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Experimental and modeling investigation of the effect of the unsaturation degree on the gas-phase oxidation of fatty acid methyl esters found in biodiesel fuels

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ABSTRACT

The oxidation of three C₁₉ fatty acid methyl esters present in biodiesel fuel was experimentally investigated using a jet-stirred reactor in order to highlight the effect of double bonds on the reactivity and product distribution. Fuel candidates were methyl-stearate, methyl oleate and methyl linoleate with no, one and two double bonds, respectively. Experiments were carried out over a wide temperature range (500–1050 K), at a pressure of 1.067 bar, at a residence time of 2 s. Methyl esters were diluted with benzene to avoid their condensation as much as possible. Inlet mole fractions of methyl ester, benzene and oxygen were 4×10^{-4} , 5×10^{-3} and 4.5×10^{-2} , respectively (with dilution in helium). However, as previously demonstrated for alkanes, the presence of benzene does not notably influence the mixture reactivity below 850 K. Many reaction intermediate products have been quantified, including species which can be formed through Waddington reaction for unsaturated reactants. The present experiments are the first ones allowing the actual measurement of large ester intrinsic reactivity in a jet-stirred reactor. They further contribute to an extensive validation of the POLIMI lumped kinetic scheme of pyrolysis and oxidation of biodiesel fuels. Two reaction classes have been added to better account for the oxidation of species with double bonds: the Waddington mechanism and the concerted decomposition reactions through cyclic transition states. The new model contains 18,217 reactions involving 461 species. Overall, a correct agreement was obtained for the reactivity of the three fuels. The model well reproduces mole fraction profiles of many reaction products. The kinetic analysis performed at low-temperature (650 K) confirmed the significant inhibitive effect of H-atom abstractions forming non-propagating allyl type radicals in this temperature region. It also showed that the inhibitive effect of these reactions increases from methyl oleate to methyl linoleate, which explains the large difference observed in the reactivity.

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1. Introduction

The continuously increasing world energy demand and the negative impact of the use of fossil fuels on the environment have led to a shift toward alternative sources of energy such as biofuels. Without waiting for new technologies, the depletion of oil resources and the preservation of the environment urge us to improve as much as possible the current engines fed with biofuels. Biodiesel, which is a blend of fatty acid methyl esters obtained from the trans-esterification of vegetable oil or animal fat, is one of the transportation fuels which are currently used in diesel engines [1]. This alternative fuel has

several advantages compared to petroleum fuels: it is a renewable energy source which can be blended with other resources like diesel fuel. It is sulfur free and it has interesting lubricating properties [2]. Biodiesel has also some disadvantages due to some of its physical properties (e.g., higher viscosity which affects the operation of injectors, the presence of unsaturations which makes biodiesel less stable and requires the addition of stabilizers for the storage) [3]. As far as emissions are concerned, the use of biodiesel instead of diesel fuel in a diesel engine leads to a decrease of particulate matter, unburned hydrocarbons, sulfur oxides, carbon monoxide and volatile organic compounds, but leads to an increase of nitrogen oxides [4].

The composition of fatty acid methyl esters found in biodiesel fuels depends on the plant it is issued [4] (Table 1). As an example, rapeseed oil methyl ester is composed of 62% of methyl oleate (C₁₉H₃₆O₂). It also contains methyl linoleate (C₁₉H₃₄O₂), methyl

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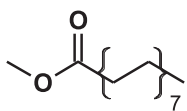
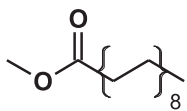
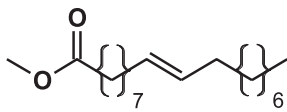
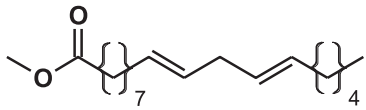
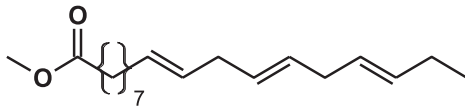
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Table 1
Average composition (wt%) of some biodiesel fuels issued from plants [4].

	Methyl palmitate $C_{17}H_{34}O_2$	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 $C_{19}H_{32}O_2$
Rapeseed oil methyl esters	4	2	62	22	10
Soybean oil methyl esters	12	4	23	54	6
Palm oil methyl esters	43	4	41	10	0

Table 2
Structure and cetane number of methyl esters [5].

Ester	Structure	Cetane number
Methyl palmitate ($C_{17}H_{34}O_2$)		86
Methyl stearate ($C_{19}H_{38}O_2$)		101
Methyl oleate ($C_{19}H_{36}O_2$)		59
Methyl linoleate ($C_{19}H_{34}O_2$)		38
Methyl linolenate ($C_{19}H_{32}O_2$)		23

linolenate ($C_{19}H_{32}O_2$), methyl stearate ($C_{19}H_{38}O_2$) and methyl palmitate ($C_{17}H_{34}O_2$). Soybean oil methyl ester also contains the same species but with a different composition: methyl palmitate and methyl oleate are the main components.

These esters have very close structures (Table 2): they are composed of a long alkyl chain (16–18 carbon atoms) attached to a methyl ester group. The difference is the number of double bonds in the chain (no, 1, 2 or 3 double bonds). As for alkenes, the degree of unsaturation (i.e., the number of double bonds) has a direct influence on the low-temperature oxidation chemistry and reactivity of methyl esters. This is responsible for the large difference which is observed in the cetane number of these species [5] (Table 2).

The literature is particularly abundant concerning the gas phase oxidation data for small methyl esters [6,4,7–12]. Methyl butanoate oxidation was extensively studied over a wide range of conditions including flow reactors, jet-stirred reactors, shock tubes, rapid compression machines and flames [4,6,9,10]. These studies enabled a better understanding of the chemistry specific to this class of biofuels. Nevertheless they also showed that methyl butanoate was not a good surrogate for the large methyl esters actually found in biodiesel fuels.

Oxidation studies involving saturated esters with an alkyl chain up to C_{10} (e.g., methyl hexanoate, heptanoate, octanoate and decanoate) are also reported in literature [4,6]. These studies showed that these species can be good candidates for surrogate of actual saturated methyl esters (e.g., methyl stearate) but not for actual unsaturated methyl esters.

There are only a few data about the gas-phase oxidation chemistry of methyl esters larger than methyl palmitate (Table 3). Fewer data can be found about their low-temperature oxidation chemistry with

reaction product analysis. Ignition delay times were measured behind shock waves for methyl palmitate, methyl stearate, methyl oleate and methyl linoleate at high temperatures (above 900 K) [13,14]. Campbell et al. [13] compared ignition delay times of methyl oleate and methyl linoleate. This study showed that the two biofuels have about the same reactivity at high-temperatures. In the same way, Wang et al. [14] observed that ignition delay times measured under similar conditions for the four methyl esters were very close and were similar to ignition delay times of real biodiesels (soybean methyl esters and animal fat methyl esters), irrespectively of the presence and number of the double bonds. In contrast, Das et al. [15] observed that sooting tendency of unsaturated methyl esters depends on the number and position of the C=C double bonds. Campbell et al. [16] also succeeded to measure ignition delay times of methyl palmitate which is a waxy solid at room temperature using their aerosol shock tube. Chong et al. [17] measured laminar flame speeds of palm methyl esters (PME) using the jet-wall stagnation flame configuration. They observed that data for PME were very close to laminar flame speeds measured for diesel fuel and blends of PME with diesel. This shows that biodiesel reactivity is similar to that of diesel at high-temperatures. Dagaut et al. [18] studied the oxidation of rapeseed methyl esters (RME) in a jet-stirred reactor at temperatures between 800 and 1400 K (after the negative temperature coefficient zone). They measured mole fractions of small reaction products but no information was reported about species containing ester functions.

Hakka et al. [19] and Bax et al. [20] have studied the oxidation of methyl palmitate and methyl oleate in a jet-stirred reactor over a wide range of temperatures (500–1100 K). Methyl esters were blended with *n*-decane to decrease the partial pressure of the

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