# GT2011-4) - , &

# EXPERIMENTAL AND MODELLING STUDIES OF THE OXIDATION OF SURROGATE BIO-AVIATION FUELS

Ida Shafagh CFD Centre University of Leeds Leeds, LS2 9JTUK Kevin J. Hughes CFD Centre University of Leeds Leeds, LS2 9JTUK

**Mohamed Pourkashanian** 

CFD Centre University of Leeds

Leeds, LS2 9JTUK

Zhen Liu CFD Centre University of Leeds Leeds, LS2 9JTUK

ABSTRACT

Jet fuels currently in use in the aviation industry are exclusively kerosene-based. However, potential problems regarding security of supply, climate change and increasing cost are becoming more significant, exacerbated by the rapidly growing demand from the aviation sector. Biofuels are considered one of the most suitable alternatives to petrochemical-based fuels in the aviation industry in the short to medium term, since blends of biofuel and kerosene provide a good balance of properties currently required from an aviation fuel. Experimental studies at a variety of stoichiometries using a flat flame burner with kerosene and kerosene/biofuel blends have been performed with product analysis by gas sampling and laser induced fluorescence detection of OH, CO and CO<sub>2</sub>. These studies have been complemented by modelling using the PREMIX module of Chemkin to provide insights into and to validate combined models describing the oxidation chemistry of surrogate fuels depicting kerosene, fatty acid methyl ester biofuels and Fischer-Tropsch derived fuels. Sensitivity analysis has identified important reactions within these schemes which where appropriate have been investigated by molecular modelling techniques available within GAUSSIAN 03.

## INTRODUCTION

The recent concerns over the disadvantages of fossil fuel for air transport, of which the most important concern their contribution to greenhouse gas emissions and their security of supply, have raised the need to look at alternative fuels as a new source of energy. To that end, potentially sustainable and environmentally friendly fuels are being considered. Bioliquid fuels derived from renewable energy Elena Catalanotti CFD Centre University of Leeds Leeds, LS2 9JTUK

Chris W. Wilson Department of Mechanical Engineering University of Sheffield S1 3JD

sources are one of the alternatives. Beside the fact that biofuels are renewable, research has also shown that diesel engines operating with biodiesel produce less CO, unburned hydrocarbons and particulates [1]. Moreover, the combustion of alternative biofuels can be considered to be carbon-neutral since their carbon content is derived from  $CO_2$  which previously existed in the atmosphere. A widely used biofuel is biodiesel which typically consists of mixtures of saturated and unsaturated methyl esters produced through a transesterification reaction between a lipid source and an alcohol, as shown in Figure 1.



Methanol

Triglyceride

Fatty Acid Methyl Esters Glycerol

# Figure 1. Transesterification reaction between a lipid source and an alcohol;

Fatty acid methyl esters (FAMEs) with the general formula  $R-C(O)O-CH_3$  with carbon chains of 12 to 22 atoms in length are the foremost constituents of biodiesel [2]. The chemical structure of biodiesel is considerably different in comparison to traditional fuels and therefore there is much need of fundamental studies to generate the basic data with regard to their oxidation mechanism. To date, only a few studies have been made to predict the combustion of biodiesel type aviation fuels using detailed chemical kinetics comparing to other hydrocarbon fuels.

Modelling the combustion of methyl esters has become an interesting subject in the past few years, because of the potential of replacing fuels based on petrochemicals with biodiesel, a complex mixture of FAMEs derived from vegetable oil. Mixtures of 80% kerosene and 20% FAMEs were widely considered as a possible option to be used in aviation, however, because of the physical properties of FAMEs and their levels of metallic contaminants this is no longer an acceptable option and in practice, only synthetic Fischer Tropsch derived fuels have a future as a kerosene replacement. Few studies have investigated the oxidation chemistry of oxygenated compounds, such as acetic and propanoic acids [3, 4], followed by detailed chemical reaction mechanisms for small fatty acid methyl esters as biofuel surrogates [5-10]. Dagaut et al. [11] developed a model for the combustion of biokerosene basing it on previous studies [12] which showed that the biofuel portion (typically rapeseed methyl esters, RME) could be well represented by hexadecane. The model showed overall a good agreement with experiments, although it did not consider the chemistry of the methyl ester group and the influence of the presence of oxygen in the fuel on the overall stoichiometry.

A reaction mechanism for the oxidation of biokerosene (AFRM v2.0) [13] has been previously developed by the authors using methyl butanoate (MB, CH<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>C(O)OCH<sub>3</sub>) as FAMEs' representative in the biofuel. One of the initial studies on MB was carried out by Fisher et al. [5]. They developed the first detailed chemical kinetic model for the combustion of MB. Since then a number of additional experimental and theoretical studies have been carried out on MB. Gail et al. [6] validated Fisher's MB oxidation reaction mechanism in a jet stirred reactor and an opposed-flow diffusion flame, resulting in some modification to the initial reaction mechanism. Metcalfe et al. [7] studied the oxidation of MB and ethyl propanoate (EP) under high-temperature in a shock tube. They found the ignition of EP to be faster than that of MB, and also improved the existing chemical kinetic mechanisms. In addition to the experimental studies a number of computations including molecular modelling studies have been carried out to investigate the different pathways of decompositions of MB at high temperatures. El-Nahas et al. [8] used a Complete Basis Set (CBS) method to evaluate the properties of unimolecular and bimolecular reactions of MB. Huynh and Violi [9] also used a theoretical approach to estimate the rate constants for various decomposition channels. Recently Dooley et al. [1] used both an experimental and theoretical approach to study the autoignition of MB in a shock tube which resulted in a number of reactions to be added to the MB reaction mechanism. They found that the autoignition of MB follows Arrhenius-like temperature dependence.

Although MB has the essential chemical characteristics of typical FAME biofuels, its relatively high oxygen content leads to a lower energy density than would be the case for real fuels, therefore there is a need to address this problem by increasing the carbon and hydrogen composition by extending the carbon chain. Herbinet et al. [10] investigated methyl decanoate with the formula

 $CH_3(CH_2)_7C(O)OCH_3$  as the surrogate. Their work includes developing an oxidation mechanism for biodiesel fuels which have been validated against experimental data and shows the early formation of carbon dioxide in the combustion of biofuels.

In this study a methyl ester with a carbon chain of thirteen carbon atoms has been chosen, methyl tridecanoate CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>C(O)OCH<sub>3</sub>, for the biodiesel surrogate. As a result of their physical properties and the complexity of their reaction pathways, from an experimental perspective it is difficult to study the reaction kinetics of such heavy molecules using classic techniques. However, it is recognised that many important combustion phenomena such as ignition, pollution and efficiency cannot be modeled unless there is a detailed chemical kinetic reaction mechanism available. Therefore, a detailed chemical kinetics mechanism was developed and tested against experimental data for both a blend (20% biofuel, 80% kerosene)<sup>a</sup> and pure kerosene, under a range of conditions in order to validate the mechanism. The required kinetic data for the development of the mechanism were obtained through quantum chemistry calculations. The reaction mechanism for the oxidation of kerosene and methyl tridecanoate (MTD) was initially developed using the AFRM v2.0 [13] as a base, and as a result of sensitivity analysis has been optimized based on data reported in the NIST chemical kinetics database [14] and the review of Baulch et al. [15] to improve the fit with the experiments.

a. This research was performed prior to the decision on lowering the FAMEs percentage in aviation fuels.

## EXPERIMENTAL SET UP

The kerosene burner used to perform the experiments was designed by Kyne [16] to produce a flame approximating to a laminar premixed flame; a schematic diagram is shown in Figure 2. The combustion performance of liquid fuels can be enhanced by atomizing the fuel prior to vaporisation. However, the stability of the resulting flame is very sensitive to the atomization process. In the kerosene burner, the volume of the atomizing section is adjustable in order to obtain optimal conditions for the atomization process to achieve a stable flame. The fuel is forced through a pipe to reach the atomizing section, where the liquid encounters a high-pressure jet of air consisting of about 30% of the total air. The kinetic energy of the air generates atomization by breaking the liquid into droplets exiting via a small nozzle. The size of the droplets depends on the velocity of the atomizing air, and therefore on the internal configuration of the burner controlled by the position of the adjustable block which differs according to the type of the fuels used and the stoichiometries. After atomization the fuel spray enters a chamber heated to 463K where it vaporises. At this stage the final mixing process occurs by introducing the residual 70% of the air into the chamber where a series of metal shavings and honeycomb straighteners enhance the mixing process while ensuring a uniform flow field prior to the fuel/air mixture reaching the burner surface. The burner matrix consists of a 2.5cm diameter disc of thickness 3mm, drilled with 130, 0.5mm diameter holes. The fuel is

delivered and metered using a Brooks Instruments mass flow controller model 5881, while the atomizing and secondary air arrive via Hastings model HFC-202 mass flow controllers. The mass flow controllers are set to flow rates of the fuel and air between 0.1227 to 0.1374 gs<sup>-1</sup> covering stoichiometries from 0.79 (lean) to 1.14 (rich). A 75µm diameter quartz probe placed above the burner is used to sample the flame via a water trap to a system of gas analysers connected to a data logging system. A 'Servomex' paramagnetic  $O_2$  analyser was used to measure the % mole fraction of oxygen in the sample. CO<sub>2</sub> and CO concentrations were measured using infrared analysers, a Hartmann and Braun Advanced Optima URS14 analyser was used in measuring CO, while a Signal series 2000 instrument was used for CO2. A Signal series 4000chemiluminescence analyser was used to measure the concentration of NO in the gas sample. Temperature measurement of the flame is performed by a silica coated type R fine wire thermocouple corrected for radiation losses. Relative OH concentration profiles are obtained via the technique of planar laser induced fluorescence (PLIF).

A Nd:YAG (Continuum Surelite III) pumped dye laser (Sirah Cobra-Stretch) is used to generate tunable laser radiation at 283.011nm to excite the Q1(6) transition of OH  $A^2 \Sigma^+ (v' = 1) \leftarrow X^2 \Pi(v'' = 0)$ . Light sheet optics generate a laser light sheet of approximately 2 cm diameter, and the resulting fluorescence from OH in the flame is imaged via a UV lens through an interference filter centered at 308nm onto a high speed gated image intensifier (Hammamatsu C9546 03) with detection by a Dantec Dynamics HiSense Mk II CCD camera. A schematic diagram of the laser experimental setup is given in Figure 3. For the quantitative determination of the concentration of OH a number of manipulations had to be made. To correct for variations in power accross the laser sheet, a quartz cuvette filled with water is used previous to each measurement, to produce a correction factor for the OH signal collected from the flame. Background noise is also subtracted from the data. Calibration is performed via comparison with a premixed methane laminar flame. For this purpose, experiments were run using a McKenna burner; and for the simulations the well validated GRI v 3.0 mechanism for methane was used [17]. Data processing is performed with Dantec Dynamics DynamicStudio V2.30 for analysis of the fluorescence data, and the gas sampling and the temperature data is transferred to PC via analog to digital converters and processed with ChartView.

### THEORETICAL STUDIES Electronic Structure Calculations

All quantum chemical calculations were performed using the Gaussian 03 program [18]. The first step to obtain the required data is to optimize the structures of the reactants, products and the relevant transition states (TS). These optimized structures are then used to execute the frequency calculations. Contributions to the thermochemical properties for the reactants and products are computed based on the vibrational, electronic, rotational and translational motions of the atoms in the molecules. Obviously the results obtained from these procedures will be dependent on the particular methods used. Here the geometries of the reactants, products and transition states involved in the set of studied reactions were optimized using Density Functional Theory (DFT) [19] at B3LYP [20-23] level (Becke 3 parameter exchange, Lyp, Yang and Parr correlation). The basis set applied was 6-311G(d,p). The estimated mean average error in atomization energy using this method is ~4.5 kcal mol<sup>-1</sup> [24]. These optimized geometries were followed by energy and vibrational frequency calculations using the same level of theory. Contributions from these harmonic vibrational frequencies results in the final thermodynamic quantities of the reaction components. A scaling factor of 0.9877 has been recommended for B3LYP/6-311G(d) calculations which was also applied to the calculations in the current study [25].

### **Rate Constant Calculations**

The unimolecular decompositions of C-14 methyl ester involving rupture of a bond and formation of unstable radicals along with H-atom abstractions are studied in the present work. For the cited unimolecular reactions there are no obvious transition states since there is no well-defined potential energy maximum along the reaction path [26]. For the unimolecular decompositions the rate constants at a given temperature are calculated using RRKM theory as implemented in KHIMERA [27, 28]. Applying this method it is possible to interpolate the required kinetic and thermochemical data along the reaction coordinates based on the electronic structure data for the reactants, products and a few additional points. The energy dependent rate coefficients are given by Equation (1):

$$k(E) = \left(\frac{m^* \sigma g_e^*}{m \sigma^* g_e}\right) \frac{N^* (E - E_0)}{h \rho(E)} \tag{1}$$

where the rate constant k is written as a function of energy,  $m^*$  and m are the number of optical isomers,  $\sigma^*$  and  $\sigma$  are the external symmetry numbers,  $g^*_e$  and  $g_e$  are the electronic degeneracies of the transition state,  $N^*(E - E_0)$  is the sum of ro-vibrational states of the transition state (i.e. the total number of states with energy  $\leq (E - E_0)$ ),  $\rho(E)$  is the density of ro-vibrational states of the reactant,  $E_0$  is the threshold energy for the reaction, and finally h is the Plank constant. As there is no barrier height for such reactions the structure of a semi-transition state should be inserted in the input file to make it possible for the program to follow the reaction path. The collision model for downward energy transfer used for master equation calculations is the exponential-down model as shown in Equation (2):

$$P_d(E, E') = \frac{1}{N(E')} \exp\left(\left|\frac{E'-E}{\alpha}\right|\right) \quad (E' > E)$$
(2)

where  $P_d(E, E')$  is the probability of downward (deactivating) collisional energy transfer from internal energy E' to E, N(E') is a normalisation factor, and  $\alpha$  is a constant equivalent to the average transfer energy of a deactivating collision  $\langle \Delta E \rangle_d$  at moderate-to-high energies.  $\langle \Delta E \rangle_d$  was set to 500 cm<sup>-1</sup>. This value is almost half way between a weak inert gas collider (~100 cm<sup>-1</sup>) and a strong collider (~1000 cm<sup>-1</sup> or greater) and is sufficient for most practical applications [28-30]. Nitrogen was chosen as the bath gas since it is the major component in air, the function of the bath gas is to facilitate energy transfer by collisions and energise the reacting molecule. This energized molecule may then react to form products, or alternatively be deenergized by further collisions. From the corresponding unimoleular decomposition reactions the rate constants for the recombination reactions were estimated using Equation (3):

$$k_r = k_d / K_{eq} \tag{3}$$

where  $k_r$  is the recombination rate constant,  $K_{eq}$  is the equilibrium constant and  $k_d$  is the decomposition rate constant. The unimolecular decomposition and their corresponding reverse reactions were studied over the temperature 500-1500 K.

Bimolecular reactions include the hydrogen abstraction reactions by flame reactive radicals. Usually such reactions possess considerable barrier height and a clear structure for the transition state which clarifies the reaction path. The electronic structure data obtained through Gaussian 03 was imported into the KHIMERA program to calculate the forward rate constants for these reactions. For calculating these rates the Transition State Theory (TST) was applied [31]. The restriction of this method is that temperature is bounded from above by the requirement that the potential barrier heights for the reactants in the direct and reverse reactions are much higher than thermal energy. It is also bounded from blow with the assumption that the



Figure 2. Schematic diagram of kerosene burner;

tunneling effect can be neglected. In addition, TST is used for the calculation of the isomerisation reactions' rates.

For the forward reactions the reaction rate is calculated from Equation (4):

$$k(T) = B(T) \exp\left[-\frac{(E_{el}^{\#} + E_{z}^{\#}) - (E_{el,X} + E_{z,X}) - (E_{el,Y} + E_{z,Y})}{RT}\right]$$
(4)

where k is the reaction rate, B is the pre-exponential factor,  $E_{el}$  and  $E_z$  are the electronic energy and zero-point correction and R is the ideal gas constant. The # sign highlights the transition state, while X and Y represent the reactants. The pre-exponential factor is calculated using Equation (5):

$$B(T) = N_A \frac{k_B T}{h} \left[ \frac{2\pi m_X m_Y k_B T}{(m_X + m_Y) h^2} \right]^{-3/2} \frac{g^{\#}}{g_X g_Y} \frac{Q^{\#}}{Q_X Q_Y}$$
(5)

where  $N_A$ ,  $k_B$ , T, h, m, g and Q are Avogadro's constant, Boltzmann constant, temperature, Plank constant, mass of the particle, degeneracy of the particle and the partition function respectively. The bimolecular reactions and their corresponding reverse reactions were studied over the temperature 300-2500 K. To express the temperature dependence of a reaction rate constant at a desired range of temperature the modified Arrhenius equation, Equation (6), can be fitted to the results obtained.

$$k(T) = AT^{n} \exp\left(-\frac{E_{a}}{RT}\right) \tag{6}$$



Figure 3. Schematic diagram of laser experimental setup;

where A is the pre-exponential factor, T is the temperature, n is the term describing the temperature dependence of the preexponential factor,  $E_a$  is the activation energy and R is the ideal gas constant. The extracted rate expression parameters were used for the simulation of the proposed mechanism performance.

# Development and Modelling the Oxidation Mechanism

Detailed chemical mechanisms consist of entire sets of reactions occurring in a combustion system for which the rate coefficient parameters are often stated in the form of the modified Arrhenius Equation as shown in Equation (6). The reaction rates are either obtained through direct measurements or estimated from theoretical considerations. There are three distinct ways of estimating reactions rates, including:

- 1. Using analogies between similar types of reactions.
- 2. Applications of theories of rate processes in a
- conventional manner.
- 3. Modern quantum chemical calculations.

A detailed chemical reaction mechanism for an asymmetric long chain molecule, such as MTD would contain several thousands of reactions for hundreds of species if approximations were not considered. In addition, considering the difficulties involved in the experimental studies of possible individual reactions for MTD, theoretical investigations represent the best option.

In quantum chemical calculations, to predict thermochemistry and reaction rate parameters, the total energy of a molecular system must be determined as a function of its geometrical configuration in space, which requires resolving the interactions between all the atoms comprising the system. Thus, a stable structure refers to the configuration with the lowest energy. A chemical reaction represents the path from one stable structure (reactant) to another (product) linked together (often) through an unstable structure called the transition state (TS). The barrier height corresponding to the TS structure is the activation energy to the reaction.

Due to the very similar structures of MTD and MB, as shown in Figure 4, it is sensible to assume that the degradation process of MTD can be described in a similar way as for MB. We have previously developed an oxidation mechanism (AFRM v2.0) to investigate the performance of the surrogate fuel, MB [13]. Therefore, AFRM v2.0 [13] was chosen as the starting point in the development of the new mechanism for those reactions involving the carbons up to position 4. Figure 5 presents a schematic representation of the oxidation process, from the parent molecule to smaller species. The final mechanism consisted of 321 species, 101 irreversible and 1538 reversible reactions, and includes kerosene, MTD, NOx, SOx and PAH oxidation chemistry. The rates for reactions related to carbons 1 to 3 were kept unchanged from the parent mechanism AFRM v2.0 [13], except for the classes of reactions listed in Table 1. For these specified reactions, reaction rate parameters were calculated using molecular modeling techniques as described before. In order to reduce to a minimum the steps for the breakdown of the MTD and keep the mechanism relatively simple, the reactions of H-atom abstractions or C-C bond dissociation involving carbons 5 to 14 were omitted, assuming that the subsequent chemistry that would arise (alkyl radical decomposition) can be encapsulated in the already existing alkyl radical breakdown reactions within the mechanism. In selecting a C-14 FAME the additional CH<sub>2</sub> groups introduced compared to MB are sufficiently removed from the ester group such that the influence of the ester group on the chemistry is negligible, and therefore the additional thermal decomposition and hydrogen abstraction data obtained are equally valid for the additional CH<sub>2</sub> groups introduced in extending MB to a C-14 FAME.



Figure 4. Methyl butanoate and methyl tridecanoate molecular structures;

For the breakdown of long chain hydrocarbons (i.e.  $C_{12}H_{25}$ ,  $C_{11}H_{23}$ ) the rates already contained in AFRM v2.0 [13] for the decomposition of  $C_{10}H_{21}$  were used. The thermodynamic data of the new species introduced in the mechanism were taken from the work of Herbinet et al. [10] for the hydrocarbon species: C<sub>9</sub>H<sub>19</sub>; C<sub>9</sub>H<sub>18</sub>; C<sub>8</sub>H<sub>17</sub>; C<sub>8</sub>H<sub>16</sub>; C<sub>6</sub>H<sub>12</sub>; C<sub>5</sub>H<sub>10</sub>. For those species whose thermodynamic data were not available, the program THERM (Thermo Estimation for Radicals and Molecules) [32] was used to produce an appropriate set of NASA polynomial coefficients. The calculations of the thermodynamic data were based on the Benson's group additivity method [33] for gas phase radicals and molecules. The NOx chemistry section is taken from the Gas Research Institutes Mechanism version 2.11 [34]. The mechanism was then extended by the addition of sulphur and polycyclic aromatic hydrocarbon (PAH) chemistry. The SOx chemistry section describes the chemistry of simple sulphur species; based on the work of Hughes et al. [35].

### **KINETIC MODELLING TOOLS**

The perfectly stirred rector simulations and the laminar flame species profile simulations were performed using the PSR and PREMIX components of CHEMKIN<sup>TM</sup> [36], a FORTRAN computer program that predicts the steady-state temperature and composition of the species in a perfectly stirred reactor. The perfectly stirred reactor consists of a small, thermally insulated chamber that has inflow and outflow, with the assumption that the mixing process is infinitely fast and thus that the rate of conversion from reactants to products is controlled by chemical reaction rates and not by mixing processes. Therefore complicating factors that would be caused by spatial temperature and concentration gradients are avoided. Additionally, the SPRINT FORTRAN code [37] was setup to perform identical simulations to PSR, and also if required homogeneous static

reactor simulations, with the advantage that it could be manipulated to aid in the sensitivity analysis by the use of automated scripts to systematically vary the rate coefficient of individual chemical reactions and explore the response of the system to these variations.

No.	Reactions
(1)	$MTD \rightleftharpoons MP3J + C_{10}H_{21}$
(2)	$MTD \rightleftharpoons TDAOJ+ CH_3$
(3)	$MTD \rightleftharpoons ME2J+C_{11}H_{23}$
(4)	$MTD \rightleftharpoons CH_3OCO + C_{12}H_{25}$
(5)	$MTD \rightleftharpoons CH_3O + C_{12}H_{25}CO$
(6)	$MTD2J \rightleftharpoons C_{11}H_{23}CHCO + CH_3O$
(7)	$MTD2J \rightleftharpoons MP2D + C_{10}H_{21}$
(8)	$MTD2J \rightleftharpoons MTD2D + H$
(9)	$RO+MTD2J \rightleftharpoons R+MTD2O^{(a)}$
(10)	$RO+MTD3J \rightleftharpoons R+MTD3O^{(a)}$
(11)	$RO+MTD4J \rightleftharpoons R + MTD4O^{(a)}$
(12)	$RO+MTDMJ \rightleftharpoons R + MTDMO^{(a)}$
(13)	MTD3J ≓ MTD2D + H
(14)	MTD3J ≓ MTD3D + H
(15)	$MTD3J \rightleftharpoons MB3D + C_9H_{19}$
(16)	$MTD4J \rightleftharpoons C_{11}H_{22} + ME2J$
(17)	$MTD2D+R \rightleftharpoons MTD3D2J + RH^{(a)}$
(18)	$MTD3D+R \rightleftharpoons MTD3D2J + RH^{(a)}$
(19)	$MTD3D2J \rightleftharpoons C_{10}H_{20}CHCHCO + CH_{3}O$
(20)	$C_nH_{2n+1}CO \rightleftharpoons C_mH_{2m+1}CHCO + H^{(b)}$
(21)	$C_nH_{2n+1}CO \rightleftharpoons CH_2CO + C_mH_{2m+1}^{(b)}$
(22)	$C_nH_{2n+1}O \rightleftharpoons C_mH_{2m+1}CHO + H^{(b)}$
(23)	$C_{10}H_{20}CHCH_2 \rightleftharpoons C_3H_4 + C_9H_{19}$
(24)	$C_{10}H_{20}CHCH_2 \rightleftharpoons C_3H_4(A) + C_9H_{19}$
(25)	$C_qH_{2q+1} \rightarrow C_2H_4 + C_1H_{2l+1}^{(c)}$
(26)	$C_qH_{2q+1} \rightarrow C_3H_6 + C_pH_{2p+1}^{(c)}$
(27)	$C_qH_{2q+1} \rightarrow C_4H_8 + C_rH_{2r+1}^{(c)}$
(28)	$C_qH_{2q} \rightarrow C_3H_5 + C_pH_{2p+1}$
(29)	$C_q H_{2q} \rightarrow C_3 H_6 + C_p H_{2p}^{(c)}$
(30)	$C_{11}H_{20} \rightarrow C_3H_4(P) + C_8H_{16}^{(d)}$
(31)	$C_{11}H_{20} \rightarrow C_3H_3 + C_8H_{17}^{(d)}$

Table 1. List of the new reactions added to AFRM v2.0 [13].

<sup>(a)</sup> R refers to OH, HO<sub>2</sub>, H, CH<sub>3</sub> and O.

<sup>(b)</sup> n = 9 to 12; m = n-1.

<sup>(c)</sup> q=8 to 12; l=q-2; p=q-3; r=q-4.

<sup>(d)</sup> For C<sub>6</sub>H<sub>10</sub>

### **RESULTS and DISCUSSIONS**

Initially the performance of the mechanism was tested using experimental data of Dagaut et al. [11] for the oxidation of a blend of 80% kerosene, with 20% RME (rapeseed methyl esters) in a Jet Stirred Reactor for a lean ( $\varphi = 0.5$ ) and a stoichiometric ( $\varphi = 1.0$ ) flame, and the results are shown in Figures 6 and 7. In both lean and stoichiometric cases the results indicated the same type of discrepancies between simulations and experiments. The main problems occurred in the CO-CO<sub>2</sub> conversion, which was too high at low temperature, as well as in a severe underprediction of CO at high temperature. In order to improve the performance of the

mechanism, sensitivity analyses were performed by sequentially varying individual reaction rate coefficients by a fixed factor, which allowed the identification of the most influential reactions responsible for the concentration profiles of each particular species at defined temperatures. The results of the sensitivity analysis are shown in Figure 8 for 850K and figure 9 for 1200K.

As expected the main reaction controlling the conversion of CO to CO<sub>2</sub> either at low and high temperature was the oxidation of CO with OH which produces  $CO_2$  and H. Second in importance at low temperature was the reaction of CO with HO<sub>2</sub>, while at high temperature the branching reaction between H and O<sub>2</sub> leading to O and OH radicals was also prominent, as was the case for the CH<sub>4</sub> concentration profile at high temperature. The importance of these three reactions is related to the fact that they govern the OH levels in the mixture; therefore modifications applied on these rates had a massive impact on the performance of the mechanism. It was observed that a reduction of the rate of these reactions would allow better prediction of CO<sub>2</sub>, CO and CH<sub>4</sub>. Other reactions were slightly modified to achieve a better fit with experiments also for minor species. Particularly interesting is the modelling of  $C_2H_2$  because of its role of precursor in the PAH formation. All the modifications in the rates were performed keeping the values consistent with the ranges reported in the NIST database [14] and the review of Baulch et al. [15].

The optimized version of the mechanism was called AFRMv2.1, and the performance was tested against the same experimental data for biokerosene as before and the previous version. The results are shown in figures 6 and 7.

Significant improvements were achieved in the overall performance, especially for main species such as CO, CO<sub>2</sub>, CH<sub>4</sub>, but also for minor species. Additional experimental data were produced in this work. Premixed laminar flames of kerosene and biokerosene were studied and the data compared with the optimized mechanism AFRM v2.1. In Figure 10 the results for stoichiometries 0.96 and 1.14 are shown. The model shows overall a good agreement with the data, although it seems to slightly under estimate the production of CO<sub>2</sub>, compensated by an over production of CO in the area closer to the burner. However the major species are reasonably well represented. OH profiles present a different trend. Kerosene is in fact well modelled in the case of the rich flame, while in the lean case it is under predicted. Whereas, biokerosene OH profiles are over-predicted in both cases, as shown in Figure 11. A comparison of the lean flames of both the fuels also shows that while experimentally the peak OH value for kerosene is higher than that reached by biokerosene, the model shows a different trend, with biokerosene reaching higher levels of OH then kerosene (Figure 12). This indicates that although progress has been made in optimisation of the model with respect to many of the major species, questions remain to be solved with respect to important intermediates such as OH.



Figure 5. Schematic representation of decomposition and oxidation of Methyl Tridecanoate (MTD)



Figure 6. Species profiles for the oxidation of biokerosene (80% kerosene, 20% MTD) in a Jet Stirred Reactor ( $\phi = 0.5$ , P = 10 atm,  $\tau = 0.5$ s, O<sub>2</sub>= 3.4246%). Filled squares represent the experiments, black lines are simulations performed with the initial MTD mechanism, red lines represent the optimized version AFRMv2.1.



Figure 7. Species profiles for the oxidation of biokerosene (80% kerosene, 20% MTD) in a Jet Stirred Reactor ( $\phi = 1.0, P = 10 \text{ atm}, \tau = 0.5s$ , O<sub>2</sub>= 3.4246%). Filled squares represent the experiments, black lines are simulations performed with the initial MTD mechanism, red lines represent the optimized version AFRMv2.1

![](_page_9_Figure_0.jpeg)

Figure 8. Sensitivity analysis performed for the main species in a lean biokerosene flame ( $\phi = 0.5$ , P = 10 atm,  $\tau = 0.5$ s, O<sub>2</sub>= 3.4246%, T = 850K);

![](_page_9_Figure_2.jpeg)

Figure 9. Sensitivity analysis performed for the main species in a lean biokerosene flame ( $\phi = 0.5$ , P = 10 atm,  $\tau = 0.5$ s,  $O_2 = 3.4246\%$ , T = 1200K);

![](_page_10_Figure_0.jpeg)

Figure 10. Comparison of experimental and simulated mole fractions of some of the main combustion products, as a function of distance from burner surface for atmospheric premixed kerosene flames. Two stoichiometries are shown: red is  $\phi$ =1.14; black is  $\phi$ =0.960. Filled squares represent the experiments, lines are simulations. The values reported are for dry gases, except for OH;

![](_page_10_Figure_2.jpeg)

![](_page_11_Figure_0.jpeg)

Figure 11. Comparison of experimental and simulated mole fractions of some of the main combustion products, as a function of distance from burner surface for atmospheric premixed biokerosene flames. Two stoichiometries are shown: red is  $\phi$ =1.14; black is  $\phi$ =0.960. Filled squares represent the experiments, lines are simulations. The values reported are for dry gases, except for OH;

![](_page_11_Figure_2.jpeg)

Figure 12. Comparison of experimental and simulated OH profiles for lean ( $\phi$ =0.960) atmospheric premixed kerosene and biokerosene flames. Dotted lines are experimental data; solid lines are simulations. Red represents kerosene; black is biokerosene;

### CONCLUSIONS

A previously developed reaction mechanism to model biofuel/kerosene mixtures was extended to model a C-14 FAME, methyl tridecanoate, that is more representative of real biofuels in terms of its molecular weight, oxygen fraction, and hence energy density. Molecular modeling tools were used to investigate and calculate rate coefficient parameters for 31 of the additional reactions associated with the MTD oxidation mechanism. The resulting mechanism was validated against literature experimental data obtained from jet stirred reactor studies, along with new data reported in this paper for species profiles measured in a burner approximating to a laminar premixed flame. Sensitivity analysis was used to identify important components of the mechanism, which were then tuned within acceptable limits to improve the predictions of the mechanism such that reasonable agreement between experiment and simulation was obtained in most cases, although unresolved questions remain in some cases, specifically the trends in OH predictions.

### ACKNOWLEDGEMENTS

We acknowledge the Higher Education Funding Council for England's (HEFCE) Higher Education Innovation Fund (HEIF 3) OMEGA partnership for the partial funding of Ida Shafagh.

#### REFERENCES

[1] Dooley, S., Curran, H., Simmie, J.M., 2008, "Autoignition measurements and a validated kinetic model for the biodiesel surrogate, methyl butanoate", Combustion and Flame, **153**, 2-32.

[2] Graboski, M.S., McCormick, R.L., 1998, "Combustion of fat and vegetable oil derived fuels in diesel engines", Progress in Energy and Combustion Science, **24**, 125-164.

[3] Mackie, J.C., Doolan, K.R.B., 1984, "High Temperature Kinetics of the Thermal Decomposition of Acetic Acid and its product", International Journal of Chemical Kinetics, **16**, 525-541.

[4] Doolan, K.R., Mackie, J.C., Reid, C.R., 1986, "High Temperature Kinetics of the Thermal Decomposition of the lower Alkanoic Acids", International Journal of Chemical Kinetics, **18**, 575-596.

[5] Fisher, E.M., Pitz, W.J., Curran, H.J., Westbrook, C.K.,

2000, "Detailed Chemical Kinetic Mechanisms for Combustion of Oxygenated Fuels", Proceedings of the combustion institute, **28**, 1579-1586.

[6] Gail, S., Thomson, M.J., Sarathy, S.M., Syed, S.A., Dagaut, P., Diévart, P., Marchese, A.J., Dryer, F.L., 2007, "A wide-ranging kinetic modeling study of methyl butanoate combustion", Proceedings of the Combustion Institute, **31**, 305-311.

[7] Metcalfe, W.K., Dooley, S., Curran, H.J., Simmie, J.M.,

El-Nahas, A.M., Navarro, M.V., 2007, "Experimental and Modelling Study of C5H10O2 Ethyl and Methyl Esters", Journal of Physical Chemistry A, **111**, 4001-4014.

[8] El-Nahas, A.M., Navarro, M.V., Simmie, J.M., Bozzelli, J.W., Curran, H.J., Dooley, S., Metcalfe, W., 2007, "Enthalpies of Formation, Bond Dissociation Energies and Reaction Paths for the Decomposition of Model Biofuels: Ethyl Propanoate and Methyl Butanoate" Journal of Physical Chemistry A, **111**, 3727-3739.

[9] Huynh, L.K., Violi, A., 2008, "Thermal Decomposition of Methyl Butanoate: Ab Initio Study of a Biodiesel Fuel Surrogate", 73, 94-101.
[10] Herbinet, O., Pitz, W.J., Westbrook, C.K., 2008, "Detailed

chemical kinetic oxidation mechanism for a biodiesel surrogate", Combustion and Flame, **154**, 507-528.

[11] Dagaut, P., Gaïl, S., 2007, "Chemical Kinetic Study of the effect of a Biofuel Additive on Jet-A1 Combustion", Journal of Physical Chemistry, **111**, 3992-4000.

[12] Dagaut, P., Gaïl, S., Sahasrabudhe, M., 2007, "Rapeseed oil methyl ester oxidation over exended ranges of pressure, temperature, and equivalence ratio: Experimental and modelling kinetic study", Proceedings of the Combustion Institute, **31**, 2955-2961.

[13] Catalanotti, E; Hughes, K.J.; Pourkashanian, M.; Uryga-Bugajska, I.; Williams, A., 2008, "Development of a High Temperature Oxidation Mechanism for Bio-Aviation Fuels", Proceedings of the ASME International Mechanical Engineering Congress and Exposition, **3**, 321-330.

[14] NIST Chemical Kinetics Database, 2008, http://kinetics.nist.gov/kinetics/index.jsp.

[15] Baulch, D.L., Bowman, C.T., Cobos, C.J., Cox, R.A., Just, Th., Kerr, J.A., Pilling, M.J., Stocker, D., Troe, J., Tsang, W., Walker, R.W., Warnatz, J., 2005, "Evaluated Kinetic Data for Combustion Modeling: Supplement II", Journal of Physical and Chemical Reference Data, **34**, 757-1397.

[16] Kyne, A., PhD Thesis "Experimental and theoretical investigation of the oxidation of kerosene", University of Leeds, 2001.

[17] Smith, G.P., Golden, D.M., Frenklach, M., Moriarty, N.W., Eiteneer, B., Goldenberg, M., Bowman, C.T., Hanson, R.K., Song, S., Gardiner, W.C.Jr., Lissianski, V.V., Qin, Z., http://www.me.berkeley.edu/gri\_mech/, 2010.

[18] Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, Jr., J.A., Vreven, T., Kudin,

K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., Pople, J.A., 2004, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford, CT.

[19] Sholl, D.S., Stecke, J.A., 2009, "Density Functional Theory: A Practical Introduction", John Wiley and Sons. p. 238.

[20] Becke, A.D., 1993, "Density-functional thermochemistry. III. The role of exact exchange", Journal of Chemical.Physics. **98**, 5648-5652.

[21] Lee, C., Yang, W., Parr, R.G., 1988, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density", Physical Review B, **37**, 785-789.

[22] Vosko, S.H., Wilk, L., Nusair, M., 1980, "Accurate spindependent electron liquid correlation energies for local spin density calculations: a critical analysis", Canadian. Journal of Physics, **58**, 1200-1211.

[23] Stephens, P.J., Devlin, F.J., Chabalowski, C.F., Frisch, M.J., 1994, "Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields", Journal of Physical Chemistry, **98**, 11623-11627.

[24] Zope, R.R., Dunlap, B.I., 2005, "Accurate molecular energies by extrapolation of atomic energies using an analytic quantum mechanical model", Physical Review B: Condensed Matter and Materials Physics, **71**, 193104/1-193104/4.

[25] Andersson, M.P., Udval, P., 2005, "New Scale Factors for Harmonic Vibrational Frequencies Using the B3LYP Density Functional Method with the Triple-.zeta. Basis Set 6-311+G(d,p)", The Journal of Physical Chemistry A, **109**, 2937-2941.

[26] Pilling, M.J., Smith, I.W.M., 1987, "Modern gas kinetics: theory, experiment and application", Oxford, Blackwell.

[27] KHIMERA v3.1, Motorola Inc., 2001.

[28] Novoselov, K.P., Shirabaikin, D.B., Unanskii, S.YA., Vladimirov, A.S., Minushev, A.KH., Korkin, A.A., 2002, "Software news and updates. CHIMERA: a software tool for reaction rate calculations and kinetics and thermodynamics analysis", Journal of Computational Chemistry, **23**, 1375-1389.

[29] Gilbert, R.G., Smith, S.C., 1990, "Theory of Unimolecular and Recombination Reactions", Oxford, Blackwell Scientific,.

[30] Pilling, M.J., Robertson, S.H., 2003, "Master Equation Models for Chemical Reactions of Importance in Combustion", Annual Review of Physical Chemistry, **54**, 245-275.

[31] Laidler, K., King, C., 1983, "Development of Transition-State Theory", Journal of Physical Chemistry, **87**, 2657-2664.

[32] Ritter, E.R., Bozzelli, J.W., 1991, "THERM: thermodynamic property estimation for gas phase radicals and molecules", International Journal of Chemical Kinetics, **23**, 767-778.

[33] Benson, S., 1976, "Thermochemical Kinetics: methods for the estimation of thermochemical data and rate parameters", second ed., John Wiley & Sons, New York.

[34] Gas Research Institute, <u>http://www.me.berkeley.edu/gri-mech/</u>, 2008.

[35] Hughes, K.J., Tomlin, A.S., Dupont, V.A., Pourkashanian, M., 2001, "Experimental and modelling study of sulphur and nitrogen doped premixed flames at low pressure", Faraday Discussion, **119**, 337-352.

[36] Kee, R.J., Rupley, F.M., Miller, J.A., 1991, CHEMKIN-2: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics. Sandia Laboratories Report: 89-8009B.

[37] Berzins, M., Furzeland, R.M., 1985, Shell Research Ltd., TNER 85058.