FIRST PRINCIPLES BASED MICROKINETIC MODELING OF METHYL BUTANOATE PYROLYSIS

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ABSTRACT

A consistent set of ab initio obtained thermodynamic and kinetic data is applied to simulate the thermal decomposition of methyl butanoate (MB). Reactor simulations were performed for the MB pyrolysis at a temperature range of 913-1113 K and the results were validated by comparison with experimental data gathered on a bench-scale flow reactor. For the development of a reaction mechanism for the MB pyrolysis the in-house developed automatic kinetic model generation software "Genesys"^[1,2] was used. All thermodynamic data required for the generation of the reaction mechanism were derived from (a) quantum chemical calculations on the CBS-QB3 level of theory^[3,4], (b) by means of group additivity^[5,6] based on CBS-QB3 data or (c) using the hydrogen bond increment method^[7]. Rate coefficients were mainly obtained from (a) ab initio calculations at high level of theory or (b) group additivity methods based on ab initio calculations. The simulated MB conversion and major product yields agree well with experimental data acquired at the bench-scale setup over the studied temperature range. The good agreement indicates the usefulness and reliability of the CBS-QB3-based group additivity methods and the potential of integrating ab initio methods with engineering tools for accurate reactor simulations.

INTRODUCTION

The increasing worldwide energy demand and the declining global oil production capacity have created the need for sustainable development of alternatives. Among the potential alternatives is biodiesel, a fuel substitute produced from renewable resources such as vegetable oils or animal fats. Because of its complex composition and the varying size of the constituent molecules, direct modelling of biodiesel chemistry is difficult. However, the investigation of the chemical characteristics of this potential fuel is of major importance. An alternative is to use model molecules that match the characteristics of the biodiesel but avoid the complexity of the mixture. Methyl butanoate (MB), CH₃CH₂CH₂C(=O)OCH₃, 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 using the in-house software "Genesys"^[1,2], to describe the pyrolysis of methyl esters. The simulation of a bench-scale reactor for MB thermal decomposition is performed using the CHEMKIN software package^[8] in order to validate the use of the ab initio based group additively models in the microkinetic modelling of ester pyrolysis. Reaction path analysis is used to identify the dominant paths for the MB thermal decomposition at the studied conditions. The predictions of this model for the MB pyrolysis are compared with available experimental data obtained in a bench-scale pyrolysis set-up in the Laboratory for Chemical Technology (LCT) of Ghent University.

BENCH-SCALE PYROLYSIS REACTOR

The bench-scale pyrolysis setup has been discussed in details in previous work^[9,10] and is used to acquire a set of experimental data for the pyrolysis of MB. For the studied process, the initial feed to the reactor is set to 257 g/h MB and 40 g/h N₂, corresponding to a dilution of 0.6 mol N₂/ mol 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 C₄- components (CH₄, C₂H₆, C₂H₄ and C₃H₆) at a first retention time lower than 10 min, methyl propenoate and methyl butanoate, at a first retention time of 20 min and 25 min respectively.



Figure 1. GC×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 N_2 / mol MB; Temperature: 1033 K)

KINETIC MODEL GENERATION

For the development of the microkinetic model for MB pyrolysis, the "Genesys" ^[1,2] software package for the automatic kinetic model generation is used. As stated by Vandewiele et al.^[1], the automated construction of kinetic models with Genesys consists of three sequential parts: (1) the input of the required information, (2) the processing step, in which the thermodynamic and kinetic data is assigned and the reaction network is generated, and (3) the post-processing step, in which the output file is produced in a format that can be read by microkinetic or reactor simulation programs. 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^[3,4] or higher accuracy methods. If data is not available, prediction techniques, such as Benson's group additivity method^[5,6] 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 Saeys et al.^[11] and extended by

Sabbe et al.^[12] User-defined correlations for tunneling coefficients can be introduced. In this work, a fourth order polynomial is used, derived from Eckart^[13] tunneling 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, several reaction families are implemented in Genesys. These have kinetic parameters based on group additive models for hydrocarbons^[12] and oxygenated compounds^[14-16]. The reaction families include (1) unimolecular decomposition reactions of MB. (2) Hydrogen abstraction reactions by hydrogen atoms and carbon- and oxygen centered radicals to hydrocarbons and oxygenates. (3) Intramolecular hydrogen abstraction reactions. (4) Hydrogen- and carbon-centered beta-scission reactions and the reverse addition reactions. (5) Alpha-scission reactions with the formation of CO. For the bond scission reactions and unimolecular initiation reactions of MB, Arrhenius parameters have been determined with the use of variational transition state theory (VTST). 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^[17] and Ali and Violi^[17]

For hydrogen shift/isomerization reactions no group additive models are available due to the strong ring strain dependency during most of these reactions, which makes them difficult to model group additively. The Arrhenius parameters for these reactions are calculated at the CBS-QB3 level of theory in the study of Huynh and Violi^[17] and Ali and Violi^[18].

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.^[19] 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. However, methyl propenoate is among the most important species during the MB decomposition. To complete the kinetic model, important reactions for the decomposition of methyl propenoate have been calculated at the CBS-QB3 level of theory by Bennadji et al.^[20].

MICROKINETIC SIMULATIONS

The microkinetic model developed in this work is used to simulate bench-scale experiments. All experiments are performed at the same feed flow rates and pressure, but at different temperature settings ranging from 913 K to 1113 K in 20 K increments in order to cover a broad conversion range. A qualitative comparison of the produced compounds obtained from the reaction mechanism generated in this study and the experimental data shows that the majority of compounds which are present in the reactor effluent of MB pyrolysis are also present in the simulations.

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

Yield (wt %)	Experimental	Simulated
CO ₂	11.14	9.09
CH ₄	10.79	9.92
СО	16.11	11.92
C ₂ H ₆	1.62	0.40
C ₂ H ₄	8.83	7.84
C ₃ H ₆	7.34	6.72
CH ₂ O	3.32	3.66
Methyl propenoate	4.60	9.24
Methyl butanoate	32.47	33.53
Other products	3.78	7.68
Total	100.00	100.00

Table 1. Comparison between simulated and experimental product yields (wt %) at 1013 K (pressure: 0.17 MPa; flow rate of methyl butanoate: 257 g/h; dilution: 0.6 mol_{N2}/mol_{MB}).

Based on these results, it can be concluded that the simulated conversion of MB, 66.47 %, is in good agreement with the experimentally observed conversion of 67.53 %. Also at the whole temperature range studied, the conversion is accurately predicted as it is shown in Figure 2.



Figure 2. Simulated (line) and experimentally obtained (dots) methyl butanoate (MB) conversion as function of reactor temperature. (pressure: 0.17 MPa; MB flow rate: 257 g/h; dilution 0.6 mol_{N2}/mol_{MB}).

Most of the product yields are predicted satisfactorily. Major products such as CO, CO₂, CH₄, C₂H₄, C₃H₆ and formaldehyde are in good agreement with the corresponding experimental yields. Major deviations pertain to unsaturated esters such as methyl propenoate. Methyl propenoate and C4:1 esters are overpredicted by the kinetic model proposed in this work. The consumption and production pathways of the unsaturated esters are very sensitive to the addition of hydrogen to the C=C double bound and reverse beta-scission. Because of the low barrier of hydrogen addition reactions, the uncertainty on the ab initio calculated rate coefficients is high. More accurate Arrhenius parameters for these reactions can improve the prediction of unsaturated esters.

CONCLUSIONS

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 applicability of the developed reaction mechanism is not restricted only to methyl butanoate thermal decomposition. It can be implemented as a seed mechanism to describe other processes based on gas phase radical chemistry involving oxygenates, such as partial oxidation or combustion processes. As such, this is a significant step towards optimization of current technologies or designing new processes involving bio-based feedstock.

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