

Lowering the Boiling Curve of Biodiesel by Metathesis

There exist some disadvantages when Biodiesel is used in vehicles equipped with diesel particulate filter (DPF). Especially during the regeneration phase, fuel bedabbles the piston walls and is taken over into the engine oil. Unlike fossil diesel fuel, biodiesel can not evaporate out of the engine oil because of its high boiling range. This leads to oil dilution and, furthermore, the formation of oligomers and oil sludge. The Thünen Institute of Agricultural Technology and the Technology Transfer Center Automotive Coburg (TAC) of the Coburg University of Applied Sciences modified the boiling behaviour of biodiesel by metathesis. This enables the new fuel to evaporate from the engine oil.

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1 MOTIVATION

Fuels from regenerative sources help to save fossil resources and therefore lower the anthropogenic greenhouse effect. In particular, fuels which can be used as drop-in fuels are of special interest. The fuels must be suitable for all generation of engines and therefore can be sold in the existing filling station network. Currently, biodiesel is the biogenic component predominantly used as blend component in diesel fuel. Unfortunately, the high boiling curve of fatty acid methyl esters (FAME) is not very well suited for modern passenger car engines with diesel particle filters (DPF). This is due to the post injection during the DPF regeneration phase which causes fuel to enter the piston walls and be taken to the engine oil by the piston rings. While the dominating part of diesel fuel can be evaporated from the oil pan, the biodiesel remains in the oil and leads to oil dilution [1]. If biodiesel stay over a longer period in the engine oil, it can lead subsequently to the formation of oligomers and polymers by thermal and oxidative processes. In extreme cases it results in oil sludge. We therefore decided to use metathesis to change the boiling behaviour of biodiesel and enable its evaporation from the engine oil [2]. The new metathesis fuel has been tested

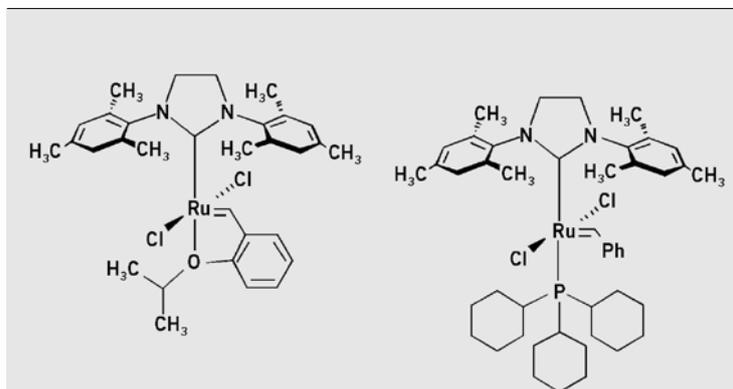


FIGURE 1 Structure of the Hoveyda-Grubbs second generation (left) and Grubbs second generation catalysts

for material compatibility as well as for its burning behaviour and its emissions in a 20 % blend with fossil diesel fuel.

2 METATHESIS REACTIONS TO MODIFY BIODIESEL

The mechanism of metathesis reactions was first described by Yves Chauvin in 1971. In 1990, Richard R. Schrock developed a more effective catalyst and two years later Robert H. Grubbs described ruthenium- based catalysts, which are also effective and more stable towards water and oxygen. All three scientists were awarded the Nobel Prize in Chemistry in 2005 [3]. Two of the catalysts developed by Grubbs are shown in FIGURE 1. The active center is the central ruthenium metal atom. During the metathesis reaction, two alkenes interchange their alkylidene rests. In case of only one alkene, the reaction is called self-metathesis. Alternatively, if two different starting alkenes are used, the reaction is called cross-metathesis, FIGURE 2. Depending on the percentage of the educts, an equilibrium of products is obtained including self-metathesis products.

To approximate the boiling curve of the biodiesel to that of diesel fuel, the cross-metathesis was used. Self-metathesis changes the

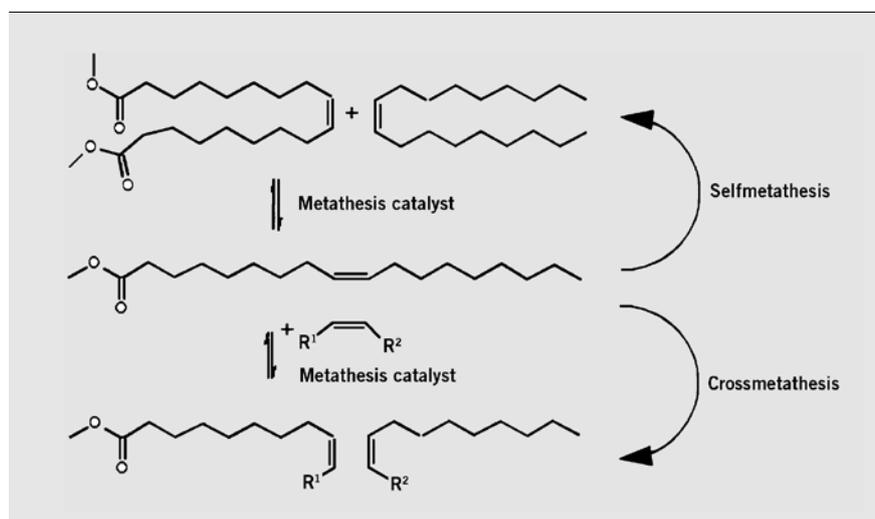


FIGURE 2 Self- and cross-metathesis reactions of oleic acid methyl ester (© Thünen Institute of Agricultural Technology)

alkylidene rests of unsaturated methyl esters in biodiesel. Using self-metathesis, the products have both lower and higher molecular weight. The higher molecular products have higher boiling points than biodiesel and are therefore tentatively undesired. Therefore, the cross-metathesis is better suited to lower the boiling curve, whereas the reaction partners must have a clearly shorter chain length compared to the methyl ester used. Therefore α -olefins are a good choice. They can easily be obtained by cracking processes in refineries.

1-hexene was used for metathesis reactions with biodiesel. Theoretical considerations have shown that the product mixture should have a boiling temperature of about 230 °C. **TABLE 1** shows the main components of the metathesis reaction from rape seed oil methyl ester (RME) and 1-hexene, measured by gas chromatography-mass spectrometry (GC-MS). Next to the listed molecules, also substances with a molar mass higher than that of biodiesel were formed in the reaction. These products could not be measured by GC-MS but were detected by size exclusion chromatography (SEC).

The metathesis reaction of biodiesel with 1-hexene was carried out with different catalysts, different catalyst loadings, different equivalents of hexene and under different reaction conditions. While the choice of catalyst and the reaction parameters influenced mainly the speed of response, the selection of the ratio between biodiesel and 1-hexene had the greatest influence on the boiling line. Overall, more than ten different metathesis fuels were generated. The boiling curves of these fuels were more or less comparable to the boiling curve of fossil diesel fuel. In **FIGURE 3**, the comparison of the boiling curves of biodiesel, fossil diesel fuel, and six metathesis fuels are shown. The boiling curves were obtained by simulated distillation (SimDis).

3 COMPATIBILITY OF MATERIALS

To get an impression of the impact of the new fuel on plastics, a durability test according to DIN EN ISO 175 was carried out with self-metathesis fuel using two polymer samples. Samples of polyamide (PA 66 Ultramid A3K) and high density polyethylene (HDPE Lupolen 4261) were stored for a period of seven days at a temperature of 70 °C in 70 mL of metathesis fuel (self metathesis,

Product	Boiling temperature [°C]	Content [%]
5-Decene + 1-Decene	172	13.3
5-Undecene	192	2.7
5-Dodecene	213	0.9
5-Tetradecene	251	15.2
4-Decenoic acid methyl ester	215	18.1
9-Octadecene	314	2.5
Methyl myristoleate	306	31.8
Hexadecanoic acid methyl ester (C16:0)	332	6.3
9-Octadecenoic acid methyl ester (C18:1)	351	9.2

TABLE 1 Reaction products of the cross-metathesis reaction of RME with 1-hexene (© Coburg University of Applied Sciences)

Metathesis_{0,0}). As reference samples were stored in fossil diesel fuel and rapeseed oil methyl ester. In addition, reference samples were stored at 22 °C and 45 % humidity in a climatic chamber. After this time, changes in mass, elastic modulus and tensile strength according to DIN EN ISO 527-2 was determined, **TABLE 2**.

The reference samples in the climatic chamber at 22 °C and 45 % humidity didn't change significantly. The polyethylene samples (HDPE) stored in the fuels showed a significant increase in sample mass, while the increase during the storage in diesel fuel showed almost twice as compared to rapeseed oil methyl ester and metathesis fuel. In relation to the mass of a test piece of about 8.8 g, the increase was just below 10 % for diesel fuel. The PA-samples showed a significantly lower swelling. Comparing the sample mass of 11.2 g, the mass growth during the fuel storage of less than 0.1 g was below 0.1 % of the original mass.

Between the reference sample in air and the samples stored in the fuel only slight differences in the modulus of elasticity and

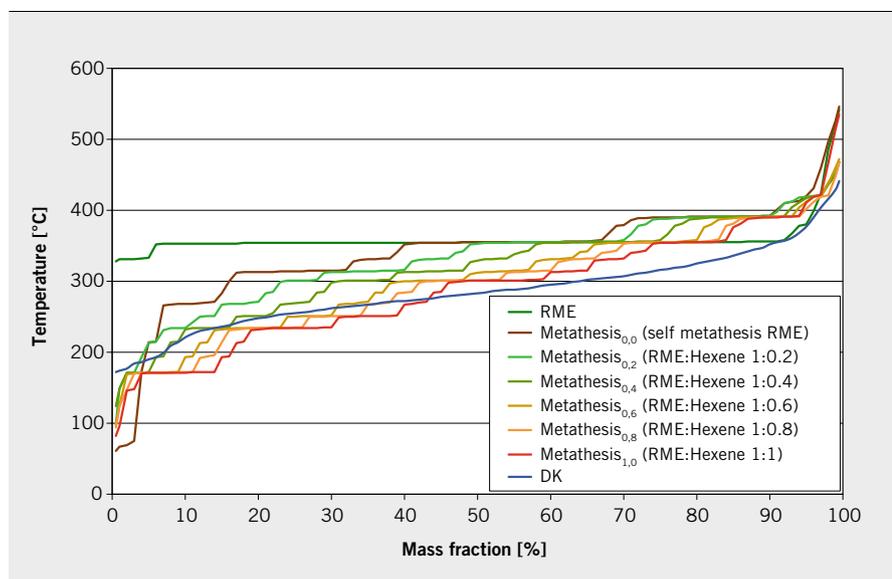


FIGURE 3 Boiling curves of biodiesel, fossil diesel fuel and a metathesis fuel (SimDis) (© Thünen Institute of Agricultural Technology)

Stored in		Reference (Air)	DF	Metathesis fuel	RME
Changes in mass (mass of sample)	PA (11.2 g)	0.01	0,04	0.05	0.07
	HDPE (8.8 g)	0.00	0.78	0,45	0.40
Elastic modulus	PA	2434	2076	2108	1906
	HDPE	793	420	553	566
Tensile strength	PA	65	64	64	61
	HDPE	27.2	23.2	24.5	25.0

TABLE 2 Results of material compatibility tests
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tensile strength were observed. The modulus of elasticity decreased slightly after storage in fuel. Thus, the samples are somehow more flexible than before. This trend can be seen in both materials. The tensile strength of PA didn't change significantly. In contrast, the tensile strength of HDPE decreased during storage in all fuels, whereas diesel fuel led to the greatest decrease. In summary, the metathesis fuel showed no higher influence on material properties as compared with RME and diesel fuel.

4 EMISSION TESTS

Since metathesis fuels will probably not be available as neat fuels in the near future, blends of 20 % metathesis fuel in diesel fuel were produced and tested. From 10 different metathesis blends, two blends were chosen for extended emission tests in a heavy-duty truck engine (Mercedes OM 904 LA, Euro IV) by a selection process that took into account: the boiling behaviour, the biogenic content and the regulated emissions from a single-cylinder engine (Farymann 18 W). The highest biogenic content had the metathesis fuel obtained from the self-metathesis. At 20 % blend of Metathese_{0,0} this fuel will be called M20. According to emission behaviour in the single cylinder engine, the fuel Metathese_{0,8}

showed the best results. At 20 % blend of Metathese_{0,8} it will be called N20.

In addition to the regulated emissions (NO_x, CO, HC and PM), the non-regulated exhaust gas components ammonia, polycyclic aromatic hydrocarbons (PAH), aldehydes, as well as mutagenicity of the exhaust and the particle size distribution were tested as well. Fossil diesel fuel (DF), biodiesel from rape seed oil (RME) and a B20 blend of RME in DF were used in comparison with the metathesis blends (M20 and N20).

In operation with metathesis fuel blends, the emissions of the OM 904 LA only showed very slight deviations from B20, **FIGURE 4**. The nitrogen oxide emissions for RME were much higher than for DF, and also the B20 or metathesis blends showed a slight increase. The opposite effect was observed with particle mass, where the use of RME led to a reduction of 25 %. However, this trend was not observed for the blends. Their particle masses were within the order of magnitude of DF at 0.01 g/kWh and within the standard deviation. A significant reduction in hydrocarbon and carbon monoxide emissions was also observed for RME. For the mixtures, a reduction was only found for HC emissions of the B20 blend. In contrast, the carbon monoxide emission of B20 and N20 showed a slight increase. Only one of the metathesis fuels showed no increase compared to diesel fuel. However, almost all regulated emissions were within the Euro IV specification that applied to the engine used. All specifications were attained for three of the four fuels used. Only the nitrogen oxide emissions of RME slightly exceeded the threshold value of 3.5 g/kWh. For non-regulated exhaust gas emissions, only slight differences between the metathesis blends and B20 could be found. The carbonyl emissions were in the same order of magnitude and therefore no significant differences between the fuels used were recognisable. In the particle size distribution, little difference could be found. The metathesis fuel blends showed a slight increase in the number of particles in the size range from 28 nm to 1000 nm compared to the B20 blend. In the range of 2 µm to 10 µm, the emission of the B20 blend was higher, **FIGURE 5**.

The individual emissions of 15 measured PAHs showed no clear changes because of high standard deviations. Therefore, the environmental effect was determined by calculating the benzo[a]pyrene

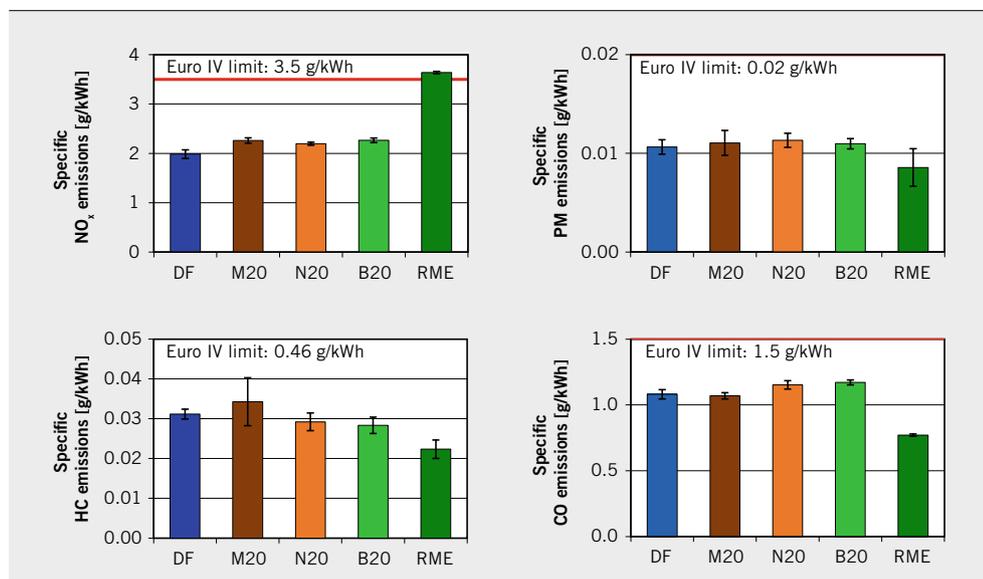


FIGURE 4 Emission of fossil diesel fuel, 20 % blends of both metathesis fuels and biodiesel in DF, and neat biodiesel, tested in an OM 904 engine with SCR catalyst (ETC test) (© Thünen Institute of Agricultural Technology)

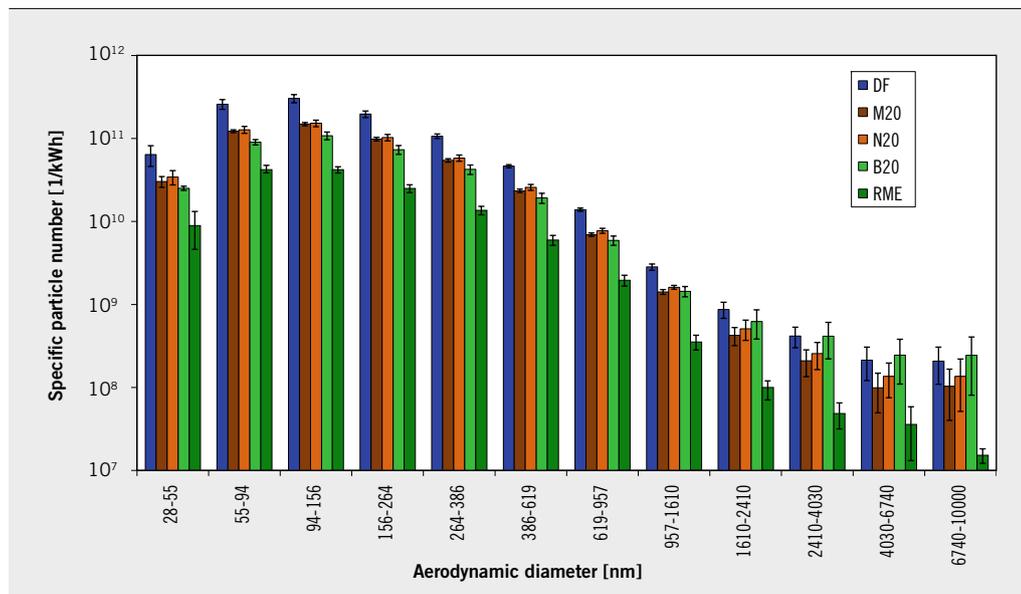


FIGURE 5 Particle size distribution of fossil diesel fuel, 20 % blends of both metathesis fuels and biodiesel in DF, and neat biodiesel, tested in an OM 904 engine with SCR catalyst (ETC test) (© Thünen Institute of Agricultural Technology)

equivalent effect [4]. This effect sums up all individual PAH emissions, multiplied by a factor depending on the health effects of the PAH, **FIGURE 6**. In addition to the effect equivalent sampled after the exhaust after-treatment system, the effect equivalent of the raw exhaust gas was also determined. Here, the benefits of the SCR catalyst system could clearly be shown. The effect equivalent of diesel fuel and the blends decreased from 30 to about 10. This decrease can be explained by the significant reduction of organic-soluble fraction by the catalyst. Together with the organic-soluble fraction, the polycyclic aromatic hydrocarbons in this fraction were also eliminated to a large extent. The RME equivalent effect in the raw exhaust gas was already below the other four fuels and the reduction by the SCR system was higher than for the other fuels. After the SCR system also the metathesis blend N20 showed a reduced effect equivalent. However, in considering the standard deviations of the PAH measurement, this behaviour could not be safely confirmed.

Regarding mutagenicity, it was to assume that a use of an SCR catalyst leads to low emissions of mutagenic substances. This is because the SCR system has a built-in oxidation catalyst, which eliminates the PAH and other mutagenic substances. Therefore, like the PAH sampling, the mutagenic samples were taken from

the raw exhaust gas and after the SCR system. The determination of mutagenicity was carried out using the Ames test with the salmonella strain TA98 [5,6]. The direct mutagenicity was measured as well as the indirect mutagenicity from metabolites using rat liver enzymes (S9 fraction). The admixture of biogenic fuels tends to a decline in direct mutagenicity in the raw exhaust gas, **FIGURE 7**. RME and also the metathesis blend M20 showed fewer mutations. The indirect mutagenicity of all fuels tested showed no significant differences. After the SCR system there was almost no mutagenic potential. Only for diesel fuel, a very low mutagenicity could be detected. In summary with regard to the mutagenicity, no negative effect on emissions was observed by using metathesis fuels.

Furthermore, studies with metathesis blends compared to diesel fuel were carried out using an AVL single cylinder research engine based on an MAN D28 engine with respect to emissions and combustion behaviour. The test engine with a displacement of 2059 cm³ was equipped with four valves per cylinder and a Bosch second-generation common-rail injection system. In addition, the motor had a supercharging using an electrically driven screw compressor, a flow heater for intake air conditioning and a temperature-controlled external exhaust gas recirculation (EGR).

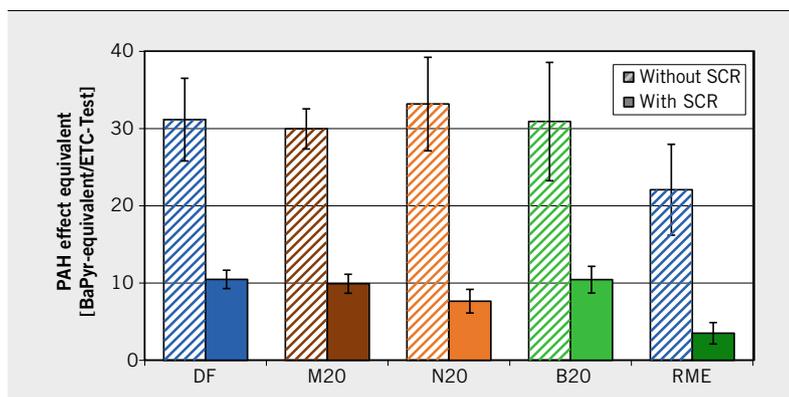


FIGURE 6 Effect equivalent of PAH emissions from particulate and condensate of the OM 904 LA in the ETC test (© Thünen Institute of Agricultural Technology)

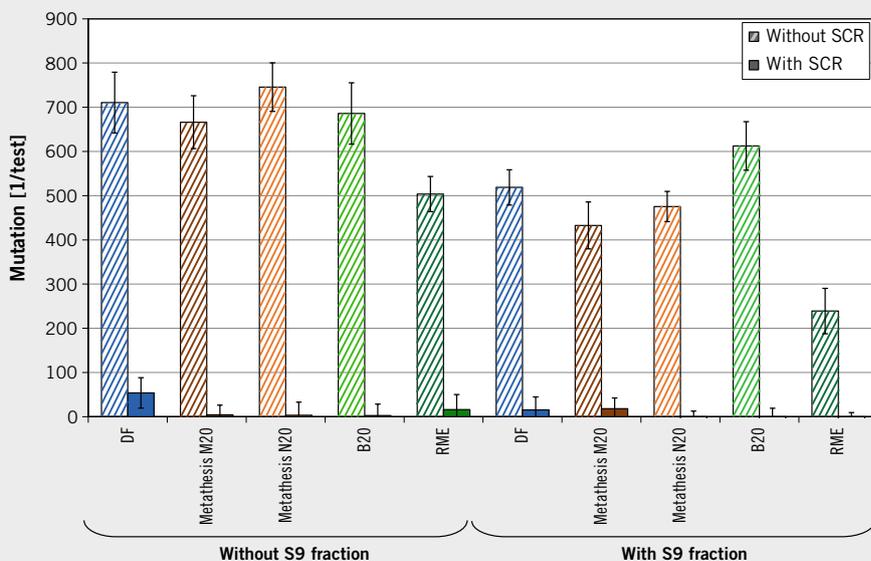


FIGURE 7 Sum of the mutagenicity in particulate and condensate from DF and RME compared to three blend fuels at the OM 904 LA in the ETC test with the bacterial strain TA98 (© Thünen Institute of Agricultural Technology)

Due to the limited availability of metathesis fuel, only the operating points 1, 3, 5, 7 and 9 of the ESC test were made. All points without the idling point 1 were tested both without and with exhaust gas recirculation.

In summary, the motor behaviour of all investigated fuels was very similar and therefore the emissions of all fuels were comparable to those of conventional diesel fuel. The particulate emissions from points without EGR were very low for all fuels. With an EGR rate of 25 %, the particulate emissions rose as expected. The metathesis blends showed a trend of lower particulate emissions than other fuels. Without EGR the nitrogen oxide emissions showed almost no differences, however, a slight increase for the metathesis blends could be found with exhaust gas recirculation. The carbon monoxide and hydrocarbon emissions were very low for almost all operating points. A slight advantage was apparent for the fuel blends. In addition, the combustion process using the different fuels showed no significant differences within the measurement accuracy of the available metrology. Slight variations in the pressure gradients can be explained by the different boost pressures with the same starting air ratio due to variations in the minimum air consumption. Differences in the ignition and the energy release could not be seen clearly, suggesting small differences in fuel-mixture generation, ignition and burnout behaviour of the investigated fuels.

5 SUMMARY

By using the metathesis reaction, the boiling curve of biodiesel can be lowered. The best fit to the boiling curve of conventional diesel fuel can be reached by using 1-hexene as reactants. The resulting metathesis fuel has been extensively studied and tested in three different diesel engines with regard to the resulting emissions. The investigations showed, that metathesis fuels are suitable for use in internal combustion engine. Boiling behaviour and material compatibility of pure metathesis fuel and also the regulated and non-regulated emissions and the burning behaviour of 20 % blends with diesel fuel demonstrated that metathesis fuels can be used without limitations.

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