



A wide range kinetic modeling study of pyrolysis and oxidation of methyl butanoate and methyl decanoate – Note II: Lumped kinetic model of decomposition and combustion of methyl esters up to methyl decanoate

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ARTICLE INFO

Article history:

Received 14 December 2011

Received in revised form 22 February 2012

Accepted 29 February 2012

Available online 23 March 2012

Keywords:

Bio-fuel

Pyrolysis and combustion kinetics

Methyl decanoate

Lumped kinetic model

ABSTRACT

The aim of this work is to develop and discuss a lumped kinetic model to simulate the pyrolysis and combustion behavior of methyl decanoate. Validation of the lumped kinetic model of methyl decanoate in a very wide range of conditions, with temperature ranging from 500 to more than 2000 K, pressures up to 16 bar and equivalent ratios from lean to pyrolysis conditions, proved that, despite the drastic simplifications, the model can properly reproduce the experimental measurements in pyrolysis as well as in an oxidation environment, in both the low temperature regime and in flame conditions. This model is an extension of the lumped model of methyl butanoate developed and discussed in the first part of this work [1]. Thus, the lumped kinetic model of methyl butanoate and methyl decanoate is also quite simply applied to simulating the combustion behavior of intermediate methyl esters, by using the lever rule between the two reference components. The overall agreement with experimental measurements is very encouraging and lays the basis for the extension to the lumped kinetic scheme to soy and rapeseed biodiesel fuels.

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1. Introduction

Energy demands are growing constantly and are predicted to increase still further in the coming years especially because of the growing needs of developing countries. More energy, which mostly comes from combustion, means more greenhouse gases, particularly carbon dioxide. However, while emissions of the latter are expected to increase in the developed world, they will mainly do so in the developing ones. Consequently, the use of alternative energy sources will grow relatively faster compared to traditional ones. In fact, the use of renewable fuels is expected to double in the next 20 years [2]. Several countries have already adopted strategies to boost production of renewable fuels. In February 2009, a European Parliament resolution set out a range of measures required to reduce greenhouse gas emissions by 25–40% by 2020 and by at least 80% by 2050. The resolution also states that EU Member States should invest in research on sustainable advanced bio-fuels [3].

Great attention is being devoted to transportation fuels and possible mixtures with alcohols and biodiesel fuels. Biodiesels are complex mixtures of multi-component alkyl esters of long-chain fatty acids, generally made by trans-esterification of soy

and rapeseed oil with methanol. Biodiesel fuels can be effectively used both as alone or blended with fossil diesel fuels [4–10].

As already mentioned in the Note I of this work [1], extensive research has gone into experimental and kinetic modeling of pyrolysis and combustion of fatty-acid methyl esters (FAME) [11–35]. As a result of this, we now have a good understanding of the intrinsic kinetics and reaction classes of pyrolysis and oxidation of methyl esters. Detailed kinetic models of pyrolysis and combustion of large methyl esters involve a huge amount of species and reactions. Thus, Herbinet et al. [6] presented a methyl decanoate mechanism including 3012 species and 8820 reactions. Very recently, Westbrook et al. [7] reported a detailed kinetic scheme of the five major components of soy and rapeseed biodiesel fuels with ~5000 chemical species and ~20,000 elementary reactions. In some cases, however, these dimensions may prevent the use of the mechanism for flame simulations.

The Note I of this work focused on the kinetic modeling of methyl butanoate (MB) with the identification of the main reaction classes of small saturated and unsaturated methyl esters, at both low and high temperatures. The second part of this work aims to extend the kinetic mechanism up to methyl decanoate (MD). The peculiarity of this kinetic mechanism lies in the lumping approach, which allows to extend and describe the primary oxidation reactions of MD using only a few new lumped molecules and radicals involved in less than 100 new reactions, correctly describing the

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system reactivity and the product distribution of major and minor intermediates. The whole kinetic mechanism of pyrolysis and oxidation of hydrocarbons and oxygenated up to heavy liquid fuels is made up of ~350 species involved in ~10,000 reactions. This kinetic model, which is available online (<http://creckmodeling.chem.polimi.it/>), allows to the study not only of the combustion of methyl esters at low and high temperatures in ideal systems, but also to the analysis of their combustion behavior in premixed and diffusion flames, without the need to deduce skeletal mechanisms from very detailed ones [36]. Similarly, the autoignition of methyl heptanoate and methyl nonanoate studied in motored CFR engines [37,38] can be directly simulated with the lumped kinetic scheme without any need for more empirical 'global reactions' [39].

Moreover, the lumped kinetic scheme allows to the study of methyl ester mixed with hydrocarbons and oxygenated species. This makes the kinetic modeling of blends of biodiesel and surrogate mixtures of real transportation fuels in internal combustion engines more feasible, without unnecessary reduction techniques.

Finally, methyl butanoate and methyl decanoate are used and assumed as reference compounds useful to describe the pyrolysis and oxidation behavior of intermediate methyl esters [21,22]. The lever rule allows the description of the intermediate methyl esters as a mixture of the reference components. This approach has proved very effective, with good results for methyl esters from pentanoate up to octanoate.

2. Lumped kinetic scheme

Because of the lack of symmetry in the molecular structure of ester molecules, the detailed kinetic scheme of the pyrolysis and oxidation of MD and larger methyl esters becomes very large. Lumped or simplified approaches are therefore necessary and allow to the number of species and reactions to be controlled. The regularity of long alkyl chains, as well as the similarities of heavy species of the same family, has already been clearly explained and verified, not only for the series of *n*-alkanes [40] but, more extensively, for the different hydrocarbon fractions in the liquid feedstocks of the steam cracking process [41].

On very simple basis, the lumped kinetic scheme of MD pyrolysis is derived by first analyzing the initiation and then the H-abstraction reactions and successive decomposition reactions of primary MD radicals.

2.1. Initiation reactions

As already discussed by El-Nahas et al. [11] and Glaude et al. [16], the activation energies of unimolecular initiation reactions, involving the C–C bonds located in α - and β -positions from the ester function, demand to overcome the bond dissociation energies (BDE) of ~92 and ~84 kcal/mol, respectively. The long alkyl chain of MD consists of 7 C–C bonds between secondary C atoms with BDE of 82–84 kcal/mol and one C–C bond with the terminal methyl group of ~86 kcal/mol. The C–C bond dissociations in the alkyl chain form the alkyl radicals from methyl up to nonyl and methyl ester radicals, from methyl formate up to radicals with 10 C atoms. Instead of including all the possible alkyl and methyl ester radicals in the kinetic scheme, we refer to the alkyl radicals already contained in the existing kinetic scheme (C_2H_5 , C_3H_7 , C_4H_9 , C_5H_{11} , and C_7H_{15}), and to four lumped radicals of methyl esters ($C_4H_7O_2$, $C_5H_9O_2$, $C_8H_{15}O_2$, and $C_{11}H_{21}O_2$). Referring to the previous kinetic scheme of methyl butanoate [1], we include only two new radicals of ester species (RME7: $C_8H_{15}O_2$, and RMDX: $C_{11}H_{21}O_2$). The intermediate radicals, not directly accounted for in the kinetic scheme, are split between the two adjacent reference

radicals, using the lever rule. Thus, hexyl radicals are equally split between pentyl and heptyl radicals, while octyl radicals are split between heptyl and decyl radicals with the ratio 2/1. The lumped initiation reactions of MD, involving both the breaking of C–C bonds on the alkyl chain and the different bonds of the ester group, are reported in Table 1. The fractional stoichiometry of the reaction R1 is derived on the basis of a C balance. Once CH_3 and CO_2 are formed from MD ($C_{11}H_{22}O_2$), then C_9H_{19} completes the balance. We simply split C_9H_{19} between $C_{10}H_{21}$ and C_7H_{15} according to the lever rule.

2.2. H-abstraction and β -decomposition reactions

H abstraction reactions on MD give rise to 10 different $C_{11}H_{21}O_2$ radicals. The initial selectivity of the different radicals depends on the different H atoms to be removed. There are three primary H atoms in the ester group, three primary H atoms in the terminal methyl group, 14 secondary H atoms, and finally two secondary H atoms close to the methyl ester group, with a BDE of 94.2 kcal/mol. Thus, the radicals corresponding to these secondary H atoms are the favored ones. We consider a single, lumped radical (RMDX: $C_{11}H_{21}O_2$) with an internal distribution derived from the relative weight of the H abstraction reactions to form the different isomers. The successive β -decomposition reaction forms either an alkene (C_kH_{2k}) and a radical of a methyl ester (RME $_{9-k}$: $C_{9-k}H_{2(9-k)+1}-COOCH_3$), or an unsaturated smaller methyl ester (UME $_{9-k}$: $C_{9-k}H_{2(9-k)}COOCH_3$) and an alkyl radical (C_kH_{2k+1}). Formaldehyde is formed directly from the β -decomposition of the isomer $C_9H_{19}COOCH_2$. The A-factors of the β -decomposition reactions (R9–R15) in Table 1 reflect the initial distribution of the $C_{11}H_{21}O_2$ radicals formed in the H-abstraction reaction R8. Only two new unsaturated methyl esters: methyl heptenoate (UME7) and methyl decenoate (UME10) are included in the kinetic scheme (aside from the methyl acrylate and methyl crotonate already involved). The remaining intermediate species are again split between the two adjacent unsaturated esters, using the lever rule. Table 1 reports the full detail of the pyrolysis reactions, involved in the high temperature oxidation mechanism. The rate of H abstraction reactions are systematically obtained as reported in Ranzi et al. [42]. According to the BDE of the H atoms, the rate of H-abstraction from different sites are simply obtained by using the reference kinetic parameters of the removal of primary H atoms and the specific correction factor of the H atoms to be removed. Thus, the primary H atoms in the methyl of ester group are assumed to be 1.5 times more reactive than the primary H atoms in alkanes. Similarly, the rate parameters to abstract the secondary H atoms in the α position to the ester group are assumed twice as reactive as the usual secondary H atoms in alkanes. Of course, the primary propagation reactions of methyl heptenoate and methyl decenoate (relevant intermediates of the primary MD decomposition) are also included in the lumped kinetic model. These successive reactions, including H and OH addition reactions, are obtained by analogy with similar initiation and propagation reactions of methyl acrylate and methyl crotonate.

3. Pyrolysis of methyl decanoate

3.1. JSR experimental data of Herbinet et al. [18]

The thermal decomposition of methyl decanoate in a jet-stirred reactor in the temperature range 773–1123 K and 106.6 kPa (fuel inlet mole fraction of 0.0218 in N_2) was recently reported and discussed by Herbinet et al. [18]. They also developed a detailed kinetic model for the thermal decomposition of methyl decanoate containing 324 species and 3231 reactions, generated using an

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