Experimental and modeling study of the pyrolysis of biodiesel: unraveling the role of double bonds

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Highlights

- Plug flow reactor
- Automatic kinetic model generation
- Methyl decanoate and methyl 4-decenoate pyrolysis

Introduction

The increasing energy demand around the world and the decreasing petroleum reserves create the need for alternative feedstocks. Additional environmental and socioeconomic concerns make biofuels, like bioethanol and biodiesel, the most viable and sustainable alternatives. These biofuels are already used for blends with petroleum diesel for usage in compression engines. Regarding the environmental concerns, the bio-based alternatives contribute significantly in reducing the emission of greenhouse gases as they are considered "carbon-neutral".

Biodiesel, the focus of this work, is produced by fermentation of triglycerides, from a vegetable source, with methanol to form fatty acid methyl esters (FAME, biodiesel) and glycerol as a byproduct. Alternatively, also bio-ethanol can be used in the fermentation process, yielding fatty acid ethyl esters (FAEE). The composition of the FAME (or FAEE) mixture depends on the source of the vegetable oil or fat that is used. Typically unsaturated, mono-saturated and poly-saturated methyl esters with a hydrocarbon chain length ranging from 14 to 24 carbons are present in the mixture [1].

Many kinetic studies have been performed to study the pyrolysis and oxidation of unsaturated methyl esters. Most studies focus on methyl butanoate to capture the chemistry that is characteristic for the methyl ester group. Other biodiesel surrogates that have been studied range from methyl hexanoate to methyl decanoate. The kinetic studies on unsaturated methyl esters, on the other hand, are scarce. Some attention has been paid to the pyrolysis and oxidation of methyl crotonate and also methyl 5-decenoate and methyl 9-decenoate have been studied [2].

In this work, a comparative study has been performed between methyl decanoate (MD) and methyl 4-decenoate (M4DE) to study the influence of the presence of a double bond in the hydrocarbon chain. Experiments for both compounds are done in a plug flow reactor. The influence of the double bond will be studied with the development of a microkinetic model with the automatic kinetic model generation tool Genesys.

Experimental methodology

A bench-scale plug flow pyrolysis reactor is used to study the pyrolysis of methyl decanoate and methyl 4-decenoate. Experimental results for MD pyrolysis have been published in previous work by Pyl et al.[3] Details regarding the experimental set-up have been discussed before [4,5]. For the pyrolysis of M4DE the pressure in the reactor is set to 0.17 MPa and temperature settings vary between 580 and 720 °C with 20 °C increments. The mass flow rate equals 50 g h^{-1} for M4DE and 152 g h^{-1} for nitrogen diluent, corresponding to a dilution of 20 mol_{N2}/mol_{M4DE}. Pyrolysis products are measured using a dedicated analysis section with a refinery gas analyzer, a light oxygenates analyzer and a 2-dimensional GC×GC coupled to either a FID detector for quantification or a TOF/MS detector for species identification. The main hydrocarbon products detected at the highest temperature are typical pyrolysis products like methane, ethylene, propylene, 1,3-butadiene, 1,3-cyclopentadiene and benzene. Carbon monoxide is the most abundant detected oxygenate, followed by carbon dioxide. Furthermore, small amounts of formaldehyde and water are detected.

Automatic kinetic model generation

Discrepancies between the pyrolysis products of methyl decanoate and methyl decenoate have been identified and explained by means of a microkinetic model. For the construction of this kinetic model, an

in-house developed software tool called “Genesys” is used [6,7].

The network generation in Genesys requires reactants and possible reaction families as user-input. For the assignment of thermodynamic and kinetic data to the kinetic model, Genesys makes use of extensive databases based on high level quantum mechanical calculations. If no species data is available, Genesys uses estimation methods like Benson’s group additivity [8] or Lay’s hydrogen bond increment method [9] to determine thermodynamic data. In case no Arrhenius parameters are found in the kinetics databases, reactivity-structure-related estimation methods are used for the determination of Arrhenius parameters. One example is the group additivity method for Arrhenius parameters developed by Saeys et al. [10] and extended by Sabbe et al. [11]

The final kinetic model is generated in CHEMKIN format and can be used for reactor simulations.

Results and Discussion

Experimentally acquired data for methyl decanoate and methyl 4-decenoate are compared in Figure 1.

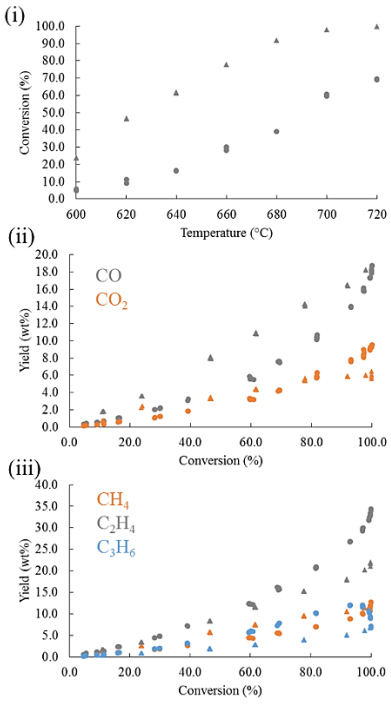

Figure 1. Experimental results for the pyrolysis of methyl decanoate (●) and methyl 4-decenoate(▲). (i) Conversion profile as function of temperature (ii) CO (grey) and CO2 (orange) yields as function of conversion (iii) CH4 (orange), C2H4 (grey) and C3H6 (blue) yields as function of conversion.

In Figure 1 (i), the conversion is presented. It is clear that the conversion of M4DE is higher compared to the one of MD. In Figure 1 (ii) and (iii), the yields of the main product species are compared. The yield of carbon monoxide is higher for the pyrolysis of M4DE compared to MD, while the yield of carbon dioxide is comparable. The yield of hydrocarbon species, such as ethylene and propylene are higher in case of MD pyrolysis, while the yield of methane slightly increases in case of M4DE pyrolysis.

Conclusion

An experimental dataset is developed for the pyrolysis of methyl decanoate and methyl 4-decenoate. A comparison of the experimental results indicates that ethylene and propylene yields are higher for the pyrolysis of the unsaturated methyl ester. A microkinetic model has been developed with in-house developed software, Genesys, for automatic kinetic model generation to confirm and explain the experimental results. .

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Keywords

Biodiesel, saturated, pyrolysis