



Experimental study of the oxidation of methyl oleate in a jet-stirred reactor

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

Laboratoire Réactions et Génie des Procédés, Nancy Université, CNRS, ENSIC, BP 20451, 1 rue Grandville, 54001 Nancy, France

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ABSTRACT

The experimental study of the oxidation of a blend containing *n*-decane and a large unsaturated ester, methyl oleate, was performed in a jet-stirred reactor over a wide range of temperature 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 (*n*-decane and methyl oleate inlet mole fractions of 1.48×10^{-3} and 5.2×10^{-4}) and under stoichiometric conditions.

The formation of numerous reaction products was observed. At low and intermediate temperatures, the oxidation of the blend led to the formation of species containing oxygen atoms like cyclic ethers, aldehydes and ketones deriving from *n*-decane and methyl oleate. At higher temperature, these species were not formed anymore and the presence of unsaturated species was observed. Because of the presence of the double bond in the middle of the alkyl chain of methyl oleate, the formation of some specific products was observed. These species are dienes and esters with two double bonds produced from the decomposition paths of methyl oleate and some species obtained from the addition of H-atoms, OH and HO₂ radicals to the double bond.

Experimental results were compared with former results of the oxidation of a blend of *n*-decane and methyl palmitate performed under similar conditions. This comparison allowed highlighting the similarities and the differences in the reactivity and in the distribution of the reaction products for the oxidation of large saturated and unsaturated esters.

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1. Introduction

The interest in the oxidation of biodiesel fuels is increasing because of their use along with conventional diesel fuels in internal combustion engines [1–4]. Biodiesel fuels are alternative renewable fuels which are obtained from vegetable oils and animal fats and are converted into fatty acid esters by trans-esterification with an alcohol (e.g. methanol). When biodiesel fuels are obtained from soybean and rapeseed, they contain five main esters with very similar structures (Table 1). These esters are made of a long alkyl chain attached to an ester group and the main differences are the length of the chain (16 or 18 carbon atoms) and the number of double bonds in the chain (no double bond, one, two, or three double bonds). Methyl oleate (C₁₉H₃₆O₂), which is the subject of this study, is the main component found in rapeseed biodiesel fuel: it represents about 60% of its mass content and appears to be a good surrogate for rapeseed biodiesel fuel. This ester has an alkyl chain of 18 carbon atoms with one double bond in the middle.

The oxidation of esters has been the subject of several experimental studies. The most studied ester is methyl butanoate [6–9]

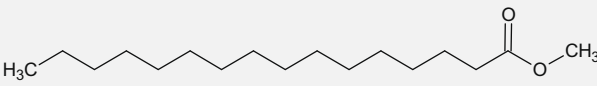
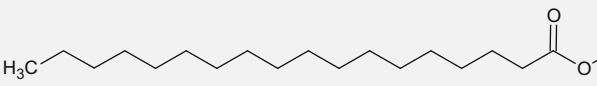
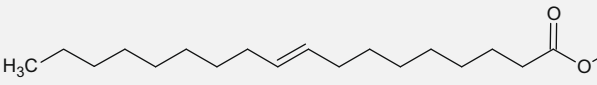
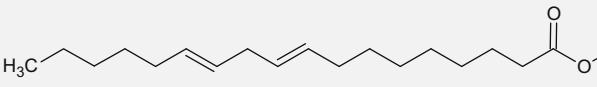
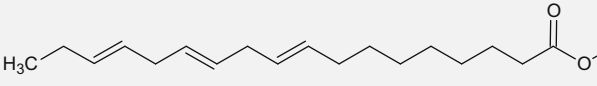
because it can be handled relatively easily to perform gas phase kinetic studies. These studies allowed making progress in the understanding of the chemistry of the oxidation of methyl esters but they also showed that methyl butanoate is too small compared to esters in real biodiesel fuels to be used as a surrogate. There are fewer studies about larger esters [10–20] and very little data about esters with double bonds [9,11,12]. Dagaut et al. [11] studied the oxidation of rapeseed biodiesel fuel in a jet-stirred reactor at temperatures from 800 to 1400 K (corresponding to the region right after the negative coefficient temperature zone), at pressures between 1 and 10 atm, at high dilution in helium and at two equivalence ratios (0.5 and 1). Reaction products were analyzed by gas chromatography and the formation of carbon oxides, hydrogen, methane, ethylene and olefins from propene to 1-hexene was reported. The formation of unsaturated esters was not mentioned in this work but other studies showed that these species could be formed during the combustion of esters [13,14,19,20].

Gaïl et al. [9] studied the oxidation of methyl crotonate (C₅H₈O₂), an ester with one double bond conjugated with the carbonyl group, in different apparatuses. These experiments were compared to methyl butanoate results obtained under identical conditions. Experiments were performed in a jet-stirred reactor at atmospheric pressure, at high dilution, at temperatures ranging

* Corresponding author. Fax: +33 383378120.

E-mail address: olivier.herbinet@ensic.inpl-nancy.fr (O. Herbinet).

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

Esters	Structure	Average composition (mass%)	
		Rapeseed	Soybean
Methyl palmitate (C ₁₇ H ₃₄ O ₂)		4	6–10
Methyl stearate (C ₁₉ H ₃₈ O ₂)		2	2–5
Methyl oleate (C ₁₉ H ₃₆ O ₂)		60	20–30
Methyl linoleate (C ₁₉ H ₃₄ O ₂)		21	50–60
Methyl linolenate (C ₁₉ H ₃₂ O ₂)		13	5–11

Note: Double bond(s) in natural molecules are in the cis conformation.

from 850 to 1400 K, at two equivalence ratios ($\Phi = 0.375$ and 0.7) and at a residence time of 0.07 s. Experiments were also performed in an opposed flow diffusion flame at atmospheric pressure (the oxidizer stream was composed of 42% O₂ and 58% N₂ and was sent through the top burner port; the fuel stream was composed of 4.7% fuel and 95.3% N₂ and was sent through the bottom). Mole fraction profiles were plotted for the reactants and for numerous reaction products (small hydrocarbons and oxygenated compounds with no more than four carbon atoms). The comparison between methyl crotonate and methyl butanoate studies showed that these esters had very close reactivities and that the formation of unsaturated species (e.g. acetylene, allene, propyne, 1,3-butadiene) was enhanced in the case of methyl crotonate.

Zhang et al. performed the study of the ignition of C₉ fatty acid esters (ethyl nonanoate, methyl nonanoate, methyl-2-nonenoate, and methyl-3-nonenoate) in a motored CFR engine [12]. Their study showed that these species exhibit different ignition behavior in the low temperature regime and that unsaturated esters were less reactive than the saturated ones according to the differences observed in the magnitude of low temperature heat release.

The purpose of this paper is to present new experimental results about the oxidation of an unsaturated ester larger than methyl crotonate. Methyl oleate was chosen because it is one of the main components found in rapeseed and soybean biodiesel fuels. The oxidation of a blend of *n*-decane and methyl oleate (74 mol%/26 mol%) was studied in a jet-stirred reactor under the same conditions than those used for a former study of the oxidation of a blend of *n*-decane and methyl palmitate [20] in order to draw comparisons between the two esters. Note that, it was necessary to dissolve methyl palmitate in *n*-decane in the previous study because this saturated ester is a solid at ambient temperature. *N*-decane was retained because it is also a common surrogate for *n*-alkanes in diesel fuels.

2. Experimental method

The experimental study of the oxidation of methyl oleate blended with *n*-decane was performed using an apparatus which has already been used in our laboratory for studies of the oxidation of several organic compounds such as iso-butene, *n*-heptane, iso-octane, toluene, *n*-decane, *n*-hexadecane and methyl palmitate

[20–24]. This apparatus has already been described in former papers [20–24] and only its main features are presented here.

2.1. Experimental apparatus specifications

The reactor used to perform this study is a fused silica jet-stirred reactor operated at constant temperature and pressure. This type of reactor has been proven to be well adapted to gas phase kinetic studies and it has been designed to be well stirred for residence times between 0.5 and 5 s [25,26]. It is composed of a sphere with an injection cross located at its center. The mixing of the gas-phase inside the reactor is achieved through turbulent jets issued from the four nozzles of the cross. In order to avoid the formation of temperature gradients in the gas phase, the reactor is preceded by an annular preheater in which the temperature of the gas mixture is increased progressively to the reaction temperature. Uncertainties on the temperature of reaction and the residence time of the gas inside the reactor are ± 2 K and $\pm 5\%$, respectively.

The oxidation of the *n*-decane/methyl oleate blend (74 mol%/26 mol%) was studied in the above described reactor over the temperature range 550–1000 K, at a pressure of 106 kPa (800 Torr), at a residence time of 1.5 s, at stoichiometric conditions, and at high dilution in helium. The inlet fuel mole fraction was set to 0.002.

2.2. Products analyses

Reaction products were analyzed by gas chromatography. The analytical procedure has already been described in details in a previous paper [20]. Analyzed species were hydrocarbons and oxygenated species with more than five heavy atoms (carbon and oxygen atoms are considered as heavy atoms) which were condensed in a trap maintained at liquid nitrogen temperature, light species such as oxygen, carbon monoxide, carbon dioxide, C₁–C₄ hydrocarbons and small oxygenated compounds (online analysis). Water was not quantified. The limit of detection was about 100 ppb for the heaviest species (flame ionization detector, FID) and about 10 ppm for carbon oxides and oxygen (thermal conductivity detector, TCD). Uncertainty estimates are about $\pm 5\%$ for species which are analyzed online and $\pm 10\%$ for species condensed in the trap.

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