1 Introduction

For a long time now, increasing the renewable components in fuel has been of as much interest as the reduction of emissions in motor vehicles. In order to increase the proportion of renewable energies and to reduce dependency on mineral oil, there is great political interest in the addition of biogenic components to fossil fuels. Diesel fuel currently makes up a quota of 7% (BioKraftQuG, 2006). A renewable energy proportion of 10% has been prescribed for the transport sector in the year 2020 by the European Union (EC guideline 2009/28).

In addition, the tightening of emissions standards places increasingly high demands on vehicle manufacturers, and also especially on the quality of the fuels used. The additive component that is currently predominantly used for diesel fuels is biodiesel. However, in its current form it is not optimally suited to modern car engines. A primary reason for this is its boiling behaviour, which for example leads to problems such as oil dilution by the addition of fuel to the engine oil, especially in the case of after-injection for the regeneration of particle filters (Tschöke et al., 2008). The biodiesel contained in engine oil can then form oligomers and polymers that deposit as oil sludge. For this reason, the boiling behaviour of biodiesel was changed in this project so that the fuel can evaporate more easily from the engine oil due to its lower boiling point. In order to attain this adaptation of the boiling curves to match that of the fossil diesel fuel, the properties of rapeseed oil methyl ester were altered both with self-metathesis and also cross-metathesis. In particular, new fuels are to be produced by homogeneous and heterogeneous catalysed cross-metathesis of fatty acid methyl esters with linear olefins that display behaviour in engine operation similar to fossil diesel fuel without allowing oil dilution and oil sludge formation. These possibilities of fuel design could form the basis for a substantial increase in the renewable proportion in diesel fuel without having negative effects on the engine. In this way, the use of plant oils and biodiesel as a fuel could be expanded.

In order to be able to evaluate the behaviour of the altered fuels, analyses of the boiling point and evaluation of the emissions in engine operation are required. Here, the emissions behaviour can not only be described by determination of the amounts of statutorily regulated exhaust gas components nitrogen oxide, particle mass, carbon monoxide and hydrocarbons. Measurement of the statutorily non-regulated components are also necessary for the estimation of the emissions behaviour and any resultant risks, since as is the case with polycyclic aromatic hydrocarbons or mutagenicity in the Ames test, they provide indications for the effect on health of diesel engine emissions. This cannot be derived from the statutorily regulated components. In addition, consideration of the particle concentration and the ammonia emissions is also necessary as these will belong to the regulated components in future (EC Regulation No. 582/2011).

In summary, the project demonstrates a sustainable development approach for fuels since the fuel design has been accompanied by engine and exhaust analysis tests right from the start.

2 Production and basic characterisation of metathesis fuels

The metathesis fuels were produced at the Karlsruhe Institute for Technology. The chemical modification of biodiesel took place using a known catalytic reaction, olefin metathesis, to reduce the boiling curve of biodiesel. This was achieved by cross-metathesis reactions of biodiesel with 1-hexene (and other olefins), which led to a shortening of the alkyl chain of the fatty acid methyl esters. Biodiesel that was synthetically modified in this way produced a boiling curve similar to that of diesel fuel extracted from mineral oil.

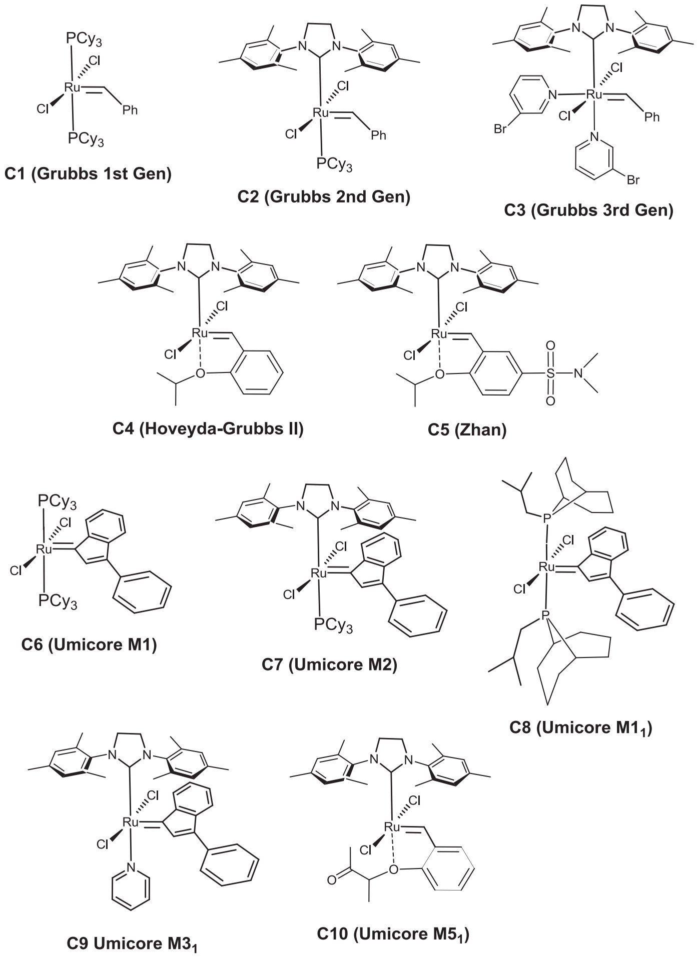
2.1 Starting materials and analytical process

a) Starting materials

- Rapeseed oil methyl ester with a fatty acid spectrum comprising 4.7% methyl palmitate, 1.6% methyl stearate, 61.2% methyl oleate, 19.2% methyl linoleate and 10.1% methyl linolenate
- 1-hexene, 97%

b) Catalysts

- Commercially-available ruthenium catalysts (see Fig. 2-1) from Sigma-Aldrich and Umicore were used



C1 (Grubbs 1st Gen) **C2 (Grubbs 2nd Gen)** **C3 (Grubbs 3rd Gen)**

C4 (Hoveyda-Grubbs II) **C5 (Zhan)**

C6 (Umicore M1) **C7 (Umicore M2)** **C8 (Umicore M1$_1$)**

C9 Umicore M3$_1$ **C10 (Umicore M5$_1$)**

Fig. 2-1: Ruthenium-based olefin metathesis catalysts used for the initial screening

c) Analysis

- Examination of the hydrocarbon composition of the samples of reaction solutions via GC (Bruker 430-GC) and/or GC-MS (Varian-431-GC/MS instrument)
- Simulated distillations (SimDis) of the metathesis samples according to the method ASTM D7169 via GC (ASG, Neusäss and TAC, Coburg)
- Determination of the ruthenium content of the synthetically modified fuels via ICP-MS (Varian 820) using ruthenium standards with 1 to 10 ppm (ASG, Neusäss, Deutschland)

2.2 Metathesis reactions

2.2.1 Cross-metathesis of biodiesel with 1-hexene

Cross-metathesis reactions of biodiesel and 1-hexene were carried out with 5 ml biodiesel, the corresponding quantity of 1-hexene and tetradecane (internal standard) in a Radleys carousel 12 Plus^{TM} carousel reactor with continuous stirring. To simplify calculation of the required quantities of reactants, it was assumed that the biodiesel only comprised methyl oleate. Reactions with catalysts **C1-C5** were carried out at 40 °C, whilst reactions with **C6-C10** took place at the somewhat higher temperature of 50 °C (it is known that C6-C10 have slightly higher initiation temperatures). The reaction temperatures were selected low to prevent 1-hexene (boiling point: 63 °C) from evaporating. After a t=0 sample was taken, in each case one of the catalysts **C1–C10** (0.02 to 0.10 mol% based on the quantity of biodiesel) was added to the reaction mixture. All reactions ran for four hours and were replicated. Samples were taken at regular intervals for GC or GC-MS analyses. In order to stop the reaction before the GC and GC-MS analysis, an excess of vinyl ethylether (50 mol%) was added to the reaction mixture.

The consumption of methyl oleate and methyl linoleate yielded a mixture of self and cross-metathesis products comprising alkenes, dienes, esters and diesters of different chain length (Fig. 2-2). Methyl oleate and linoleate had a proportion of 80.4% of the unsaturated fatty acids in the utilised biodiesel in a ratio of 3:1. The entire fatty acid profile can be found in Table 6-1 in the appendix. The possible resultant compounds are designated as self-metathesis product (SM_1 to SM_6) and cross-metathesis product (CM_1 to CM_6). Here, it should be noted that after a metathesis reaction all double bonds are present as cis / trans mixtures, as shown in Fig. 2-2. The compounds produced in this way have clearly different boiling points and should therefore render a modified boiling curve compared to that of the starting product (biodiesel).

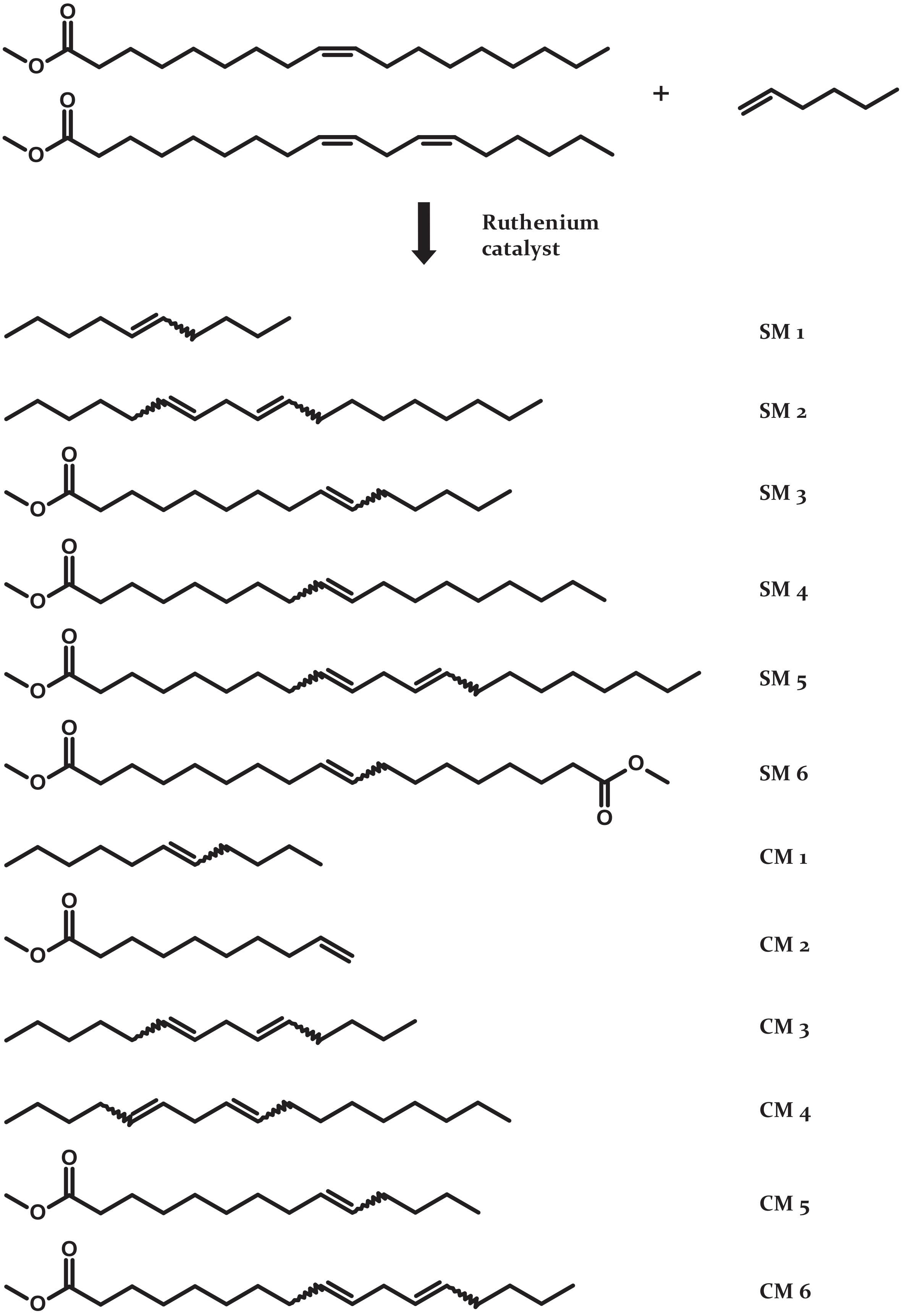


Fig. 2-2: Product mixture resulting from cross-metathesis of biodiesel with 1-hexene

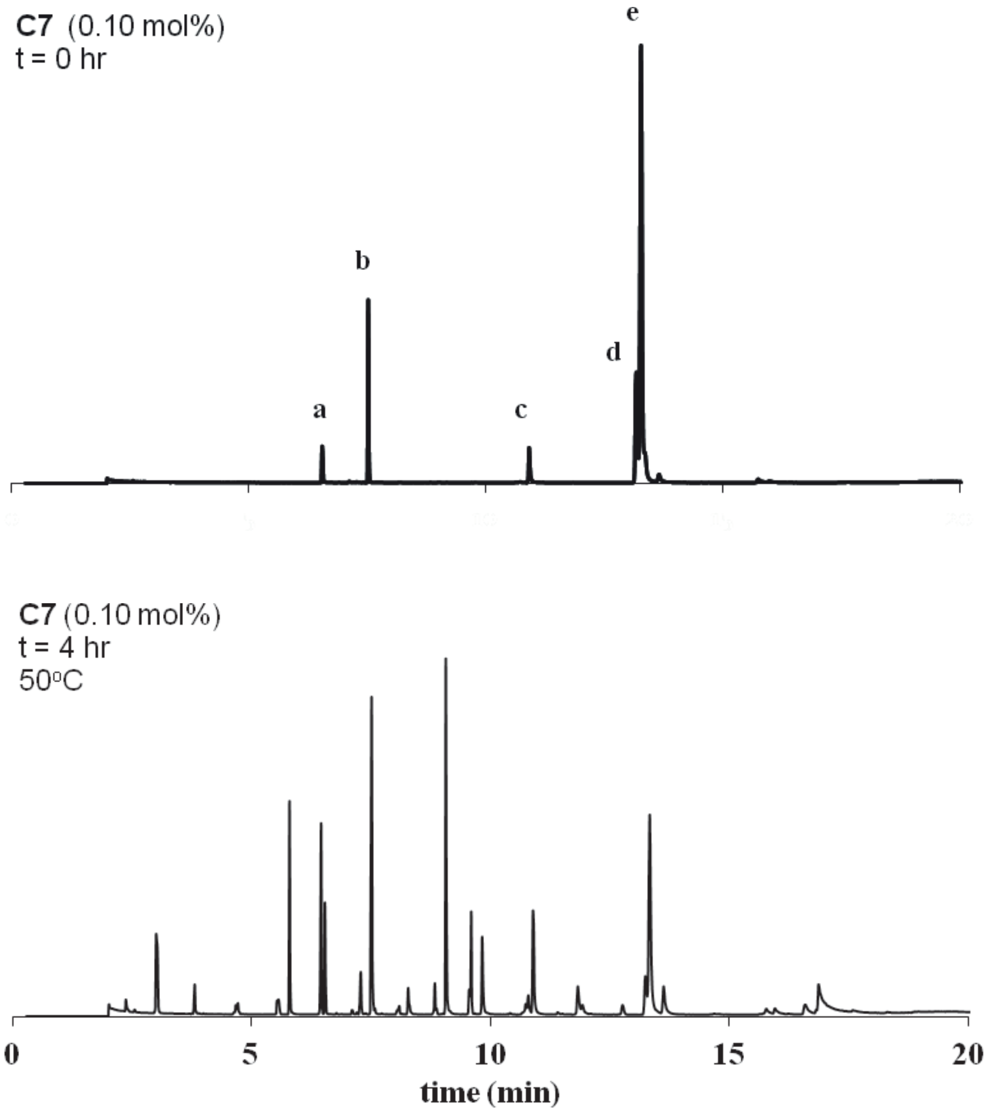


Fig. 2-3: GC-MS of biodiesel before the addition of catalyst (top) and after the cross-metathesis reaction of biodiesel with 1-hexene (bottom); (a) tetradecane, (b) BHT, (c) methyl palmitate, (d) methyl linoleate, (e) methyl oleate

Fig. 2-3 shows a representative GC-MS chromatogram of biodiesel before and after the addition of one of the catalysts (**C7**). At t=0 only tetradecane (standard), BHT (antioxidation agent in the THF used for sample preparation) and the fatty acid methyl ester of the biodiesels was detected. After four hours' reaction time, the cross-metathesis yielded new products of different chain length, as expected and desired.

In order to identify the most suitable catalyst for this reaction, all catalysts shown in Fig. 2-1 were first screened. The catalyst loading was initially set to 0.10 mol% and tested with a mixture of biodiesel and 1-hexene in a molar ratio of 1:1. All reactions were replicated and displayed good reproducibility.

Fig. 2-4 shows the results of this catalyst screening. As clarified in the diagram, **C2**, **C4**, **C7**, **C9** and **C10** allow almost complete conversion even at the low catalyst loading of 0.10 mol%. These catalysts were then used for the next phase of testing and further optimisation tests.