



# FIRST PRINCIPLES BASED MICROKINETIC MODELLING OF METHYL BUTANOATE PYROLYSIS

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## Introduction

The increasing worldwide energy demand and reduced amount of petroleum reserves have created the need for sustainable development of alternatives. One of the possible alternatives is biodiesel, a fuel substitute produced from renewable resources such as vegetable oils or animal fats. The chemical reaction of triglycerides with methanol gives a mixture of saturated and unsaturated methyl esters containing hydrocarbon chains with 12 or more carbon atoms [1].

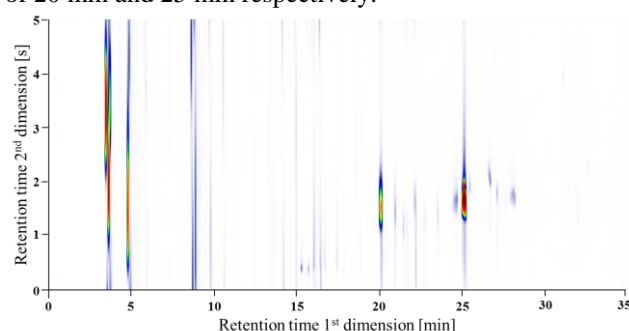
Kinetic modelling can provide insight into the chemical characteristics of this fuel alternative. The kinetic model contributes to the design and optimization of processes in which biodiesel is involved. Because of its complex composition, the direct modelling of biodiesel is difficult. First, an understanding of the reactivity of the oxygenated part of these molecules is required. For this, a model molecule is used that matches the characteristics of biodiesel and avoids the complexity of the mixture. Methyl butanoate (MB),  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_3$ , is a relatively short methyl ester that still incorporates all essential chemical structure features of a typical biofuel. It can therefore be used as a convenient model compound for the complex biofuel methyl ester mixture.

In this work, an ab initio based group additive model is built to describe the pyrolysis of methyl esters. The kinetic model is validated by comparison with a new set of experimental data gathered on the bench-scale setup.

## Bench-scale pyrolysis reactor

The bench-scale pyrolysis setup is used to acquire a new set of experimental data for the pyrolysis of MB. The setup has been discussed in detail in previous work [2, 3]. For the pyrolysis of MB, the initial feed to the reactor is set to 257 g/h MB and 40 g/h  $\text{N}_2$ , corresponding to a dilution of 0.6 mol $\text{N}_2$ /mol $\text{MB}$ . The pressure is set to 0.17 MPa. In order to cover the complete conversion range, the temperature setting varies from 913 K to 1113 K in 20 K increments. For each studied condition, at least three repetition experiments are performed. The resulting chromatogram at 1033 K is given in Figure 1. The major components at this temperature are  $\text{C}_4$ -components ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_6$ ) at

a first retention time lower than 10 min, methyl propanoate and methyl butanoate, at a first retention time of 20 min and 25 min respectively.



**Figure 1. Gc x Gc chromatogram acquired from bench-scale experiments for the pyrolysis of MB. (pressure: 0.17 MPa; MB flow rate: 257 g/h; dilution 0.6 mol $\text{N}_2$ /mol $\text{MB}$ ; Temperature: 1033 K)**

## Kinetic model generation

For the development of the microkinetic model for MB pyrolysis, the Genesys [4, 5] software package for automatic kinetic model generation is used. The termination of the kinetic model generation is achieved with the rule-based criterion.

For the determination of thermodynamics and kinetics of all compounds and reactions in the model, Genesys makes use of user-defined databases. Thermochemistry data for hydrocarbon and oxygenated compounds is calculated with the CBS-QB3 composite method or higher accuracy methods. If data is not available, prediction techniques, such as Benson's group additivity method [6] and the hydrogen bond increment method developed by Lay et al. [7] are applied to determine thermochemical properties for molecules and radicals respectively. Rate coefficients for elementary reactions are determined with the use of group additive values for Arrhenius parameters based on the group additive method developed by Saeyns et al. [8] and extended by Sabbe et al. [9] User-defined correlations for tunnelling coefficients can be introduced. In this work, a fourth order polynomial is used, derived from Eckart [10] tunnelling coefficients. Reverse rate coefficients are calculated based on the rate coefficient for the forward direction of the

reaction and on the thermodynamic equilibrium coefficient, to assure thermodynamic consistency.

Starting from an extended literature review for the thermal decomposition of MB, seven reaction families are implemented in Genesys. These have kinetic parameters based on group additive models for hydrocarbons [11] and oxygenated compounds [12]. The reaction families include (1) carbon-centred radical additions to hydrocarbons and oxygenates (2) hydrogen radical additions to hydrocarbons (3) hydrogen abstractions by carbon-centred radicals and (4) by hydrogen atoms from hydrocarbons and (5) hydrogen abstractions by carbon-centred radicals, (6) by hydrogen atoms and (7) by oxygen-centred radicals from oxygenates.

For the bond scission reactions and reverse radical recombination reactions of MB, Arrhenius parameters from the work of Huynh and Violi [13] and Ali and Violi [14] are applied. These Arrhenius parameters have been determined with the use of variational transition state theory. Rate coefficients for bond scission reactions for which no data is available, are assumed to be equal to the rate coefficients of structurally similar reactions that are reported in the studies of Huynh and Violi [13] and Ali and Violi [14]. Also for hydrogen shift reactions, no group additive models are available due to the strong ring strain dependency during most of these reactions. The ab initio study of Huynh and Violi [13] and Ali and Violi [14] also provides Arrhenius parameters for these reactions.

The accuracy of group additivity methods for smaller species is limited and it is recommended to use thermodynamic and kinetic data for those species determined from experimental resources or high level ab initio calculations. To improve the accuracy of the generated kinetic model it is opted to use the base mechanism for the decomposition of smaller compounds containing up to two carbon atoms from the work of Metcalfe et al. [15] This mechanism is merged with the mechanism resulting from the Genesys simulations.

The group additive framework used in these simulations contains mainly data for saturated oxygenates. The decomposition of small unsaturated methyl esters, such as methyl propenoate, is not well described because of the limited amount of group additive values available for unsaturated oxygenates. Methyl propenoate is an important species during MB decomposition. To complete the kinetic model, important reactions for the decomposition of methyl propenoate, proposed by Bennadji et al. [16], are included.

## Microkinetic simulations

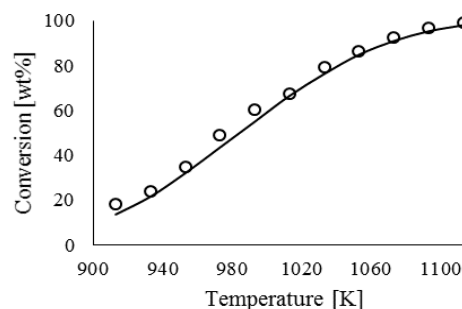
The microkinetic model developed is used to simulate bench-scale experiments. All experiments are performed at the same feed flow rates and pressure, but at different temperatures ranging from 913 K to 1113 K in 20 K increments in order to cover a broad conversion range.

Table 1 provides a comparison between simulated and experimentally observed product yields for the bench-scale experiment at 1013 K. Only products within an experimental yield of 1 wt% or higher are compared.

**Table 1. Comparison between simulated and experimental product yields (wt%) at 1013 K (pressure: 0.17 MPa; MB flow rate: 257 g/h; dilution: 0.6 mol<sub>N2</sub>/mol<sub>MB</sub>)**

| Yield (wt%)                   | Experimental | Simulated |
|-------------------------------|--------------|-----------|
| CO <sub>2</sub>               | 11.14        | 9.09      |
| CH <sub>4</sub>               | 10.79        | 9.92      |
| CO                            | 16.11        | 11.92     |
| C <sub>2</sub> H <sub>6</sub> | 1.62         | 0.40      |
| C <sub>2</sub> H <sub>4</sub> | 8.83         | 7.84      |
| C <sub>3</sub> H <sub>6</sub> | 7.34         | 6.72      |
| CH <sub>2</sub> O             | 3.32         | 3.66      |
| Methyl propenoate             | 4.60         | 9.24      |
| Methyl butanoate              | 32.47        | 33.53     |

Based on these results, it can be concluded that the simulated conversion of MB 66.47 % is in good agreement with the experimental observed conversion of 67.53 %. Also at other temperatures, the conversion is accurately predicted (Figure 2).



**Figure 2. Simulated (lines) and experimentally obtained (dots) methyl butanoate conversion as function of reactor temperature. (pressure: 0.17 MPa; MB flow rate: 257 g/h; dilution 0.6 mol<sub>N2</sub>/mol<sub>MB</sub>)**

Most of the product yields are predicted satisfactorily. Major products such as CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub> and formaldehyde are in good agreement with experimental yields. Major deviations pertain to three products: C<sub>2</sub>H<sub>6</sub>, methyl propenoate and CO. Methyl propenoate is overpredicted by the model, whereas ethane and carbonmonoxide are both underpredicted by the model. A possible explanation for the discrepancy is a missing elementary reaction from methyl propenoate to ethane and CO.

## Conclusion

The thermal decomposition of methyl butanoate was studied using the automatic kinetic model generation software Genesys and using novel ab initio based

group additive values for thermodynamic and kinetic parameters. The simulated MB conversion and major product yields agree well with experimental data acquired at the bench-scale setup over the studied temperature range (913 K – 1113 K). The majority of the major products are simulated within less than 10% relative deviation from the experimental values.

## Acknowledgements

The SBO proposal “ARBOREF” supported by the Institute for promotion of Innovation through Science and Technology in Flanders (IWT) is acknowledged.

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