



# Experimental study of the oxidation of large surrogates for diesel and biodiesel fuels

Mohammed Hichem Hakka, Pierre-Alexandre Glaude, Olivier Herbinet\*, Frédérique Battin-Leclerc

Département de Chimie Physique des Réaction, Nancy Université, CNRS, Ecole Nationale Supérieure des Industries Chimiques (ENSIC), BP 20451, 1 rue Grandville, 54001 Nancy, France

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## ABSTRACT

The experimental study of the oxidation of two blend surrogates for diesel and biodiesel fuels, *n*-decane/*n*-hexadecane and *n*-decane/methyl palmitate (74/26 mol/mol), has been performed in a jet-stirred reactor over a wide range of temperatures covering both low, and high-temperature regions (550–1100 K), at a residence time of 1.5 s, at quasi atmospheric pressure with high dilution in helium (hydrocarbon inlet mole fraction of 0.002) and at stoichiometric conditions.

Numerous reaction products have been identified and quantified. At low and intermediate temperatures (less than 1000 K), the formation of oxygenated species such as cyclic ethers, aldehydes and ketones has been observed for *n*-decane, *n*-hexadecane, and methyl palmitate. At higher temperature, the formation of these species was not observed any more, and small amounts of unsaturated species (olefins and unsaturated methyl esters) have been detected.

Results obtained with methyl palmitate and *n*-hexadecane have been compared in order to highlight similarities and differences between large *n*-alkanes and methyl esters.

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## 1. Introduction

Biodiesels are new alternative renewable fuels that could answer some of the energy issues that the world is currently facing [1,2]. They are new potential sources of energy that can help to reduce the dependence on petroleum, and it has been demonstrated that their use in diesel engines allows decreasing the amount of some pollutants (carbon monoxide, soot) formed during the combustion. Nitrogen oxide emissions seem to be slightly higher under some engine conditions [3,4].

Biodiesels are composed of fatty acid esters obtained from vegetable oils and animal fats through a process of trans-esterification with an alcohol (e.g., methanol and ethanol) [1]. Biodiesels are mainly produced from rapeseed oil in European countries and from soybean oil in the United States. When methanol is used, they contain five main esters: methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate. The structures of these molecules and the average composition [5] of rapeseed and soybean biodiesels are shown in Table 1. All these esters have very similar structures: a long alkyl chain attached to a methyl ester group. Differences are the length of the alkyl chain (15 atoms of carbon for methyl palmitate and 17 atoms of carbon for the other esters) and the number of double bonds in the chain (no double bond for methyl palmitate and methyl stearate, one double bond

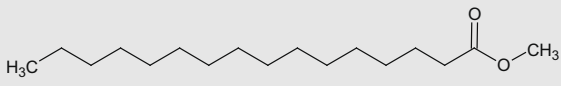
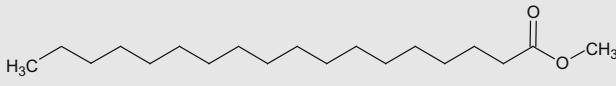
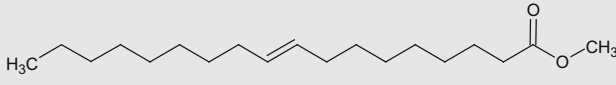
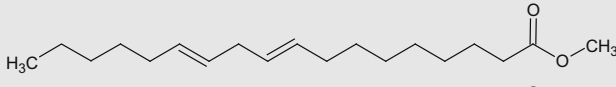
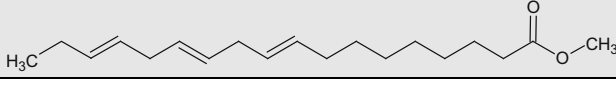
for methyl oleate, two double bonds for methyl linoleate and three double bonds for methyl linolenate).

In contrast to *n*-alkanes [6–10], experimental studies of the combustion of biodiesel fuels or of their individual components are still very scarce. Methyl butanoate (C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>) combustion has been the subject of several studies in the past years because it has a much shorter alkylic chain than esters present in real biodiesels (its vapor pressure is much higher, making gas phase kinetic studies easier). These studies led to a better understanding of the specific chemistry, due to the presence of the ester group, but they also demonstrated that methyl butanoate is not a good surrogate for biodiesels because the alkylic chain is too short and the influence of the ester group on the chemistry is emphasized. In the 1950s the combustion of methyl butanoate was studied in closed vessels [11]. Pressure data were recorded as a function of time. These experimental results were used by Fisher et al. in the validation of a detailed kinetic mechanism for the oxidation of this species [12]. While the experimental studies have mainly been performed under conditions corresponding to the high-temperature region, this mechanism, written by analogy with *n*-alkanes, included all relevant pathways for both low- and high-temperature regions. Metcalfe et al. [13] measured ignition delay times for methyl butanoate and ethyl propanoate in a shock tube over the temperature range 1100–1670 K and at pressures of 1.0 and 4.0 atm. They proposed a new version of the methyl butanoate mechanism based on that developed by Fisher et al. [12]. Gail et al. [14] studied the oxidation of methyl butanoate in three

\* Corresponding author. Fax: +33 383378120.

E-mail address: [Olivier.Herbinet@ensic.inpl-nancy.fr](mailto:Olivier.Herbinet@ensic.inpl-nancy.fr) (O. Herbinet).

**Table 1**  
Structures of methyl esters and average composition in rapeseed and soybean biodiesels [5].

Esters	Structure	Average composition (mass%)	
		Rapeseed	Soybean
Methyl palmitate (C <sub>17</sub> H <sub>34</sub> O <sub>2</sub> )		4.3	6–10
Methyl stearate (C <sub>19</sub> H <sub>36</sub> O <sub>2</sub> )		1.3	2–5
Methyl oleate (C <sub>19</sub> H <sub>34</sub> O <sub>2</sub> )		59.9	20–30
Methyl linoleate (C <sub>19</sub> H <sub>32</sub> O <sub>2</sub> )		21.1	50–60
Methyl linolenate (C <sub>19</sub> H <sub>30</sub> O <sub>2</sub> )		13.2	5–11

different apparatuses. Experiments were performed in a jet-stirred reactor (atmospheric pressure, dilute conditions, temperature range 800–1350 K, equivalence ratio  $\phi$  1.13, residence time  $\tau$  0.07 s), in a variable pressure flow reactor ( $P = 1.266$  MPa, dilute conditions,  $\phi = 0.35$  and 1.00,  $\tau = 1.8$  s), and in an opposed-flow diffusion flame. Reaction products were sampled at the outlet of the jet-stirred and flow reactors and withdrawn with a quartz microprobe within the opposed flow diffusion flame. Species were analyzed by gas chromatography (flame ionization detector) and FTIR. Mole fraction profiles were plotted for the reactants (methyl butanoate and oxygen) and for numerous reaction products. Gail et al. also proposed a new version of the Fischer et al. [12] mechanism with validation using their experimental data. In a more recent paper, Gail et al. [15] studied the oxidation of methyl butanoate and methyl crotonate (C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>), an ester with one double bond conjugated with the carbonyl group, in a jet-stirred reactor (atmospheric pressure, large dilution, temperature range 850–1400 K, two equivalence ratios  $\phi = 0.375$  and 0.7, residence time 0.07 s) and in an opposed-flow diffusion flame. Mole fraction profiles were plotted for the reactants and for several reaction products. This comparison study showed that the formation of unsaturated species was enhanced in the case of methyl crotonate. A model of the oxidation of these species has been developed from mechanisms previously published in the literature. A kinetic analysis of this mechanism showed that the reactions pathways are very similar for both molecules and highlighted the role of the ester function and of the double bond in the unsaturated ester. Farooq et al. [16] studied the high-temperature decomposition of three esters (methyl acetate, methyl propionate and methyl butanoate) in a shock tube (temperature range 1260–1653 K, pressures 1.4–1.7 atm and reactant concentrations 2–3%, in argon). CO<sub>2</sub> yield measurements were performed using a laser based method and compared to yields calculated from several mechanisms. The auto-ignition of methyl butanoate in a rapid compression machine was studied by Walton et al. [17] (experiments at  $T = 935$ –1117 K,  $P = 4.7$ –19.6 atm, and  $\phi = 0.3$ –0.4) and ignition delay times were compared to a new model derived from that of Metcalfe et al. [13]. Dooley et al. [18] studied the auto-ignition of methyl butanoate in a shock tube (at 1 and 4 atm, over the temperature range 1250–1760 K, at  $\phi = 1.5$ , 1.0, 0.5, and 0.25, and at fuel concentrations 1.0% and 1.5%) and in a rapid compression machine (temperature range 640–949 K at compressed gas pressures of 10, 20, and 40 atm,  $\phi$  of 1.0, 0.5, and 0.33, and fuel concentrations of 1.59% and 3.13%). These new experimental results and other data

from the literature were used to produce a model of the oxidation of methyl butanoate. Vaughn et al. [19] measured droplet ignition delay times for several methyl esters and real biodiesels. This study provided interesting results, since they demonstrated that large methyl esters such as methyl decanoate (C<sub>11</sub>H<sub>22</sub>O<sub>2</sub>), methyl dodecanoate (C<sub>13</sub>H<sub>26</sub>O<sub>2</sub>), methyl oleate, and soybean biodiesel have very close reactivities, whereas ignition delay times for methyl butanoate are much longer. This confirms that methyl butanoate is not a good surrogate for biodiesel fuels.

Experimental studies of the oxidation of methyl esters larger than methyl butanoate are very scarce. HadjAli et al. [20] studied the low-temperature auto-ignition of a series of methyl esters from methyl butanoate to methyl heptanoate in a rapid compression machine. Experiments were performed over the temperature range 650–850 K and at pressures from 4 to 20 bar. They observed that the reactivity of the ester increased with the number of carbon atoms in the alkyl chain as for the *n*-alkanes. Ignition delay times of methyl hexanoate were compared with ignition delay times of a series of *n*-alkanes (*n*-butane, *n*-pentane, and *n*-heptane). This comparative study showed that the first stage delay times of methyl hexanoate were very close to those of *n*-heptane. The delay times at temperatures less than 670 K were also very close to those of *n*-heptane, but a major difference was the position of the negative-temperature-coefficient region, which occurred at lower temperature in the case of methyl hexanoate. Dagaut et al. [21] performed the study of the oxidation of rapeseed oil methyl ester (RME) in a jet-stirred reactor working at pressures between 1 and 10 atm, at temperatures from 800 to 1400 K, at high dilution in helium, and at two equivalence ratios (0.5 and 1). The formation of numerous reaction products has been observed. These products are carbon oxides, hydrogen, methane, ethylene, and larger olefins from propene to 1-hexene. The formation of unsaturated esters is not reported in this paper, whereas Dagaut and Gail [22] observed this type of species (methyl esters with one double bond at the extremity of the alkyl chain) when studying the oxidation of a blend of Jet-A1 and RME in a jet-stirred reactor. The formation of these species is expected because they can be formed by the same pathways as those leading to olefins during the oxidation of alkanes. Dagaut et al. [21] used a detailed kinetic model for the oxidation of *n*-hexadecane from [23] to reproduce the RME experimental data. The agreement was good for most species, except for the early production of carbon dioxide due to the presence of the ester group in RME. The formation of unsaturated esters has also been observed by Pedersen et al. [24] during the study of the

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