrogates formed from these species, and the reduction of the larger chemical kinetics mechanisms. Finally, the paper is concluded highlighting the main challenges in the field and the future prospects.

2. CHEMICAL KINETICS MODELING OF COMBUSTION

The fundamental phenomenological studies in combustion may largely focus on physical and chemical aspects. In the chemical aspects, the modeling of the reaction paths and steps leading from the fuel molecule to the final saturated combustion products is the basic objective of the chemical kinetics modeling (Law, 2006).

Real fuels, such as diesel and biodiesel, are made of several different chemical species, ranging typically from 9 to 23 carbon atoms (John Bacha and Mills, 2007). Furthermore, their chemical compositions vary according to their raw material and production process. This restrains the development of chemical kinetics models that reproduce exactly the real fuels. Less complex fuels that mimic some of the target fuel chemical combustion characteristics are used instead. They are called fuel surrogates (Farrell *et al.*, 2007).

One of the most used computational tool available to solve combustion kinetics problems is CHEMKIN® (Design, 2013). Created originally at SANDIA National Laboratories in the 70's, it became freely available from 1980 in its FORTRAN 77 implementation. Since 2014, it is a proprietary software owned by ANSYS. Most of the papers cited in the following used CHEMKIN® (Fisher *et al.*, 2000; Gaïl *et al.*, 2007; Dooley *et al.*, 2008; Gaïl *et al.*, 2008; Metcalfe *et al.*, 2007; Herbinet *et al.*, 2008; Sarathy *et al.*, 2007; Seshadri *et al.*, 2009; Dayma *et al.*, 2008, 2009; Herbinet *et al.*, 2010; Luo *et al.*, 2010; Westbrook *et al.*, 2011a; Ismail *et al.*, 2013; An *et al.*, 2014; Chang *et al.*, 2015; Cheng *et al.*, 2015; Jiaqiang *et al.*, 2016; Liu *et al.*, 2016). CANTERA (Goodwin *et al.*, 2018) is an open source alternative to CHEMKIN. It was created originally by David G. Goodwin at the California Institute of Technology in the 80's. It is now provided under a permissive 3-Clause BSD license, ensuring that it remains freely available. It has language interfaces to Python, C++, Fortran and MatLab.

Both CHEMNKIN® and CANTERA receive as input data the properties of the elements, the thermodynamics and transport properties of the chemical species, and the reactions and parameters of the chemical reaction mechanism. Those data are used to calculate thermodynamic, transport and production and destruction rates of chemical species, which in turn are used to solve the basic conservation equations of mixture mass, mass of chemical species, linear momentum and energy for the problems of interest. A more detailed explanation is out of the scope of this article and can be found in detail in the CHEMKIN and CANTERA manuals (Kee *et al.*, 1986; Cantera, 2018) and described summarily in textbooks (Merker *et al.*, 2005; Law, 2006; Williams, 2018).

The development of a detailed chemical kinetics model occurs hierarchically, starting from kinetics models of smaller species and adding reactions to construct models for larger species. The core of the chemical kinetics mechanisms for hydrocarbons is formed by the carbon monoxide wet oxidation mechanism, i.e., the mechanism for the oxidation of carbon monoxide CO and hydrogen H_2 with oxygen O_2. The basic mechanism comprises 14 species and 33 reactions (Frassoldati, 2007; O'Connaire and Westbrook, 2004). Then, the mechanisms for formaldehyde (CH_2O), methanol (CH_3OH) and methane (CH_4) are added, followed by more complete versions of C_2 to C_4 mechanisms, and so on. The final result are mechanisms with increasing complexity. Several repositories, for example, those at LLNL (https://combustion.llnl.gov/mechanisms), CRECK (http://creckmodeling.chem.polimi.it/menu-kinetics/menu-kinetics-detailed-mechanisms) and C3 (http://c3.nuigalway.ie/combustionchemistrycentre/mechanismdownloads/) present the complete mechanisms for several species.

The final acceptance of a chemical reaction mechanism as a reliable description of the chemistry of combustion requires the testing and comparison to chemical kinetics measurements, an activity broadly referred to as the *mechanism validation*. The use of the chemical mechanism at temperatures, pressures and compositions outside the range in which it was validated is not warranted (Lu and Law, 2009). Validation should ideally include the comparison to detailed, non intrusive, measurements of temperature (T) and concentration of chemical species (c_i) for different pressures (P) and equivalence ratios (Φ), as typically obtained in one-dimensional flames and flow reactors (Herbinet and Dayma, 2013). It allows the identification of intermediate species, the study of the formation of pollutants, and the range of temperature, pressure, and speed at which combustion occurs, including the conditions for the formation of cold flames. Global combustion parameters are also used to validate chemical reaction mechanisms, such as the laminar flame speed (LF), and its dependency on temperature, pressure, stoichiometry and flame stretch rate, and the ignition delay time (IDT).

The ignition delay time (IDT) is an important parameter specially in the study of fuels for internal combustion engines (Merker *et al.*, 2005). The ignition delay time (IDT) is defined as the time interval from the elapsed time when the air-fuel mixture reaches a pressure and temperature condition sufficient to ignite it to when the mixture actually auto-ignites. This is important to determine the conditions that lead to auto-ignition in compression ignition (diesel) engines and those that lead to knocking in spark ignited (gasoline) engines. The ignition delay has a determining effect on performance, efficiency, and emissions (Kalghatgi, 2014, 2015).

In the biodiesel modeling literature, the main experiments used to unveil molar fractions are the Variable Pressure Flow Reactor (VPFR) (Marchese *et al.*, 2004), the Jet Stirred Reactor (JSR - a type of perfect stirred reactor, PSR) (Dagaut *et al.*, 2007; Hakka *et al.*, 2009; Glaude *et al.*, 2010; Bax *et al.*, 2010; Rodriguez *et al.*, 2016), and the Opposed Flow (or, Counter Flow) Flame Burner (CFB) (Sarathy *et al.*, 2007; Gaïl *et al.*, 2007, 2008; Dayma *et al.*, 2011). IDT is measured in High-Pressure Shock Tubes (HPST) (Metcalfe *et al.*, 2007; Dooley *et al.*, 2008; Campbell *et al.*, 2013, 2014; Wang *et al.*, 2014) and Rapid Compression Machines (RCM) (Dooley *et al.*, 2008). Optical mono-cylinder and full internal combustion engines are also used to unveil spray characteristics, ignition patterns, heat release, cycle variability and production of emissions along individual cycles and steady-state operation. These are valuable input to the development of applications, but these engine measurements combine several physical and chemical effects simultaneously, making it more difficult to sort out the chemical contributions only. Also, the modeling and simulation of a complete engine is more challenging and time-consuming than simulating a dedicated chemical reactor, which is specifically designed to evidence chemical phenomena only (Chang *et al.*, 2015; Liu *et al.*, 2016; Jiaqiang *et al.*, 2016).

The need to model the chemical kinetics of mixtures of larger species and the hierarchical nature of the mechanisms have produced increasingly complex structures. The numbers of species and reactions increase exponentially with the increase of the size and complexity of the fuel molecules. Curran *et al.* (1998, 2002) discussed the chemical kinetics modeling of the main chemical surrogate of liquid transportation fuels, denoted Primary Reference Fuel, or PRF. PRF comprises all the mixtures of iso-octane and n-heptane, which are the reference chemical species used to measure the Octane number of fuels (RON and MON). They systematically described the 25 types of reactions that form the basis of chemical kinetics combustion models of n-heptane and iso-octane. This classification is useful to build new models because it allows assuming that analogous reactions have the same reaction constants. The rules of Curran *et al.* (1998, 2002) were adapted to describe the combustion of esters and used to build several biodiesel surrogates (Westbrook *et al.*, 2011a).

Developing a chemical kinetics model manually, by adding relevant species and reaction data one at a time, even when guided by general rules such as those in Curran *et al.* (2002), is potentially tedious and largely subject to human error. The need to develop kinetics models for larger molecules led to the emergence of software capable of automatically generating mechanisms (Warth *et al.*, 1998; Gao *et al.*, 2016). The most used software for the construction of biodiesel kinetics models is EXGAS (Glaude *et al.*, 2010; Herbinet *et al.*, 2011). The result of the application of these automated methodologies are enormous mechanisms. For example, CRECK's mechanism for PRF, PAH and methyl-esters comprises 417 species and 15742 reactions (Grana *et al.*, 2012a) and LLNL's mechanism for methyl decanoate, methyl-5-decenoate, methyl-9-decenoate and n-alkanes involves, approximately, 4800 species and 20,000 reactions (Westbrook *et al.*, 2011b). The use of such large mechanisms in numerical simulations of applications is generally time and cost prohibitive. The reduction of the comprehensive detailed mechanism and the development of skeletal mechanisms have become a reasonable alternative to improve the usage of numerical simulations in the design and optimization phases of applications.

Mechanism reduction is broadly based on finding out which reactions are more important for the prediction of a given target and adjusting the kinetics constants of the Ahrrenius model to maintain the characteristics of the original detailed model (Law, 2006; Lu and Law, 2009). Lu and Law (2009) published a review of methods of reduction of detailed chemical kinetics mechanisms. In that work, the methodologies were divided into four categories, each with several subdivisions. Skeletal reduction eliminates the less important species and/or reactions of the detailed model, thus leaving a subset of species and major reactions, called the skeletal model. Lumping consists in combining species with similar behavior in a single effective species, aiming at reducing the number of variables to be solved. Time-scale analysis consists in applying quasi-stationary state and partial equilibrium approximations to reduce the number of differential equations to be integrated by the model, thus avoiding possible numerical instabilities caused by short living species. Finally, stiffness reduction consists of reducing numerical instability and increasing coverage of the mechanism by using on-the-fly reduction techniques. From these strategies, the first three are the most used. On-the-fly methods are still on an early development stage.

Given this general background, the chemical kinetics modeling of chemical surrogate species for biodiesel are presented next.

3. METHYL BUTANOATE

The first kinetics model for a biodiesel surrogate was developed by Cornell University and Lawrence Livermore National Laboratory (LLNL) in USA. This was also the first organized effort to develop a comprehensive kinetics model to describe the combustion of esters. Elizabeth Fisher *et al.* (2000) focused on methyl butanoate ($C_2H_4O_2$) and methyl formate, the former ($C_2H_4O_2$) being chosen as a biodiesel surrogate. The final model has 264 species and 1219 reactions. It was built using the rules developed by Curran *et al.* (1998, 2002). The sub-mechanism of methyl butanoate was added to a pre-existing mechanism of n-heptane, and reactions involving hydrocarbons having more than four carbons were removed. Thermodynamic properties were estimated using group additivity. The kinetics model was used to simulate experiments of constant volume and isothermal static reactors obtained from works published in the 1950s and 1960s. Experimental conditions were: initial temperature varying from $520K$ and $740K$, initial pressure varying from $P = 13kPa$ to $P = 54kPa$, and rich mixtures. The target evaluated was the maximum value of the derivative of the pressure as a function of time $(dP/dt)_{max}$. The predictions obtained with the final mechanism diverged from the available measurements. New simulations were made using propane and propene, whose chemical kinetics were already validated. The divergence between experiments and predictions was maintained, suggesting that the experiments may have methodological problems or be affected by random errors. Fisher *et al.* (2000) concluded expressing the need for new experiments with more precise instruments to validate the model.

The model of Fisher *et al.* (2000) was validated by a later study developed in two other American universities, Rowan University and Princeton University. Marchese *et al.* (2004) used a Variable Pressure Flow Reactor (VPFR) to measure species formation and reactivity as a function of temperature. Operating conditions were more similar to a real diesel engine. The model was able to predict reactivity at stoichiometric conditions, but underestimated it for poor mixtures and overestimated it for rich mixtures. Real biodiesel presents Negative Temperature Coefficient (NTC), but neither the methyl butanoate predictions nor the methyl butanoate experiments reproduced this behavior. The study emphasized the importance of more accurate experiments to validate this kinetics model, and the elaboration of models that describe diesel and biodiesel blends, considering that biodiesel is usually mixed with fossil diesel in the applications.

Vaughn *et al.* (2006), also from Rowen University, explored other possible biodiesel surrogates comparing the ignition delay time (IDT) of fuel droplets of methyl butanoate, methyl decanoate ($C_{11}H_{22}O_2$), methyl dodecanoate ($C_{13}H_{26}O_2$), methyl oleate ($C_{19}H_{36}O_2$) and soy commercial biodiesel. Experiments were performed in a tube furnace at atmospheric pressure and temperature up to $1273K$. This study concluded that methyl butanoate do not reproduce real biodiesel IDT, therefore it is not an adequate surrogate for that characteristic. Methyl decanoate IDT was similar to biodiesel IDT up to about 1150 K. At high temperatures, methyl decanoate IDT is lower than biodiesel IDT. Methyl dodecanoate also presents lower IDT than biodiesel at higher temperatures and presents higher IDT at lower temperatures. Methyl oleate was the ester that better reproduced biodiesel IDT at all studied temperatures. Vaughn *et al.* (2006) concluded that methyl oleate would be the most adequate surrogate among the species studied, however, it's long carbon chain makes its kinetics harder to describe. They highlighted that their experiment improved the comprehension of the fuel's behavior, but several other studies are needed to develop a chemical kinetics model.

The effect of unsaturation in the combustion of methyl-esters was studied experimentally by Sarathy *et al.* (2007), researchers at the University of Toronto (Canada) and the ICARE/CNRS-Orleans (France). They used a jet stirred reactor (JSR) to test premixed combustion and measure molar fractions of several species as a function of temperature, and an opposite flow diffusion burner to study non-premixed combustion and measure molar fractions as a function of distance from the stagnation plane. The operating conditions of the JSR were: 0.075 mol % of fuel diluted in nitrogen, mean residence time $\tau = 0.07$ s, $\Phi = 1.13$ and atmospheric pressure. The opposed flow diffusion flame burner was at atmospheric pressure and 4.7 mol % of fuel diluted in nitrogen. Two substances with the same length chain were studied: saturated methyl butanoate and unsaturated methyl crotonate ($C_5H_8O_2$). Sarathy *et al.* (2007) reported that methyl crotonate produced more soot precursors than methyl butanoate. This result suggests that unsaturated esters are more prone to soot production than saturated ones.

Results obtained by JSR and opposed flow diffusion flame experiments operating under the same conditions of Sarathy *et al.* (2007), and VPFR results by Marchese *et al.* (2004) were compared to simulations to create two updated versions of the methyl butanoate model by Fisher *et al.* (2000). The first mechanism described only methyl butanoate combustion. It was published by Gaïl *et al.* (2007) in a joint work developed by the University of Toronto, ICARE, Rowan University and Princeton University. It involves 295 species and 1498 reactions. Some reaction rate constants were modified, to improve agreement with measured molar concentrations. Furthermore, a C_4 sub-mechanism taken from the literature was used to describe the kinetics of 1-butene and 1,3-butadiene. The second mechanism (Gaïl *et al.*, 2008) was developed by University of Toronto and ICARE. It also included methyl crotonate reactions and presented a more detailed study of reaction pathways. It involves 301 species and 1516 reactions.

Other two updated versions of the methyl butanoate model by Fisher *et al.* (2000) were published in parallel by a group from the Combustion Chemistry Center (C3) at National University of Ireland (NUI) in Galway. Metcalfe *et al.* (2007) studied two isomers, methyl butanoate and ethyl propanoate. They measured IDT using a shock tube. The equivalence ratio range was $0.25 \leq \Phi \leq 1.5$, and temperatures in the range 1100 K $\leq T \leq 1670$ K, 1.0 atm $\leq P \leq 4.0$ atm. The kinetics model parameters were changed to better reproduce the measurements. They also developed an ethyl propanoate sub-mechanism. Dooley *et al.* (2008) modified the methyl butanoate model by Metcalfe *et al.* (2007). They used the experimental data by Marchese *et al.* (2004); Sarathy *et al.* (2007); Gaïl *et al.* (2007); Metcalfe *et al.* (2007), and presented new shock tube and rapid compression machine (RCM) experiments. The shock tube was used to measure IDT at high temperatures (1250 K $\leq T \leq$ 1760 K) while the RCM was used to measure IDT at low to intermediate temperatures (640 K $\leq T \leq$ 949 K). Shock tube equivalence ratios and pressure were the same as Metcalfe *et al.* (2007). RCM was operated at 10 atm $\leq P \leq$ 40 atm, $0.33 \leq \Phi \leq 1.0$ and fuel concentrations of 1.59 mol % and 3.13 mol %. The methyl butanoate model by Dooley *et al.* (2008) involves 275 species and 1545 reactions. Sub-mechanisms were updated according to the literature. Transport parameters of added species were taken from the literature or estimated using either data from similar chemical species, or the group-additivity method.

Both Gaïl *et al.* (2007) and Dooley *et al.* (2008) reached the same conclusion as Vaughn *et al.* (2006). Since methyl butanoate do not present NTC, it does not represent biodiesel auto-ignition and it is not the most adequate biodiesel surrogate. Gaïl *et al.* (2007) suggested that unsaturated esters, with longer carbon chain than methyl butanoate, would form more adequate biodiesel surrogates. Dooley *et al.* (2008) highlighted that kinetics studies of methyl butanoate are important to understand general aspects of the combustion of esters and are starting points to develop more accurate biodiesel surrogates. In fact, experimental and computational works on methyl butanoate combustion are still being developed in order to better understand the behavior of this ester, to improve methyl butanoate sub-mechanisms in larger esters models, and to compare the combustion with different fuels (Walton *et al.*, 2011; Yu *et al.*, 2012; Kumar and Sung, 2016; Lele *et al.*, 2018; Salamanca *et al.*, 2019).

4. ALKANES, ESTERS UP TO 19 CARBON ATOMS AND MULTICOMPONENT SURROGATES

The first experimental data of molar species formation during real biodiesel combustion were obtained at ICARE/CNRS and the Heriot Watt University (Scotland) (Dagaut *et al.*, 2007). They used a JSR operating at residence time of 0.07 s, 0.1 s and 1 s; 1 atm $\leq P \leq 10$ atm; 800 K $\leq T \leq 1400$ K and $0.25 \leq \Phi \leq 1.5$; high degree of dilution (0,05 mol %) to study rapeseed biodiesel combustion. This study observed similarities between biodiesel and large alkanes, therefore Dagaut *et al.* (2007) proposed n-hexadecane ($C_{16}H_{34}$) as a biodiesel surrogate. A pre-existent n-hexadecane model used as diesel and kerosene surrogate was updated to reproduce biodiesel's pressure dependence data. The chemical kinetics model has 225 species and 1841 reactions. The comparison between the concentration of species measured for the fuel oxidation and those predicted for the surrogate oxidation showed a good agreement. The main differences between predictions for n-hexadecane and measurements for biodiesel were in the formation of oxygenated species, due to lack of ester group in n-hexadecane. Dagaut *et al.* (2007) concluded that n-hexadecane is an adequate surrogate for species formed during biodiesel combustion, but the similarities between the surrogate and the real fuel would increase if an ester and a saturated species were blended with the original alkane. However, this would increase substantially the model complexity.

Based on previous papers that suggested that longer chain esters would be more adequate biodiesel surrogates (Gaïl *et al.*, 2007; Dagaut *et al.*, 2007; Vaughn *et al.*, 2006), two kinetics models of esters more complex than methyl butanoate were published in 2008: methyl hexanoate ($C_7H_{14}O_2$) (Dayma *et al.*, 2008) and methyl decanoate ($C_{11}H_{22}O_2$) (Herbinet *et al.*, 2008). The methyl hexanoate model was published by two French groups from the Université Pierre et Marie Curie and ICARE/CNRS. It was hierarchically built by adding sub-mechanisms of the methyl butanoate model of Fisher *et al.* (2000). It has 435 species and 1875 reactions. It was validated against measured species in JSR experiments for rich and poor mixtures, $P = 10$ atm, $\tau = 1$ s and 500 K $\leq T \leq 1000$ K (Dayma *et al.*, 2008). In the following year, the same groups used this model as a basis to develop a model of methyl heptanoate ($C_8H_{16}O_2$) (Dayma *et al.*, 2009). Comparing those two works, it becomes clear how the increase in the size of the fuel molecule impacts the complexity of the kinetics model. The mechanism for methyl heptanoate increased to 1087 species and 4592 reactions. It is two and a half times the size of the methyl hexanoate model. The methyl heptanoate model was also validated against JSR measurements, using the same temperatures and pressures used in methyl hexanoate experiments. Residence time was 0.7 s. Both methyl hexanoate and methyl heptanoate behaved like long-chain hydrocarbons in JSR experiments. As temperature increases, their combustion follows three regimes: cold flame, NTC and high-temperature oxidation.

Dayma *et al.* (2009) pointed out that the mechanism developed by their research group was being expanded to include longer chain esters. Thence Dayma *et al.* (2011) published a methyl octanoate ($C_9H_{18}O_2$) model with 2781 reactions and 383 species. It was validated against JSR and opposed-flow diffusion flame data. In the following year, the methyl heptanoate mechanism was expanded using EXGAS, an automatic computational tool used to build kinetics models. The new mechanism can describe the combustion of esters up to methyl decanoate ($C_1 1H_{22}O_2$). The model presented 7171 reactions and 1251 species. Experimental validation was done by comparing the model with experimental data from previous wors Dayma *et al.* (2008, 2009) and new data from the combustion of methyl decanoate obtained in a JSR (Glaude *et al.*, 2010).

The first methyl decanoate model was developed by LLNC and published by Herbinet *et al.* (2008). This ester had already exhibited suitable behavior for low temperatures in the work of Vaughn *et al.* (2006). The model was build following Curran *et al.* (1998) rules. Pre-existent models of n-heptane, iso-octane and methyl butanoate were merged, and some kinetics parameters and subroutines taken from other papers were added. Due to the complexity of the molecule studied (long-chain, asymmetry), the model is quite extensive, presenting 3012 species and 8820 reactions. The validation was made comparing computational results with the experiments carried out in other works:

a Comparison with experimental JSR data obtained from the combustion of rapeseed biodiesel Dagaut *et al.* (2007) and a blend of rapeseed biodiesel and aviation kerosene Jet A1. Simulation condition were $P = 10$ atm, $\Phi = 0.5$ and 0.1, and $\tau = 1$ s Carbon flux was defined as target property. Target fuel general formula considered was $C_{17.92}H_{33}O_2$). Two different surrogates were simulated. First, pure methyl decanoate with the simulated dilution adjusted by a correction factor. Second, an equimolar mixture of methyl decanoate and n-heptane. The bi-component surrogate was considered more adequate, even though a good general agreement between experimental data and simulations was observed for both fuels.

b Comparison with experimental results of methyl decanoate in an internal combustion engine (Szybist *et al.*, 2007), compression ratio between 4.4 and 5.6 and equivalence ratio of 0.25. These simulations consumed a lot of computational time (about 160 CPU hours for each computation) due to the model complexity. A good agreement between measurements and simulations was observed.

Herbinet *et al.* (2008) concluded that both methyl decanoate and n-hexadecane are suitable biodiesel surrogates. Methyl decanoate reproduces the formation of CO and CO_2 better. They highlighted the importance of new experiments to validate this model, and the possibility to extend their model to develop a kinetics model for esters up to 18 carbons.

Herbinet *et al.* (2010) used their previous work (Herbinet *et al.*, 2008) as a basis to develop a new model that describes the combustion of the unsaturated esters methyl-5-decenoate and methyl-9-decenoate ($C_{11}H_{20}O_2$). The objective was to reproduce the effect of unsaturation in the biodiesel combustion. The model has 3329 species and 10806 reactions and was validated against measurements in JSR published by Dagaut *et al.* (2007). Methyl-5-decenoate was not reactive enough to reproduce biodiesel combustion. Methyl-9-decenoate is more reactive than methyl decanoate, and methyl decanoate is more reactive than methyl-5-decenoate. In isolation, methyl decanoate is the most adequate biodiesel surrogate of the three possible surrogates studied. A mixture of 25 % methyl decanoate, 25 % methyl-9-decenoate and 50 % n-heptane was also proposed as biodiesel surrogate, presenting a good agreement with the JSR data of Dagaut *et al.* (2007).

Esters longer than methyl decanoate were first analyzed in purely experimental works. ICARE's JSR was used to measure species formed during the combustion of two esters. Hakka *et al.* (2009) studied blends of n-decane and methyl palmitate ($C_{17}H_{34}O_2$), and also blends of n-decane and n-hexadecane (74/26 mol %/mol %). The difference between methyl palmitate and n-hexadecane is only the ester group. Sarah Bax *et al.* (2010) evaluated blends (78/22 mol %/mol %) of n-decane and methyl oleate ($C_{19}H_{36}O_2$). Both experiments used high dilution in helium, quasi-atmospheric condition, a temperature range of 500 K $- 1100$ $[K]$ and residence time $\tau = 1.5$ s. Hakka *et al.* (2009) observed that n-hexadecane and methyl palmitate had similar reactivities and NTC behavior, thus n-hexadecane is an adequate biodiesel surrogate. Bax *et al.* (2010) compared methyl oleate with the methyl palmitate results obtained by Hakka *et al.* (2009) and concluded that methyl oleate is less reactive than methyl palmitate before NTC region. This may be attributed to methyl oleate's unsaturation. Hakka *et al.* (2009) and Bax *et al.* (2010) mentioned the possibility of using EXGAS to develop a kinetics model that describes the combustion of methyl palmitate, methyl oleate and other large esters found in real biodiesel, but Bax *et al.* (2010) remarked that this model "would contain more than 50,000 reactions and 6000 species making its use very difficult".

Ester models are much larger than n-alkane models with the same number of carbons because the esters of interest are not symmetric. A comparison between the size of models for esters developed using EXGAS was presented by Herbinet *et al.* (2011). They compared a detailed model for saturated esters up to 19 carbons generated by EXGAS to experimental data available in the literature. The biggest ester studied was methyl palmitate, and PSR simulation was compared with the measurements of Hakka *et al.* (2009). The model has 6203 species and 43,444 reactions. Herbinet *et al.* (2011) concluded that esters larger than methyl decanoate and large n-alkanes are adequate surrogates for the saturated large esters present on biodiesel. They highlighted that those surrogates do not reproduce the specificity of the behavior of unsaturated esters and that at the time EXGAS was not capable of building a model for those esters.

The development of a kinetics model able to describe the combustion of the five main components of several biodiesels, methyl stearate ($C_{19}H_{38}O_2$), methyl oleate ($C_{19}H_{36}O_2$), methyl linoleate ($C_{19}H_{34}O_2$), methyl linolenate ($C_{19}H_{32}O_2$) and methyl palmitate ($C_{17}H_{34}O_2$), was undertaken by LLNL, Reaction Design, ICARE/CNRS, and C3-NUI (Westbrook *et al.*, 2011a). It comprises approximately 5000 species and 20000 reactions. Using this mechanism, esters can be combined in different proportions, according to the composition of biodiesel. The kinetics model was constructed hierarchically, merging submodels. A breakdown of small molecules was selected as the nucleus. Then a pre-existent model for alkanes up to n-hexadecane was added. The rules by Curran *et al.* (1998) and the unsaturation effects described by Herbinet *et al.* (2010) were used to estimate remaining reaction rates. Sub-mechanisms are divided into high-temperature mechanisms (similar to hydrocarbons mechanisms, with some corrections due to the presence of the ester group and the unsaturations) and low-temperature mechanisms (which have their kinetics characteristics). The model was validated comparing the simulation with measurements in JSR found in the literature (Dagaut *et al.*, 2007; Hakka *et al.*, 2009; Bax *et al.*, 2010) and doing some purely computational experiments. Westbrook *et al.* (2011a) concluded the paper informing improvements to the model in progress. Their model was a milestone in the development of complex kinetics models for biodiesel, but there is still much work being done to explore details of the combustion of long-chain esters and actual biodiesel made of different raw materials.

The Stanford University aerosol shock tube and the shock tube from Rensselaer Polytechnic Institute (USA) were used to obtain IDT from different esters. The model by Westbrook *et al.* (2011a) was updated to reproduce IDT of methyl oleate and methyl linoleate measured by Campbell *et al.* (2013) using an aerosol shock tube. The experimental conditions were: high dilution in argon, 1100 K $\leq T \leq$ 1400 K, 3.5 atm $\leq P \leq$ 7.0 atm and 0.6 $\leq \Phi \leq$ 2.4. The original model by Westbrook *et al.* (2011a) underpredicted IDT. This was corrected by adjusting the kinetics parameters. The same aerosol shock tube was used to measure IDT of methyl palmitate, methyl decanoate, methyl laurate ($C_{13}H_{26}O_2$), and methyl myristate ($C_{15}H_{30}O_2$). Campbell *et al.* (2014) used the same pressure of Campbell *et al.* (2013), 1026 K $\leq T \leq$ 1388 K, and 0.3 $\leq \Phi \leq$ 1.4. The IDT of methyl palmitate, methyl stearate, methyl oleate, and methyl linoleate were measured in different conditions by Wang *et al.* (2014). They also measured IDT for two reference biodiesel fuels, one derived of soy and other derived of animal fats. They used a shock tube operating at 900 K $\leq T \leq$ 1350 K, $P = 10$ atm and $P = 20$ atm, 0.25 $\leq \Phi \leq$ 1.0. All those experimental data are important to improve and validate kinetics models. Other papers testing IDT, kinetics routes, emissions and other physicochemical properties of large esters, biodiesel from different raw materials and blends of diesel and biodiesel have been published recently (Abboud *et al.*, 2018; Zhang *et al.*, 2018; Li *et al.*, 2019).

5. REDUCING AND SIMPLIFYING CHEMICAL KINETICS MODELS

The interest in reducing biodiesel kinetics models started after the methyl decanoate model of Herbinet *et al.* (2008) and intensified after the multicomponent model of Westbrook *et al.* (2011a). The detailed chemical kinetics models were too heavy to simulate complex problems. A reduced model maintains the most important characteristics of the detailed model, with fewer species and reactions. The reduced model must be validated in comparison with the original detailed model. A reduced model can not be used in conditions beyond those used to develop the detailed model (Lu and Law, 2009).

Researchers at the University of California at San Diego (UC), Princeton University and LLNL evaluated experimentally the combustion of methyl decanoate in a counterflow configuration Seshadri *et al.* (2009). The model by Herbinet *et al.* (2008) was too complex to simulate this configuration, therefore it was reduced to a skeletal model of only 125 species and 713 reactions. The directed relation graph methodology (DGR) was employed

The DRG methodology was also used by researchers at UT, LLNL, and University of Connecticut Sarathy *et al.* (2011). They presented new experimental data for methyl decanoate in an opposed-flow diffusion flame, measuring the profiles of several species and the temperature. The model of Herbinet *et al.* (2008) was improved with new kinetics data and then reduced to a model with 648 species and 2998 reactions. The reduced model was validated comparing opposite-flow simulations with the experimental data, and simulations of the detailed and reduced model in PSR and plug flow reactors operating with $900\ \mathrm{K} \leq T \leq 1800\ \mathrm{K}$, $0.25 \leq \Phi \leq 2.0$ and $101\ \mathrm{kPa} \leq P \leq 1013\ \mathrm{kPa}$.

The tricomponent model of Herbinet *et al.* (2010) was repeatedly reduced by researchers from UC, the University of Illinois at Chicago and Argonne National Laboratory (USA) Luo *et al.* (2010, 2012). The first paper used DRG, DRG-aided sensitivity analysis (DRGASA) and isomers lumping to produce a model with 118 species and 837 reactions. This model was validated comparing the simulations of autoignition, PSR and other homogeneous conditions of the original model and the reduced model. It did not cover temperatures under 1000 K (Luo *et al.*, 2010). The second paper used the same methodology but changed DRGASA parameters to include temperatures from 700 K. They also modified some parameters of the Luo *et al.* (2010) model. The new model has 115 species and 460 reactions. It was validated by comparing the simulation of PSR and autoignition with the detailed model and with experimental data of ignition delay, molar fraction and laminar flame speed obtained in the literature. It reproduces NTC and can simulate a turbulent 3D spray (Luo *et al.*, 2012).

A different approach to produce a compact model was presented by Ismail *et al.* (2013). The authors of this work integrate The University of Nottingham Malaysia Campus (Malaysia) and the Polytechnic of Milan (Italy). They chose two esters with a long chain as "main surrogates", a saturated ester (methyl palmitate) and an unsaturated ester (methyl linoleate), and two short-chain esters as "sub surrogates", methyl butanoate and methyl-2-butenote. A preexisting model of "sub surrogates" was reduced using the DRG with error propagation and sensitivity analysis (DRGEPSA). Two main reactions were added to the reduced model to describe "main surrogates" decomposition and connect "main surrogates" to "sub surrogates". Finally, a simplified n-heptane model was added and some parameters were adjusted. The final model has 113 species and 399 reactions and was validated comparing pressure and NOx emissions of a real motor fueled with biodiesel and blends of diesel and biodiesel made of different raw materials, such as coconut, palm, and soy.

A more compact model for the combustion of methyl stearate, methyl oleate, methyl linoleate, methyl linolenate, and methyl palmitate was developed by a group from the Politecnico di Milano (Italy). Chiara Saggese *et al.* (2013) built their model adding species and reactions to a previously validated model of esters from methyl butanoate to methyl decanoate developed by their group (Grana *et al.*, 2012b). They also based their work on the model by Westbrook *et al.* (2011a) but focusing on lumped species and reactions. The result is a model with about 420 species and 13000 reactions, which can be applied more easily than the model of Westbrook *et al.* (2011a). The model of Saggese *et al.* (2013) was validated comparing simulations with the PSR experiments by Dagaut *et al.* (2007); Hakka *et al.* (2009); Bax *et al.* (2010) and pyrolisis data found elsewhere. Later, in a joint work by CNRS and the Politecnico di Milano, Anne Rodriguez *et al.* (2016) made PSR experiments of methyl stearate, methyl oleate, and methyl linoleate. The experimental conditions were $500\ \mathrm{K} \leq T \leq 1050\ \mathrm{K}$, $P = 1.067$ bar, $\Phi = 1$ and $\tau = 2$ s. Those measurements were used to validate and make small improvements in the model of Saggese *et al.* (2013). The kinetics model was compared to previous experimental data (Campbell *et al.*, 2013, 2014; Wang *et al.*, 2014).

The reduced model of Luo *et al.* (2012) did not reproduce the formation of soot. So a different reduced version of the tri-component model of Herbinet *et al.* (2010) was published by researchers from the National University of Singapore An *et al.* (2014). The original model was reduced and then blended with an n-heptane model. The blended model was reduced again by directed relation graph with error propagation and sensitivity analysis (DRGEPSA), peak analysis, isomers lumping, elimination of non-important reactions and adjustment of reaction rates. This model was validated comparing the simulation with experimental data of IDT and CO, CO_2, NO_x and unburned hydrocarbons emissions obtained from a real motor.

Rsearchers from the University of Nottingham Malaysia and the Technical University of Denmark, published another reduced model based on Herbinet *et al.* (2010) model Cheng *et al.* (2015). This model has 92 species and 360 reactions.

The reduction was made using DRG, isomers lumping and sensitivity analysis. Validation was done comparing simulation to experimental data of shock tube, JSR, 2D spray formation and smoke distribution. The IDT simulation results are closer to experimental data than the previous model of An *et al.* (2014). Cheng *et al.* (2015) model innovation is the ability to simulate different proportions of the surrogate components, being able to simulate biodiesel made of different raw materials (coconut, palm, rapeseed, and soybean) and diesel-biodiesel blends.

Another tri-component surrogate was published in the compact model by researchers from the University of Technology (China) and the University of Wisconsin–Madison (EUA) for methyl decanoate, methyl-5-decenoate and n-decane ($C_{10}H_{22}$) Chang *et al.* (2015). Methyl-5-decenoate was chosen due to its unsaturation and the similarities between its combustion and methyl decanoate combustion. N-decane is useful to balance C/O/H proportion. This model assumes that saturated biodiesel esters decompose in methyl decanoate and n-decane, and unsaturated esters decompose in methyl-5-decenoate and n-decane. The model with 60 species and 172 reactions was built by merging sub-mechanisms of each of the components of the surrogate with small-molecule subroutines. The validation was done by comparing the simulations with measured ignition time in a shock tube, fraction of the molecules in a JSR and peak pressure and emission of NOx in a motor using soybean biodiesel.

Researchers from the Hunan University (China) and the National University of Singapore Liu *et al.* (2016); Jiaqiang *et al.* (2016) developed a reduced models based on the detailed model by Westbrook *et al.* (2011a). Liu *et al.* (2016) used DRGEPSA, isomers lumping, computational singular perturbation (CSP) and reaction rate adjustment to produce a 92 species and 242 reactions model that describes methyl linoleate combustion. This reduced model was merged with Chang *et al.* (2015) model. Repeated and unimportant species and reactions were excluded. The new model has 106 species and 263 reactions. It can describe the combustion of methyl linoleate, methyl decanoate, methyl-5-decanoate, and n-decane. Jiaqiang *et al.* (2016) updated the model of Liu *et al.* (2016) with small molecules information. The model of Jiaqiang *et al.* (2016) has 134 species and 475 reactions. Both mechanisms were validated comparing simulation results with experimental data obtained in literature: IDT for methyl linoleate and pressure and emissions of a motor operating with waste oil biodiesel and blends of diesel and biodiesel.

The more recently published papers focus on reduced models for CFD applications, blends of diesel and biodiesel and biodiesel from different raw materials. There are also studies about blends of diesel, biodiesel and alcohols (Alviso *et al.*, 2017; Manojkumar *et al.*, 2018; Zehni *et al.*, 2018).

Table 1 presents a summary of the detailed and reduced chemical reaction mechanisms developed for biodiesel surrogates. Figure 1 presents a map of the number of species and number of reactions of the detailed and reduced mechanisms. We note an approximate power growth of the size of the mechanisms in which the number of reactions is proportional to the 0.9 and 1.6 power of the number of species for the detailed and reduced mechanisms respectively. When compared to the 0.9 power for the detailed mechanisms, we note that the reduced mechanisms have relatively a larger number of reactions per species. This is in agreement with the main purpose of the reduction strategies which is to reduce the number of species, thus reducing the number of equations of conservation of mass of species that need to be solved in a given application.

Figure 2 presents the evolution of the size of the detailed and reduced chemical reaction mechanisms expressed as the number of species. We note the strong effort culminating with the larger detailed mechanisms around 2010. Also, we note that the effort in developing reduced mechanisms followed the trend of trying to use the chemical mechanisms for simulation studies of applications of biodiesel fuels after 2010.

Finally, figure 3 presents the same evolution of the size of the mechanisms in relation to the number o carbon atoms in the esters modeled. The modeling reached the esters with 19 carbon atoms with the possibility of modeling their blends also around 2010. We note, however, that although the detailed mechanisms had a consistent growth of the chemical species needed to model the chemical kinetics, the reduction efforts aimed at keeping the number of species bounded to less than 150 species, which is about a maximum number to run cost effective simulations of the applications.

6. CONCLUSION

The first surrogate proposed to biodiesel was methyl butanoate. Soon, it was discovered that it does not reproduce NTC behavior and therefore is not an adequate biodiesel surrogate. However, the kinetics models are built hierarchically, and this species is an important component of the combustion of larger esters. Therefore there is still need for an accurate modeling of the oxidation of this molecule and improvements on the methyl butanoate kinetics are still been done and updated in large esters models.

The second stage in the development of biodiesel surrogates was the exploration of the combustion of larger esters and alkanes with large carbon chains. Methyl decanoate and n-hexadecane were more often proposed as single component biodiesel surrogates in reduced models, or as part of multicomponent surrogates. The effect of unsaturation is reproduced by methyl crotonate or some of the $C_{11}H_{20}O_2$ isomers. Alkanes, such as n-heptane or n-decane, may be used to balance the C/H/O ratio.

The larger detailed kinetics model in existence was developed by Westbrook *et al.* (2011a). It describes the combustion of the five main esters that compose soy and rapeseed biodiesel. However, due to its size, its use in the simulation of

Table 1: Summary of the detailed and reduced chemical reaction mechanisms developed for biodiesel surrogates.

Detailed mechanisms				
Chemical species	**Number of species**	**Number of reactions**	**Date**	**Reference**
methyl butanoate ($C_2H_4O_2$), methyl formate ($C_2H_4O_2$)	264	1219	2000	Fisher *et al.* (2000)
methyl butanoate ($C_2H_4O_2$)	295	1498	2007	Gaïl *et al.* (2007)
methyl butanoate ($C_2H_4O_2$)	301	1516	2008	(Gaïl *et al.*, 2008)
methyl butanoate ($C_2H_4O_2$)	275	1545	2008	Dooley *et al.* (2008)
n-hexadecane ($C_{16}H_{34}$)	225	1841	2007	Dagaut *et al.* (2007)
methyl hexanoate ($C_7H_{14}O_2$)	435	1875	2008	Dayma *et al.* (2008)
methyl decanoate ($C_1 1H_{22}O_2$)	3012	8820	2008	Herbinet *et al.* (2008)
methyl heptanoate ($C_8H_{16}O_2$)	1087	4592	2009	Dayma *et al.* (2009)
methyl decanoate ($C_1 1H_{22}O_2$)	1251	7171	2010	Glaude *et al.* (2010)
methyl decanoate, methyl-5-decenoate, methyl-9-decenoate ($C_{11}H_{20}O_2$)	3329	10806	2010	Herbinet *et al.* (2010)
methyl octanoate ($C_9H_{18}O_2$)	383	2781	2011	Dayma *et al.* (2011)
methyl palmitate ($C_{17}H_{34}O_2$)	6203	43444	2011	Herbinet *et al.* (2011)
methyl stearate, methyl oleate, methyl linoleate, methyl linolenate, and methyl palmitate	5000	20000	2011	(Westbrook *et al.*, 2011a)
Reduced mechanisms				
Chemical species	**Number of species**	**Number of reactions**	**Date**	**Reference**
methyl decanoate ($C_1 1H_{22}O_2$)	125	713	2009	Seshadri *et al.* (2009)
methyl decanoate ($C_1 1H_{22}O_2$)	648	2998	2011	Sarathy *et al.* (2011)
methyl-5-decenoate, methyl-9-decenoate ($C_{11}H_{20}O_2$)	118	837	2010	Luo *et al.* (2010)
methyl-5-decenoate, methyl-9-decenoate ($C_{11}H_{20}O_2$)	115	460	2012	Luo *et al.* (2012)
methyl palmitate, methyl linoleate, methyl butanoate and methyl-2-butenote	113	399	2013	Ismail *et al.* (2013)
methyl stearate, methyl oleate, methyl linoleate, methyl linolenate, and methyl palmitate	420	13000	2013	Saggese *et al.* (2013)
methyl stearate, methyl oleate, methyl linoleate, methyl linolenate, and methyl palmitate	92	360	2015	Cheng *et al.* (2015)
methyl decanoate, methyl-5-decenoate and n-decane ($C_{10}H_{22}$)	60	172	2015	Chang *et al.* (2015)
methyl linoleate, methyl decanoate, methyl-5-decanoate, and n-decane	106	263	2016	Liu *et al.* (2016)
methyl linoleate, methyl decanoate, methyl-5-decanoate, and n-decane	134	475	2016	Jiaqiang *et al.* (2016)

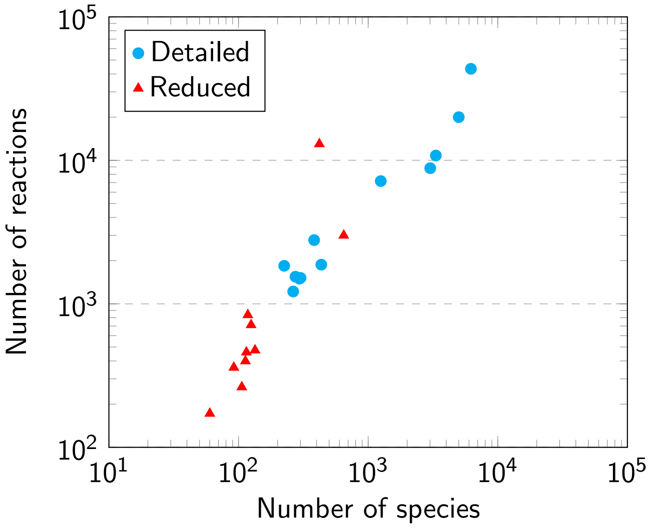

Figure 1: Number of chemical reactions as a function of the number of chemical species for the detailed and reduced chemical kinetics mechanisms for biodiesel surrogates.

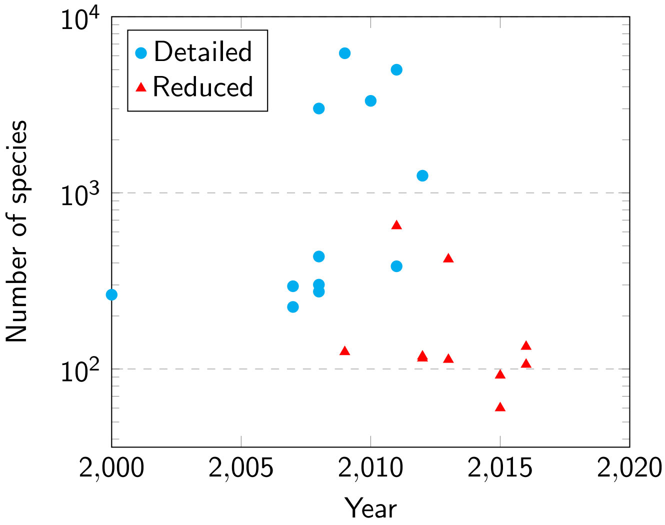

Figure 2: Size of the detailed and reduced chemical kinetics mechanisms for biodiesel surrogates, expressed as the number of chemical species, as a function of the year they were published.

complex phenomena, as those that occur in internal combustion engines, is very time and cost prohibiting. Then, a more compact model for those esters was developed by Saggese *et al.* (2013). Both models are still being improved, according to new experimental data obtained.

Finally, biodiesel composition varies strongly with the raw material used. Most studies focused on biodiesel from oil crops, especially, rapeseed and soybean. Studies done in Asian research groups also focused on coconut, palm, and waste oil. In Brazil, the most used biodiesel raw material is soybean, followed by beef tallow (Empresa de Pesquisa Energética,

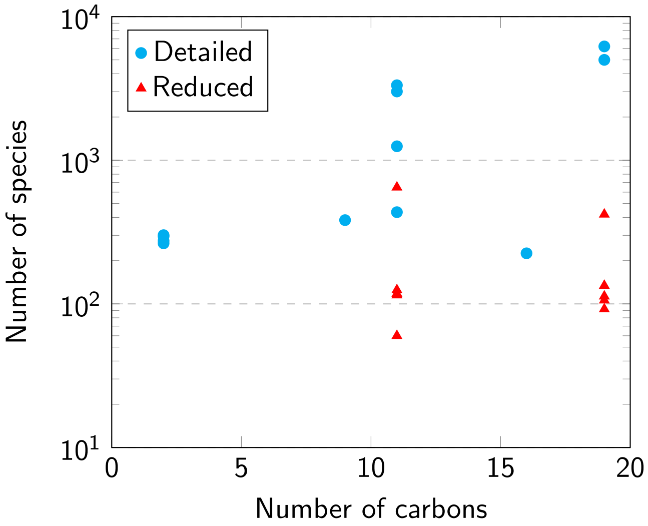

Figure 3: Size of the detailed and reduced chemical kinetics mechanisms for biodiesel surrogates, expressed as the number of chemical species, as a function of the number of carbon atoms in the ester's molecule.

2018). There are only a few experimental data on the basic combustion of biodiesel from animal sources. Biodiesel from algae and different seeds also have different chemical compositions and can have a regional interest duo to economic, environmental or social aspects. All kinetics models must be experimentally validated, therefore it is important to obtain experimental data for the real fuels obtained from different feed stocks, their corresponding surrogates, and the blends of biodiesel and diesel oil. Besides, reduced models are developed according to the target properties and interests of the studies. There are several strategies to reduce kinetics models and, as a consequence, reduce the computational cost of simulating chemical kinetics. These are important research frontiers being currently explored.

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