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A lumped approach to the kinetic modeling of pyrolysis and combustion of biodiesel fuels

Chiara Saggese, Alessio Frassoldati, Alberto Cuoci,
Tiziano Faravelli, Eliseo Ranzi *

Dipartimento di Chimica, Materiali ed Ingegneria Chimica "G. Natta" Politecnico di Milano,
Piazza Leonardo da Vinci 32, 20133 Milano, Italy

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Abstract

The aim of this work is to discuss a lumped approach to the kinetic modeling of the pyrolysis and oxidation of biodiesel fuels, i.e. rapeseed and soybean methyl esters. The lumped model is the natural extension of the kinetic scheme of methyl butanoate and methyl decanoate and takes also a great advantage from the detailed kinetic scheme of biodiesel fuels [Westbrook et al. Combustion and Flame 158 (2011) 742–755]. The combustion of methyl palmitate and methyl stearate is very similar to the one of methyl decanoate, while large unsaturated methyl esters are significantly less reactive at low and intermediate temperatures. The formation of resonantly stabilized allylic radicals from unsaturated methyl esters constitutes a critical element very useful to characterize the reactivity of the different fuels. The extension of the previous kinetic model of hydrocarbon and oxygenated fuel combustion to the methyl esters required the introduction of ~60 lumped species and ~2000 reactions. The dimension of the overall kinetic scheme (~420 species involved in ~13,000 reactions) allows a more flexible and direct application of the model without the need of kinetic reductions. The comparison of model predictions and different sets of experimental data from one side allows to verify the reliability of the proposed model, from the other side calls for further experimental and theoretical work on this subject.

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Keywords: Biodiesel fuel; Kinetic modeling; Lumped kinetics; Oxidation; Pyrolysis

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1. Introduction

The interest in the biodiesel combustion is increasing worldwide due to its renewability. The two most commonly used biodiesel fuels are soy methyl ester (SME) in US and rapeseed methyl ester (RME) in Western Europe. The five major components of typical biodiesel are both saturated and unsaturated methyl esters, specifically methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl linolenate. The development of a chemical kinetic mechanism to describe the combustion of these components is very tough, due to the complexity of the oil mixture. Among many attempts in the literature [1], a recent and excellent kinetic modeling work [2] reports a very detailed kinetic scheme of the five major components of soy biodiesel and rapeseed biodiesel fuels. The resulting reaction mechanism contains more than 4800 chemical species and ~20,000 elementary chemical reactions. The large

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* Corresponding author.
E-mail address: eliseo.ranzi@polimi.it (E. Ranzi).

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number of reactions and species, in respect of heavy *n*-alkanes, is mainly due to the lack of symmetry in the molecules. Useful thermochemical data of fatty acid methyl esters and oxygenated radicals were reported [3]. The dimension of the detailed kinetic schemes often limits their applicability and validation possibilities and calls for simplifications. Several reduction techniques, including the chemical lumping, are thus applied to make viable the use of large kinetic schemes for practical applications [4].

Therefore the combustion of biodiesel fuels obtained from RME and SME could take a great advantage by using a lumped kinetic model, which includes the combustion chemistry of fatty acid methyl esters (FAME), retaining the peculiar features of the reacting system.

2. Biofuel characterization and selection of reference species

Biodiesel fuels can be produced from a wide variety of vegetable oils. They are constituted by different fatty acids which produce long-chain monoalkyl esters by means of a transesterification reaction usually with methanol. Biodiesel fuels are complex mixtures and their characterization is the first step for predicting combustion performances. Interesting reviews on biodiesel production give useful information on the typical composition of fatty acid common oil source [5–8]. Table 1 summarizes the chemical structures and formulas of methyl esters of common fatty acid, while Table 2 reports the reference composition of several common biodiesel fuels. The most common methyl esters contained in biodiesel fuels are those derived from palmitic, stearic, oleic, linoleic and linolenic acid. This holds for biodiesel feedstocks, such as soybean, sunflower, rapeseed, palm, and peanut oils. Some tropical oils, such as coconut oil, contain significant amounts of shorter chain acids, such as lauric and myristic acid.

The lumped kinetic scheme of methyl butanoate (MB) and methyl decanoate (MD), validated in a wide range of experimental conditions, also proved the possibility to use MB and MD as reference components to properly reproduce the ignition and combustion behavior of intermediate methyl esters [9–11]. Similarly, methyl palmitate (MPA) is assumed as a further reference component to reproduce, together with methyl decanoate, also the intermediate methyl esters of lauric and myristic acid. Due to their large presence in the common biodiesel fuels [2], methyl stearate (MSTEA), methyl oleate (MEOLE), methyl linoleate (MLINO), and methyl linolenate (MLIN1) are considered as further reference fuels to be analyzed and included in the lumped kinetic model.

3. Lumped kinetic model

The detailed kinetics of methyl esters involves a huge number of species and reactions, due to the lack of symmetry in their structure, thus these kinetic schemes can take a great advantage from a lumped or simplified approach. Based on the regularity of long alkyl chains [12,13], the lumped kinetic scheme of large methyl esters refers to the same reaction classes already analyzed and discussed in the previous kinetic scheme of smaller methyl esters. Here we simply discuss the chain initiation and H abstraction reactions to form the primary radicals. At high temperatures, these radicals rapidly decompose, while at low temperatures they follow the typical branching reaction paths of peroxy radicals with the ketohydroperoxide formation.

3.1. Kinetic model

Instead of including in the kinetic scheme all the possible isomers of radicals and molecules, the lumped species refer not only to the different isomers with the same formula but also to adjacent species of the same family. Intermediate species, not directly accounted for in the lumped scheme, are splitted between the two closest reference species, with the lever rule. On these bases, only a limited number of new reference or intermediate species allows to extend the previous kinetic model

Table 1
The chemical structures of methyl esters of common fatty acid.

Fatty acid	FAME chemical structure	Chemical formula
Lauric [12:0]	$CH_3(–CH_2–)_{10}CO–OCH_3$	$C_{13}H_{26}O_2$
Myristic [14:0]	$CH_3(–CH_2–)_{12}CO–OCH_3$	$C_{15}H_{30}O_2$
Palmitic [16:0]	$CH_3(–CH_2–)_{14}CO–OCH_3$	$C_{17}H_{34}O_2$
Stearic [18:0]	$CH_3(–CH_2–)_{16}CO–OCH_3$	$C_{19}H_{38}O_2$
Oleic [18:1]	$CH_3(–CH_2–)_7CH{=}CH(–CH_2–)_7CO–OCH_3$	$C_{19}H_{36}O_2$
Linoleic [18:2]	$CH_3(–CH_2–)_3(CH_2–CH{=}CH)_2(–CH_2–)_7CO–OCH_3$	$C_{19}H_{34}O_2$
Linolenic [18:3]	$CH_3–(CH_2–CH{=}CH)_3(–CH_2–)_7CO–OCH_3$	$C_{19}H_{32}O_2$
Arachidic [20:0]	$CH_3(–CH_2–)_{18}CO–OCH_3$	$C_{21}H_{42}O_2$
Behenic [22:0]	$CH_3(–CH_2–)_{20}CO–OCH_3$	$C_{23}H_{46}O_2$
Erucic [22:1]	$CH_3(–CH_2–)_7CH{=}CH(–CH_2–)_{11}CO–OCH_3$	$C_{23}H_{44}O_2$

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