GROUP-ADDITIVE KINETIC MODELING OF BIODIESEL PYROLYSIS: METHYLDECANOATE CASE STUDY

Kevin M. Van Geem*, Steven P. Pyl, Maarten K. Sabbe, Zhiming Zhou, Marie-Françoise Reyniers and Guy B. Marin
Ghent University
Krijgslaan 281, S5, 9000 Ghent, Belgium

Abstract
This work presents the application of a consistent ab initio based kinetic and thermodynamic group additive method for the simulation of the pyrolysis of the biodiesel model component methyldecanoate. Comparison between the experimentally determined product yields and reactor simulations over a wide range of process conditions shows that the main product yields can be predicted within 5% of the experimentally observed yields. A sensitivity analysis and rate of production analysis allow to identify the dominant reaction pathways in the radical reaction network. Also commonly used assumptions such as the μ-hypothesis and the quasi steady state approximation (QSSA) for μ-radicals are verified.

Keywords
Group additive modeling, fundamental kinetic model, pyrolysis, biodiesel, methyldecanoate

Introduction
Large-scale detailed kinetic models find increasing use in the modeling of combustion processes, atmospheric chemistry, soot formation, and other areas of industrial or environmental interest. Because such reaction networks may contain up to thousands of reactions and species, constructing them by hand can be tedious and error-prone. That is why reaction network generation has evolved from manual construction (Rice & Herzfeld, 1934) to computer-aided generation using advanced algorithms for the selection of the relevant reactions. (Broadbelt et al., 1994; Green et al., 2001; Hillewaert et al., 1988; Klein et al., 2006) These algorithms generate a reaction network starting from the feedstock molecules and a given set of reaction rules, yielding all possible intermediates and reactions.

Providing these detailed reaction networks with accurate values for the required thermodynamics and kinetics in the desired range of conditions is one of the largest challenges in the modeling of industrial processes based on radical chemistry. As experimental determination of rate coefficients is very time consuming and, in particular for radical reactions, very complicated, experimental kinetic data are by far too scarce to describe the necessary kinetics. Generally a combination of experimentally determined, predicted and fitted data is applied in order to overcome the lack of available kinetic and thermochemical data. (Sundaram & Froment, 1979) (Broadbelt et al., 1995; Clymans & Froment, 1984; Dente et al., 1979) Quantum chemistry provides an opportunity to provide these reaction schemes with consistent data, thanks to the advances in methods in computing power last decennia. The use of quantum chemistry to calculate rate coefficients for gas phase radical reactions is particularly attractive since it avoids difficult experimentation techniques and the need to rely on assumed reaction schemes. However, calculating accurate kinetics and

* To whom all correspondence should be addressed
thermodynamics for the thousands of reactions for radical chemistry is beyond computational possibilities. Therefore, engineering approximations are introduced that have the advantage that for the larger species and reactions in the network, for which accurate quantum chemical calculations are computationally too expensive, the thermodynamics and kinetics can be reliably determined based on studying the chemistry of smaller species. This methodology has been extended to describe the pyrolysis of oxygenates and in particular for methyl esters. The present work has focused on pyrolysis because of the limited attention on this aspect in current kinetic databases, in particular for combustion. The processes involved in pyrolysis are of key importance for the treatment of Soot/PAH formation, since the products of such reactions are their precursors. Moreover from an experimental point of view it is difficult to study oxidation at high temperatures without a thorough understanding of the competing pyrolysis reactions.(Tsang, 2010) Therefore experiments with methyldecanoate are used to address the main challenges of modeling combustion and pyrolysis of renewable feeds. Topics such as reaction network size and the considered level of detail in combination with assigning appropriate kinetic and thermodynamic data in these comprehensive reaction networks are discussed.

**Experimental**

The bench scale pyrolysis set-up has been described extensively. (Pyl et al., 2011) It consists of three parts: the feed section, the furnace/reactor section and the analysis section. The flow rate of methyldecanoate is controlled by a coriolis mass flow controller (S) (Bronkhorst, The Netherlands). The reactor is a 1.475-m long, 6-mm internal diameter tube, made of Incoloy 800HT (Ni, 30-35; Cr, 19-23; and Fe, >39.5 wt %). The diluent, i.e. N₂ in this work (3), is heated to the same temperature as the evaporated feed. The analysis section of the pyrolysis set-up enables on-line qualification and quantification of the entire product stream, i.e. a wide boiling mixture containing H₂, CO, CO₂, alcohols (methanol, ethanol and heavier), aldehydes and ketones (formaldehyde, acetaldehyde, acetone, etc.), esters, and hydrocarbons ranging from methane to polyaromatic hydrocarbons (PAH). The enormous boiling range of the product constituents makes a complete and accurate analysis of pyrolysis reactor effluents a difficult task. Three different gas chromatographs are required: a refinery gas analyzer (RGA,17), a light oxygenates analyzer (LOA, 10) and the GC×GC-FID/TOF-MS (11) described above. The analytical equipment is positioned at different positions on the reactor effluent line. The GC×GC setup, has been discussed previously. (Van Geem et al., 2010) Approximately 200 different components could be identified because of reduced peak overlap thanks to the increased separation power of the GC×GC, see Figure 1.

![Figure 1. On-line GC×GC FID chromatogram for pyrolysis of methyldecanoate (MD) at 680°C and dilution of 1 mole N₂ per mole methyldecanoate](image)

**Results and Discussion**

**Reaction network generation**

Generally a detailed reaction network is generated by allowing the feedstock components to react according to different reaction families. Examples are hydrogen abstraction reactions either intra- and intermolecular, addition reactions (intra- and intermolecular) etc. Rice and coworkers (Rice & Herzfeld, 1934); (Kossiakoff & Rice, 1943) showed that pyrolysis of hydrocarbons proceeded through a free radical mechanism and that only a limited number of important reaction families need to be distinguished e.g. carbon-carbon and carbon-hydrogen bond scissions of molecules and the reverse radical- radical recombinations, hydrogen abstraction reactions, both intra- and intermolecular, radical addition to olefins and the reverse β scission of radicals, both intra- and intermolecular, etc. Cyclization reactions are considered as intramolecular additions, while isomerization reactions are considered as intramolecular hydrogen abstractions.

The reaction network is generated starting from pool of molecules, all reaction possibilities are identified. For every forward reaction introduced in the network the corresponding reverse reaction is also incorporated in the network. These reactions result in a number of formed radicals and molecules. The new radicals are added to the radical pool and the molecules are added to the molecule pool. In the next iteration the new species react with each other and with other species of the radical and molecule pool and the network is constructed gradually. A problem of this type of approach is that in principle the reaction network can become infinite, because addition reactions continuously lead to the formation of new species not yet included in the reaction network. Similar to that reported by Broadbelt et al. (1994) , this problem has been overcome by using a carbon count stop criterion for the formed species to limit the network growth. Because almost no products with 12 or more carbon atoms are identified in the methyldecanoate pyrolysis experiments the maximum carbon number of species is set to 11. The
The resulting reaction network consists of over 4000 reactions between more than 1000 species.

**Group Additive Methodology**

The reaction network forms the heart of any fundamental simulation model and determining the net reaction rates requires that both the thermochemistry and kinetics for each of the elementary steps in the reaction network are known. Calculating all required parameters by ab initio methods is infeasible due to the large number of reactions. Therefore, a group additive method is applied that links the thermodynamics and kinetics for larger species to mostly high-accuracy ab initio data for smaller species. In previous work, consistent group additive models have been constructed for the prediction of thermochemistry and kinetics for the radical gas phase chemistry of hydrocarbons. (Sabbe et al., 2008; Sabbe et al., 2005; Sabbe et al., 2007) These models are based on the ab initio calculation of a consistent set of thermodynamic and kinetic data for the most important reaction families involved in radical hydrocarbon chemistry. The methodology is based on Benson group additivity and has proven its reliability for hydrocarbon thermochemistry, and the kinetics of radical additions and hydrogen abstractions. In the current work this group additive method has been extended to include group additive values for the thermochemistry of oxygenates relevant to our case study and a group additive method for new reaction families including decarbonylation and decarboxylation. The group additive values for these last two reaction families have been determined based on literature data and a limited number of ab initio calculations.

**Validation**

Table 1 shows a summary of some grouped product yields for two different conditions. These data have been used for validating the automatically generated reaction network.

<table>
<thead>
<tr>
<th>Product</th>
<th>T=600°C</th>
<th>T=800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>1.0</td>
<td>12.8</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>CO</td>
<td>0.8</td>
<td>17.9</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.5</td>
<td>9.0</td>
</tr>
<tr>
<td>CH$_2$O</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Olefins</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$-C$_4$</td>
<td>6.40</td>
<td>42.9</td>
</tr>
<tr>
<td>C$<em>5$-C$</em>{11}$</td>
<td>2.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Methyl Esters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$-C$_4$</td>
<td>2.4</td>
<td>0.8</td>
</tr>
<tr>
<td>C$<em>7$-C$</em>{11}$</td>
<td>85.6</td>
<td>8.7</td>
</tr>
<tr>
<td>Mono-aromatics</td>
<td>0.1</td>
<td>5.4</td>
</tr>
<tr>
<td>Poly-aromatics</td>
<td>0.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

**μ-hypothesis and QSSA for μ-radicals**

A commonly applied assumption in modeling pyrolysis is the μ-hypothesis for large aliphatic radicals, i.e. bimolecular reactions are neglected for these radicals. These large radicals are called μ-radicals because they are involved in monomolecular reactions only. (Ranzi et al., 1983) Generally radicals with more than 5 carbon atoms are considered μ-radicals. Small radicals, such as the ethyl or propyl radical, are usually allowed to react by both unimolecular and bimolecular pathways. Benzyl and methyl radicals on the other hand are usually assumed to react only bimolecularly, i.e. their unimolecular reactions are neglected. (Laidler, 1987) In the reduced mechanism no bimolecular reactions involving long chain radicals are included. Hence, they are not fast enough compared to the unimolecular reaction possibilities and can be neglected.

To overcome the stiffness problem of the continuity equations the radical concentrations are often computed using the quasi-steady-state approximation (QSSA) (Bodenstein & Lutkemeyer, 1924). There is some concern about the accuracy of this approximation, so in some pyrolysis models the QSSA is only assumed to hold for the μ-radicals. (Clymans & Froment, 1984) In the present model the concentration of all species is calculated exactly using a stiff integrator, and KINALC (Turányi, 1997) is used to estimate the errors introduced by applying the QSSA for each species in the reaction network. Based on these calculations it seems indeed possible to assume the

A reasonable agreement, within 5% relative of the experimentally observed yields, is obtained between simulated and experimentally measured product yields as can be seen from Figure 2.

To get further insight in the chemistry of methyldecanoate pyrolysis rate of production (ROP) and sensitivity analysis (SA) are used to obtain a skeletal mechanism. The sensitivity analysis reveals that the simulated yields are in particular sensitive to the initiation reactions of methyldecanoate.

**Figure 2. Simulated (lines) versus experimentally (shapes) determined yields/conversion for MD pyrolysis**
QSSA for most of the radicals considered in the reaction network.

Conclusions

The present work demonstrates the use of a group additive method for estimating the rates of large kinetic models for methyldecanoate pyrolysis. The proper agreement between calculated and experimentally determined product yields illustrates the potential of our approach. The automatically generated reaction network can be reduced to a more manageable size using ROP and SA, while commonly applied assumptions such as QSSA for most of the radical intermediates and the μ-radical hypothesis further allow to reduce the computational load without losing accuracy.

Acknowledgments

Financial supports from the BOF Bilateral Scientific Cooperation (ECUST/LCT), the Long Term Structural Methusalem Funding by the Flemish Government (No. BOF09/01M00409), and the “111” Project by the Chinese Government (No. B080201) are acknowledged.

References


