Modeling study of the low-temperature oxidation of large methyl esters from C_{11} to C_{19}

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Abstract

The modeling of the low-temperature oxidation of large saturated methyl esters really representative of those found in biodiesel fuels has been investigated. Models have been developed for these species and then detailed kinetic mechanisms have been automatically generated using a new extended version of software EXGAS, which includes reactions specific to the chemistry of esters. A model generated for a binary mixture of n-decane and methyl palmitate was used to simulate experimental results obtained in a jet-stirred reactor for this fuel. This model predicts very well the reactivity of the fuel and the mole fraction profiles of most reaction products. This work also shows that a model for a middle size methyl ester such as methyl decanoate predicts fairly well the reactivity and the mole fractions of most species with a substantial decrease in computational time. Large n-alkanes such as n-hexadecane are also good surrogates for reproducing the reactivity of methyl esters, with an important gain in computational time, but they cannot account for the formation of specific products such as unsaturated esters or cyclic ethers with an ester function.

Keywords: Methyl esters; Methyl palmitate; Biodiesel fuels; Modeling; Oxidation

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1. Introduction

Due to the depletion of fossil fuels, the development of renewable energy is more vital than ever [1] and [2]. The production of biofuels such as methyl esters is encouraged by the European Union in order to incorporate them in existing diesel fuels. Molecules produced from vegetable oils are methyl esters with a long carbon chain such as methyl palmitate ($C_{17}H_{34}O_2$) and methyl stearate ($C_{19}H_{38}O_2$). Due to the large size of the related kinetic mechanisms, it is necessary to determine the optimal model in terms of size and performance which could be used to simulate the oxidation of these large methyl esters and to investigate the differences with the combustion of alkanes induced by the ester function. While biodiesel fuels deriving from soybean and rapeseed oils contain mainly methyl esters from C_{17} to C_{19} [3], there is almost no study of the oxidation of compounds really representative of these species.

Herbinet et al. [4] developed the first model for the oxidation of a middle size saturated methyl ester, methyl decanoate, including all pertinent reactions to low and high temperature regions. The model has been validated against limited available data and suggests that large methyl esters and n-alkanes of similar size have very similar reactivity. This model was reduced and used to model extinction and ignition of laminar non-premixed flames containing methyl decanoate [5]. Very recently, Glaude et al. [6] performed an experimental study of the oxidation of methyl decanoate in a jet-stirred reactor. They showed that their results were well reproduced by the model of Herbinet et al. [4], and they used also these data to validate a new version of EXGAS for the automatic generation of detailed kinetic model of methyl ester oxidation (EXGAS-ALKANES-ESTER[1] called EXGAS in this paper).

The purpose of this paper is to describe and test detailed kinetic mechanisms for the oxidation of large methyl esters from C_{11} to C_{19} automatically generated with software EXGAS [6]. A model thus generated is compared with experimental results of the oxidation of methyl palmitate (blended with n-decane) obtained in a jet-stirred reactor [7]. The models for methyl esters from C_{11} up to C_{19} are then used to compare the reactivity and the mole fractions of reaction products and to investigate if methyl esters such as methyl decanoate can be good surrogates for larger methyl esters.

2. Models generated with EXGAS

Models for the oxidation of methyl esters from methyl decanoate ($C_{11}H_{22}O_2$) to methyl stearate ($C_{19}H_{38}O_2$) were generated with software EXGAS. The rules used for the generation have already been comprehensively described in [6] and only the main features are given here. Models generated with

[1] Software EXGAS-ALKANES-ESTERS automatically generates detailed kinetic mechanisms for the oxidation of linear and branched alkanes, and linear methyl esters and is freely available for academic researchers (valerie.warth@ensic.inpl-nancy.fr).

EXGAS are made of three parts: a comprehensive primary mechanism, where the only molecular reactants considered are the initial organic compounds and oxygen; a C_0–C_2 reaction base, including all the reactions involving radicals or molecules containing less than three carbon atoms [8]; and a lumped secondary mechanism, containing the reactions consuming the molecular products of the primary mechanism, which do not react in the C_0–C_2 reaction base. The molecules formed in the primary mechanism and consumed in the secondary mechanism, with the same molecular formula and the same functional groups, are lumped into one unique species, without distinguishing between the different isomers [9]. This avoids an explosion of the number of molecules in the models. Globalized reactions in the secondary mechanism were considered in order to promote the formation of radicals having more than two carbon atoms, the reactions of which are already included in the primary mechanism [10].

The rules used for the generation of the primary mechanism are the same as the ones which are used in the case of the oxidation of alkanes [11] and no new specific reaction was considered. However some changes were made in the estimation of the kinetic data in order to take into account the presence of the ester group. These changes affect:

1. The activation energies of the unimolecular initiations which involve the breaking of the C–C bonds located in the α- and β-positions from the ester function (bond dissociation energies were taken equal to 93.4 and 85.0 kcal/mol, respectively, according to the values recently calculated by El-Nahas et al. [12]).

2. The activation energy of oxidations of radicals (yielding an unsaturated molecule and HO_2) and metatheses involving an H-atom carried by the atom of carbon just neighboring the ester function. Since the energy of the corresponding C–H bond (94.3 kcal/mol [13]) is close to that of a tertiary H-atom (e.g., 95.7 kcal/mol in isobutene [13]), the activation energies used for oxidations were the same as the ones for tertiary H-atoms. For H-atom abstractions, the correlations were taken the same as those used for the abstraction of a tertiary H-atom from alkanes, except in the case of the abstractions by •O• and •H atoms and by •OH, $\bullet HO_2$ and $\bullet CH_3$ radicals. In this case, the rate parameters have been evaluated using an Evans–Polanyi correlation proposed by Dean and Bozzelli [14]. Evans–Polanyi correlations have been proposed to give more accurate kinetic parameters as they take into account the real bond energies of the C–H bonds involved in the reaction. As the C–H bond energy in the α position of the ester function is slightly lower than the C–H bond energy in the case of a tertiary H-atom, the kinetic constants evaluated using the Evans–Polanyi correlation are larger and reactions faster (of about a factor 1.7 at 650 K and 2 at 1000 K).

3. The activation energy of radical intramolecular isomerizations. The activation energy for abstracting an H-atom from the carbon atom located in the α-position from the ester function has been taken equal to that for the abstraction of a tertiary H-atom in an alkyl radical. Quantum calculations were carried out to estimate the strain energy in cyclic transition states including the atoms of the ester group [6].

4. The activation energy of radical decompositions by β-scission. Quantum calculations were performed to estimate the activation energy of the reactions of decomposition involving the different types of bonds of the ester group [6].

New rules were implemented in the secondary mechanism for the consumption of the species formed in the primary mechanism and which did not exist in the case of alkanes: hydroperoxides, cyclic ethers, ketones and aldehydes bearing an ester function, as well as unsaturated methyl esters. As in the case of alkanes [10], the general idea is to promote the formation of radicals, the reactions of which are already included in the primary mechanism, i.e., C_2+ alkyl radicals and C_2+ methyl ester alkyl radicals. The rules of decomposition of the species formed in the primary mechanism as well as the associated kinetic parameters are presented in detail in [6]. Models generated with EXGAS were already validated from available shock tube, rapid compression machine, and jet-stirred reactor experimental data for methyl esters from C_5 to C_{11} [6] and [15]. Models used in this study were generated with the same version of EXGAS and using the same set of kinetic parameters.

Because of the loss of the symmetry due to the presence of the ester group, models for the oxidation of methyl esters are much larger than models for the oxidation of n-alkanes. As an example the model generated for methyl decanoate ($C_{11}H_{22}O_2$) is composed of 1247 species and 7775 reactions against 655 species and 4435 reactions for n-undecane ($C_{11}H_{24}$). The methyl decanoate model of Herbinet et al. [4], which was build in a different way than models generated with EXGAS, is much larger than the one generated in this study: it includes 3012 species and 8820 reactions. The numbers of species and reactions (Table 1) increase drastically with the size of the molecule resulting in a large increase in CPU time for the largest methyl esters. An increase of two in the number of carbon atoms in the ester molecule results in an increase by a factor of 2.4 for the computational time in a PSR, e.g., a factor of 33 from methyl decanoate to methyl stearate.

Table 1. Numbers of species and reactions in the models generated with EXGAS.

	$C_{11}H_{22}O_2$	$C_{13}H_{26}O_2$	$C_{15}H_{30}O_2$	$C_{17}H_{34}O_2$	$C_{19}H_{38}O_2$
species	1247	2012	3061	4442	6203
reactions	7775	13004	20412	30425	43444

3. Validation against methyl palmitate experimental data

Very little experimental data are available for the validation of kinetic models in the case of large esters. However, experimental data of the oxidation of methyl palmitate (blended with n-decane) in a jet-stirred reactor were recently published [7]. We present here a simulation of these data using a model generated by EXGAS for a binary mixture composed of methyl palmitate and n-decane ([Fig. 1] and [Fig. 2]). Experiments were carried out at a pressure of 106 kPa, a residence time of 1.5 s and at stoichiometric conditions. The initial mole fraction of the fuel was 0.002 (dilution in helium) and the mole composition of the blend was 0.74 n-decane and 0.26 methyl palmitate. Simulations were performed with the code PSR of the software package Chemkin [16].

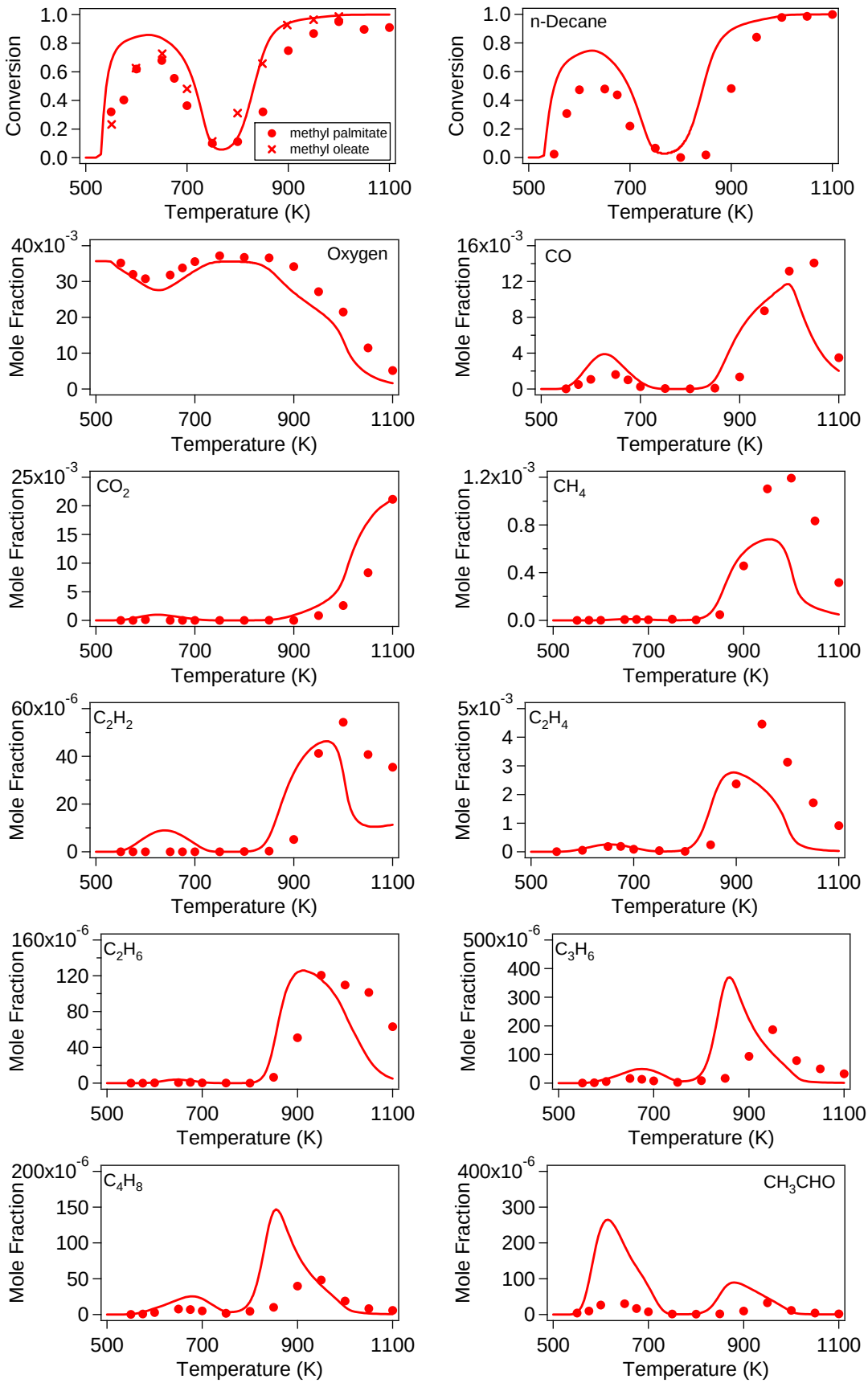


Fig. 1. Comparison of computed and experimental conversions of reactants and mole fractions of products for the oxidation of a blend of methyl palmitate and n-decane in a jet-stirred reactor (• and ×: experimental data; —: methyl palmitate model).

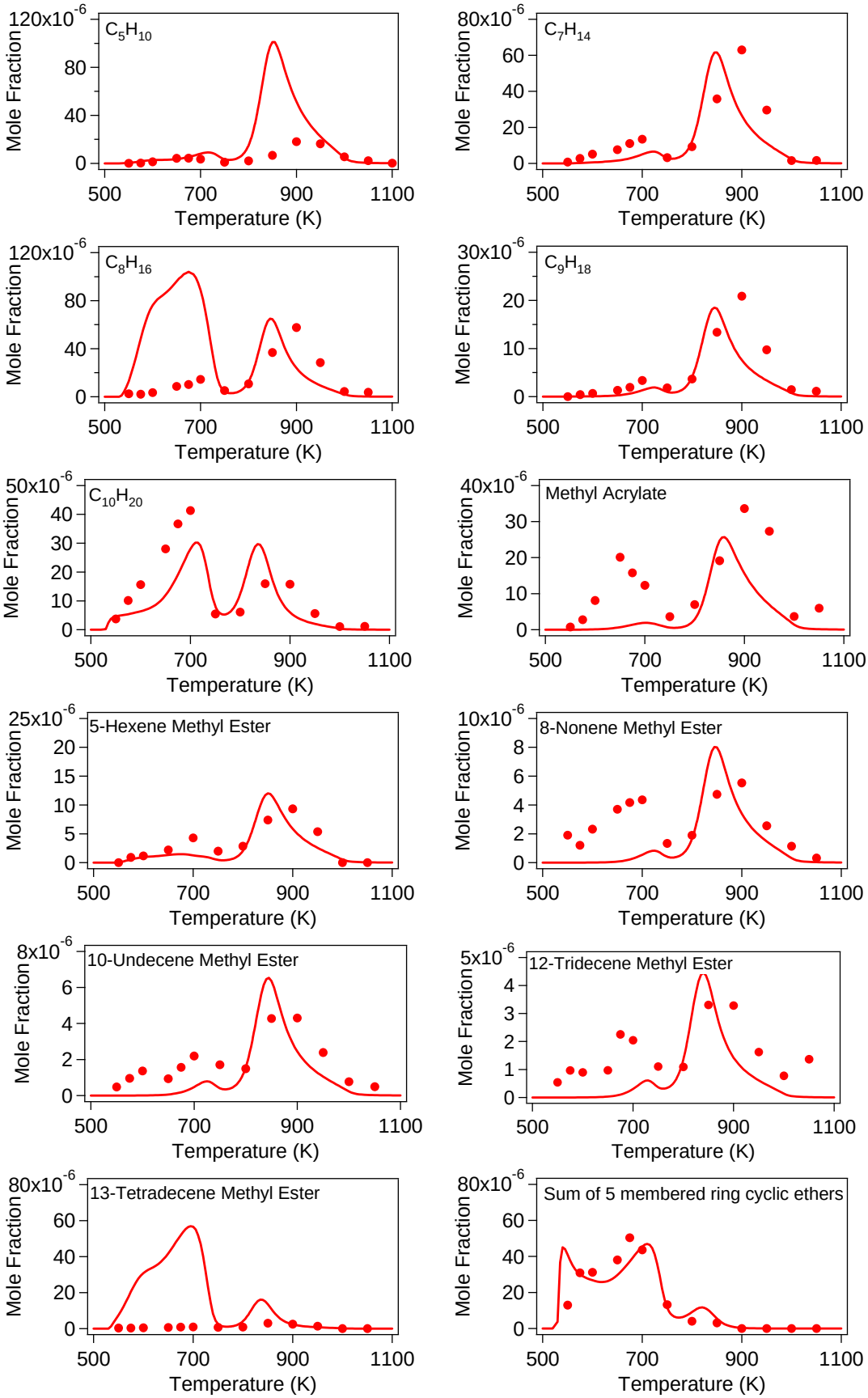


Fig. 2. Comparison of computed and experimental mole fractions of products (Part II) for the oxidation of a blend of methyl palmitate and n-decane in a jet-stirred reactor (•: experimental data; —: methyl palmitate model).

As far as the reactivity is concerned, the model captures well the mole fraction profiles of methyl palmitate, n-decane and oxygen (Fig. 1). The conversion of both reactants is over-predicted at low temperature (around 650 K) and in the region following the negative temperature coefficient (NTC) zone. The model is too reactive at high temperature (above 1000 K) as shown by the too high consumption of intermediate species (e.g., carbon monoxide, alkenes, and unsaturated esters).

The model also reproduces well the mole fraction profiles of most reaction products such as 1-alkenes (e.g., 1-heptene, and 1-nonene in Fig. 2) and unsaturated esters with the double bond at the end of the chain (e.g., 5-hexene methyl ester in Fig. 2). It can be seen that the formation of some intermediate species is strongly over-predicted in the low temperature region. This is the case for species such as acetaldehyde (Fig. 1), 1-octene, and 13-tetradecene methyl ester (Fig. 2). These discrepancies are due to the rules of decomposition of lumped species in the secondary mechanism. As an example, all the $C_{17}H_{32}O_5$ ketohydroperoxides formed in the low temperature chain branching reactions are lumped into one species called $C_{17}H_{32}O_5$KPS in the model. This species decomposes into an OH radical, a CO molecule, a large $C_8H_{14}O_3$ ester with an aldehyde function and an n-octyl radical. This reaction channel to n-octyl radical contributes then to the over-estimation of the formation of an important amount of 1-octene. The discrepancies in the mole fractions of some reaction products are also due to the change in the initial mole fraction of the fuels made to keep the carbon content constant when going from methyl decanoate to methyl stearate. Note that the lumping technique has little effect on the reactivity as the rate of consumption of a lumped species is the sum of the rates of consumption of all possible isomers. The lumping strategy is not affected by the fact that methyl esters are not symmetric: there are twice more isomers than in the case of linear alkanes of similar size but their individual amounts are twice lower. Thus the concentrations of the lumped species and their consumption rates are about the same for symmetric and non-symmetric species.

The model predicts well the global amount of $C_{17}H_{32}O_3$ five-membered ring cyclic ethers (Fig. 2). All possible isomers are formed in similar amounts except for the cyclic ether with the ring including the four atoms of carbon located at the end of the alkyl chain (which is less formed than the other ones) and for the cyclic ether including the four atoms of carbon just neighboring the ester function (the formation of which is favored by the lower energy of the C–H bonds in the α-position of the ester group). The larger amount of this ether is not in agreement with the experimental data as only very small quantities were observed [7].

According to the kinetic analysis performed at 650 K under the conditions of the experimental study, methyl palmitate is quasi-integrally consumed by H-abstractions by OH radicals. Note that the abstraction of the H-atoms in the α-position of the carbonyl group is easier than the ones of other H-atoms and that 18.5% of the fuel is consumed through this reaction. Chain branching is obtained through the sequence of reactions: addition of radicals from the reactant to O_2 forming ROO radicals; isomerizations of ROO radicals to QOOH radicals through H-shift; second additions of QOOH radicals to O_2 forming OOQOOH radicals; and isomerizations to a lumped $C_{17}H_{32}O_5$ ketohydroperoxide molecule plus OH. Note that many pathways lead to the formation of the lumped $C_{17}H_{32}O_5$

ketohydroperoxide molecule due to the large length of the chain, but the main ones are sequences which involves first and second isomerizations through a six-membered ring transition state.

The experimental conversion of methyl oleate, an ester with one double bond in the middle of the chain, which has been studied in a jet-stirred reactor [17], is also reported in Fig. 1. It can be seen that reactivities of both esters are very similar except above the NTC where methyl oleate is slightly more reactive than methyl palmitate. Consequently the model generated for methyl palmitate also reproduces well the conversion of methyl oleate. The comparison with the reaction products is not presented in this paper, but it can be deduced from the comparison between methyl palmitate and methyl oleate experimental data [17] that the generated model can also well reproduce the mole fraction profiles of the main species such as CO, CO_2, and ethylene. Note that the present model cannot account for the formation of products specific to unsaturated esters, such as dienes and esters containing two double bonds.

4. Comparison of the reactivity of large esters in a jet-stirred reactor

Models for neat methyl esters from C_{11} to C_{19} (with an odd number of atoms of carbon), generated with EXGAS, were used to compare their reactivity and the mole fractions of some reaction products in a jet-stirred reactor. Simulations were performed at temperatures ranging from 500 to 1100 K, at a pressure of 106 kPa and under stoichiometric conditions with dilution in helium. In the case of methyl decanoate, the inlet mole fraction of the fuel was 0.0023. Inlet mole fractions of other methyl esters were calculated in order to keep constant the carbon content of each reacting mixture. Simulations were also run with the model for n-hexadecane [10] in order to compare a large n-alkane with large methyl esters.

All these species exhibit a very similar conversion curves with the S shape due to the NTC (Fig. 3). Their reactivities are very close over the range of studied temperatures with the main differences observed around 780 K, where the conversion is minimum due to the NTC behavior. The reactivity increases from methyl decanoate to methyl stearate with that of other intermediate methyl esters lying in between. The reactivity of n-hexadecane is also very similar to the reactivity of large methyl esters. The conversion of this n-alkane is slightly larger than the ones of the studied methyl esters at low temperature (below 750 K), but lower at the minimum of conversion in the NTC zone. There is almost no difference at high temperature (above 800 K). Dagaut et al. also showed that the oxidation of a rapeseed biodiesel fuel can be successfully modeled by a detailed kinetic of the oxidation of n-hexadecane [18].

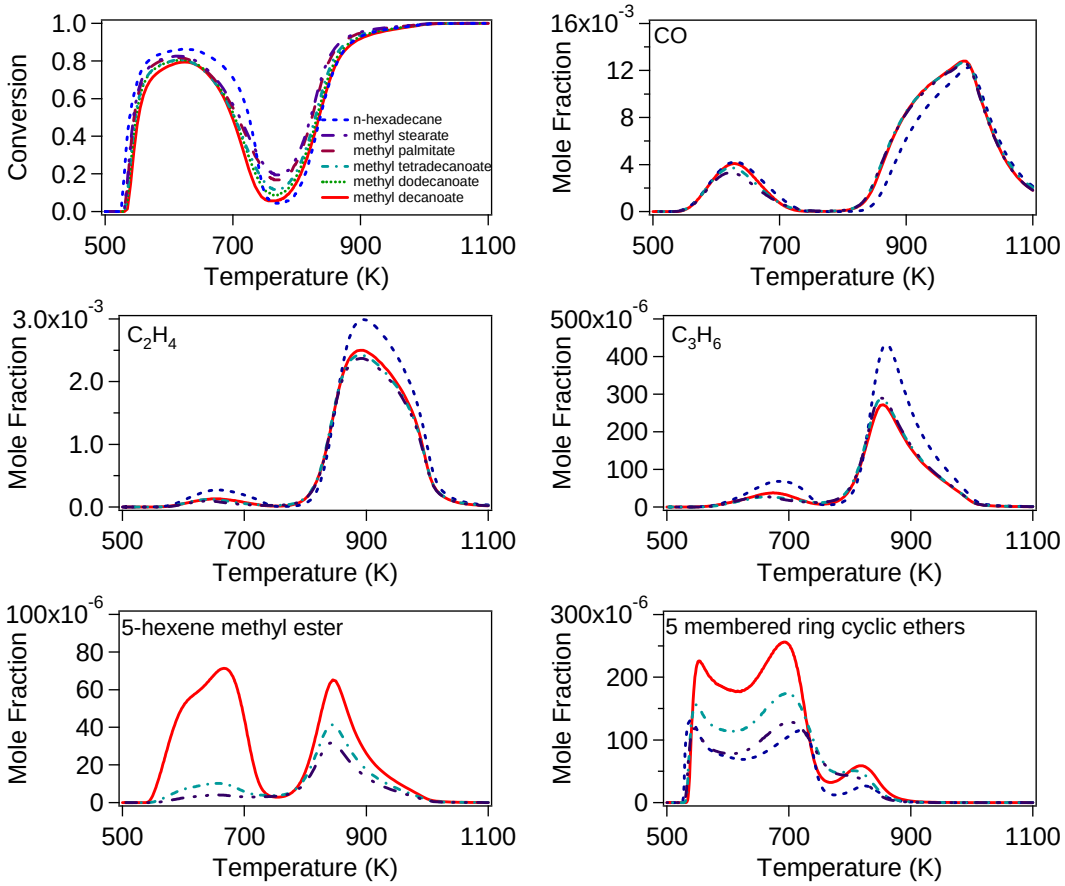


Fig. 3. Comparison of the conversion and of the mole fractions of some reaction products for methyl esters from C_{11} to C_{19} (with an odd number of atoms of carbon) and n-hexadecane in a jet-stirred reactor. Mole fractions are only presented for methyl decanoate, methyl tetradecanoate, methyl stearate, and n-hexadecane.

Figure 3 also displays the mole fraction profiles of some reaction products, CO, ethylene, propene, 5-hexene methyl ester and the sum of five-membered ring cyclic ethers with the same skeleton as the reactant. Mole fraction of CO, ethylene, and propene are very similar whatever the methyl esters. The main differences can be observed for 5-hexene methyl ester (due to some decomposition routes globalized in the secondary mechanism and favoring the formation of species with n/2 carbon atoms, n being the number of carbon atoms in the reacting species) and for cyclic ethers. For these last species, the mole fractions are different but the carbon contents are very similar due to the difference in the numbers of carbon atoms in the molecules. As an example, the amount of cyclic ethers computed with the methyl decanoate model is about twice larger than the one computed with the methyl stearate model but methyl decanoate has about twice less carbon atoms than methyl stearate. Methyl decanoate seems thus to be a good surrogate for the reactivity of larger unsaturated methyl esters with a substantial decrease in computational time.

Mole fraction profiles obtained with the n-hexadecane model are also very similar to those obtained with the models for methyl esters. The main differences are observed for ethylene and propene.

Their mole fractions are smaller in the simulations performed with the ester models due to the loss of symmetry in the initial reactants (esters lead to alkenes and unsaturated esters, whereas n-hexadecane only leads to alkenes). n-Hexadecane seems also to be a good surrogate for the reactivity of large unsaturated methyl esters but it cannot reproduce the mole fraction profiles of products specific to esters.

5. Conclusions

Detailed kinetic mechanisms for the oxidation of large saturated methyl esters from C_{11} to C_{19} were automatically generated with the software EXGAS including the reactions specific to the chemistry of esters and using a single set of kinetic parameters. These models contain many species and reactions because of the size of the reactants and because of the loss of the symmetry due to the ester function.

The data computed with the model generated for methyl palmitate were compared with experimental mole fraction profiles obtained in a jet-stirred reactor. The agreement between computed and experimental results was satisfactory for the conversion of the reactants and the mole fraction of most reaction products. This study showed that methyl esters larger than methyl decanoate are very good surrogates for the large saturated, and to a lesser extent unsaturated, esters found in biodiesel fuels as they predict well the reactivity and the mole fraction profiles of most species. This study also confirmed that large n-alkanes can be used to model the reactivity of large saturated esters, but that they cannot account for the formation of some specific reaction products such as unsaturated esters.

Biodiesel fuels also contain unsaturated methyl esters such as methyl oleate ($C_{19}H_{36}O_2$) and methyl linoleate ($C_{19}H_{34}O_2$). The present version of EXGAS is not able to account for the specific chemistry due to the presence of double bonds in the chains and further works about esters could consist in implementing specific rules in the software. Nevertheless previous work [17] shows that the presence of one double bond in the middle of the alkyl chain has very little effect on the reactivity of this type of large molecules.

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References

[1] A.K. Agarwal, Prog. Energy Combust. Sci. 33 (2007), pp. 233–271.

[2] M.S. Graboski and R.L. McCornick, Energy Combust. Sci. 24 (1998), pp. 125–164.

[3] A. Demirbas, Prog. Energy Combust. Sci. 31 (2005), pp. 466–487.

[4] O. Herbinet, W.J. Pitz and C.K. Westbrook, Combust. Flame 154 (2008), pp. 507–528.

[5] K. Seshadri, T. Lu and O. Herbinet et al., Proc. Combust. Inst. 32 (1) (2009), pp. 1067–1074.

[6] P.A. Glaude, O. Herbinet, S. Bax, J. Biet, V. Warth and F. Battin-Leclerc, Combust. Flame 157 (11) (2010), pp. 2035-2050.

[7] M.H. Hakka, P.A. Glaude, O. Herbinet and F. Battin-Leclerc, Combust. Flame 156 (11) (2009), pp. 2129–2144.

[8] P. Barbé, F. Battin-Leclerc and G.M. Côme, J. Chim. Phys. 92 (1995), pp. 1666–1692.

[9] V. Warth, N. Stef, P.A. Glaude, F. Battin-Leclerc, G. Scacchi and G.M. Côme, Combust. Flame 114 (1998), pp. 81–102.

[10] J. Biet, M.H. Hakka, V. Warth, P.A. Glaude and F. Battin-Leclerc, Energy Fuel 22 (2008), pp. 2258–2269.

[11] F. Buda, R. Bounaceur, V. Warth, P.A. Glaude, R. Fournet and F. Battin-Leclerc, Combust. Flame 142 (2005), pp. 170–186.

[12] A. El-Nahas, M.V. Navarro and J.M. Simmie et al., J. Phys. Chem. A 111 (2007), pp. 3727–3739.

[13] Y.R. Luo, Handbook of Bond Dissociation Energies in Organic Compounds, CRC Press, Boca Raton (2003).

[14] A.M. Dean and J.W. Bozzelli, Combustion Chemistry of Nitrogen. In: W.C. Gardiner, Editor, Gas-phase Combustion Chemistry, Springer-Verlag, New York (2000).

[15] M.H. Hakka, H. Bennadji and J. Biet et al., Int. J. Chem. Kinet. 42 (4) (2010), pp. 226–252.

[16] R.J. Kee, F.M. Rupley, J.A. Miller, Chemkin II: A Fortran Chemical Kinetics Package for the Analysis of a Gas-phase Chemical Kinetics, SAND89-8009B, Sandia Laboratories, 1993.

[17] S. Bax, M.H. Hakka, P.A. Glaude, O. Herbinet and F. Battin-Leclerc, Combust. Flame 157 (6) (2010), pp. 1220–1229.

[18] P. Dagaut, S. Gaïl and M. Sahasrabudhe, Proc. Combust. Inst. 31 (2) (2007), pp. 2955–2961.