METHODS TO MODIFY FAME FUELS – SURVEY ON RECENT DEVELOPMENTS

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Introduction

In recent years the limits for exhaust emissions of diesel engines have been tightened as well for passenger cars as for trucks and buses. In particular, the introduction of the particle filter led to the fact that in the passenger car sector no releases for biodiesel (in Germany mainly: RME - rapeseed oil methyl ester; B100) were given. In order to offer further income opportunities for the agricultural sector, to substitute fossil fuels, and to reduce the emission of greenhouse gases an increase in the use of biogenic components in the transport sector must be strived for. Therefore, the actual blending of 5% to 7% of biodiesel into fossil diesel fuel should be enhanced to 10% or more.

However, an increase of the RME content in blends with fossil diesel fuel or GTL (Gas-to-Liquid fuel, originating from natural gas) leads to unexpected problems like sedimentation, fuel filter blocking etc. This problem, its chemical backgrounds, and possible ways to overcome it will be addressed in this contribution. A further possibility for modification of RME is offered by a chemical treatment of the fuel that leads to shorter chain lengths of the fatty acids. Olefin metathesis, a well established catalytic conversion, can lead to such improvements, as will be discussed within this contribution. This treatment leads to fuels with improved boiling curves.

Problems with FAME biofuels

Figure 1 shows the boiling lines of some neat fuels and mixtures of different vegetable oils that can be used in diesel engines. A comparison of the curves for fossil diesel fuel (DF) and rapeseed oil methyl ester (RME) reveals distinct differences: while DF starts boiling with 165 °C and then vaporizes relatively continuously with increasing temperature, the boiling for RME begins at 300 °C and 95% of the fuel vaporizes between 335 °C and 350 °C. Besides the observation of great differences one can also state that the high boiling curve was the reason to stop the releases of biodiesel (B100) for current passenger cars. The biodiesel that gets into the engine oil during the regeneration cycle for the particle filter remains in the oil, even for higher oil temperatures, and leads to a decrease of the lubrication ability and to polymerization. The FAME (Fatty Acid Methyl Ester) coconut oil methyl ester, which shows a more favorable boiling curve (cf. Figure 1), is unsuitable as fuel, as its melting point lies too high and coconut oil is (at present) rather expensive. Detailed data for various vegetable oils, their fatty acid composition and their properties can be obtained from the literature, cf. Knothe et al., 2010, or Mittelbach and Remschmidt, 2004.

Besides the neat fuels we find today fuel blends that are composed of a fossil component and a biofuel. For instance, an addition of 7% (v/v) of biodiesel to DF is standard in Germany. Farmers and the biodiesel producers are interested in blends with higher biogenic proportion. In our experiments these blends showed a visible change of color when they were exposed to sunlight, cf. Munack et al., 2009. Figure 2 demonstrates, at the extinction of 500 nm wavelength, this ageing process as a chemical reaction of order zero. Apparently some substances (which were identified as anti-oxidative compounds, like carotiniods and tocopherols) were degraded. This can be seen by the parallel decline of all curves during the first weeks. After this, an increase of the curves happens and shows the formation of new products. These products partly form precipitates. The sedimentation in dependence of the blend was described by Fang and McCormick (2006) at the example of soy oil methyl ester and ultra low sulfur diesel fuel. In our experiments, we used RME and GTL, cf. Figure 3. While Fang and McCormick found a maximum of the sediments in the range of 20% of the biofuel, our results point to a maximum in the range of 10 to 15%. It should be mentioned here, that the results are not directly comparable, as Fang and McCormick used soy oil methyl ester in low-sulfur diesel fuel whereas our experiments were conducted with rapeseed oil methyl ester in GTL. The first cited authors describe a polymerization mechanism with the formation of dimers and trimers. Peyton et al. (2008) also observed sedimentation. They found oxidized products like azelaic acid monomethyl ester and hexanoic acid. These products were also detected in neat biofuel (B100), but therein no precipitation appeared. The authors conclude that in B100 there are enough polar molecules that are able to solubilize the oxidized molecules.

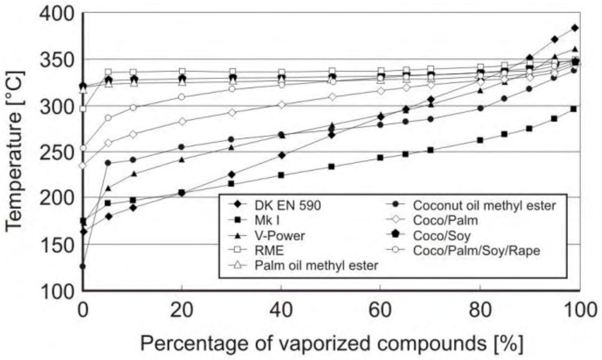

Figure 1: Boiling curves of various diesel fuels (Fischer, 2007)

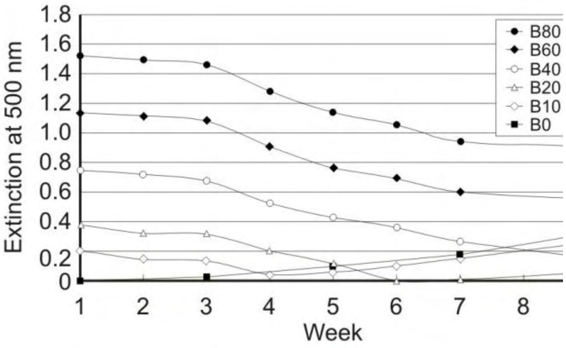

Figure 2: Ageing process in sunlight for different blends

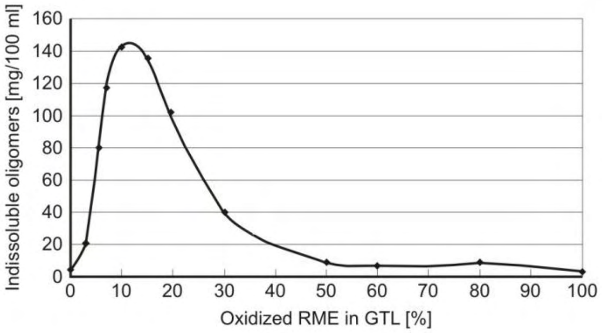

Figure 3: Precipitates in blends of GTL and oxidized RME

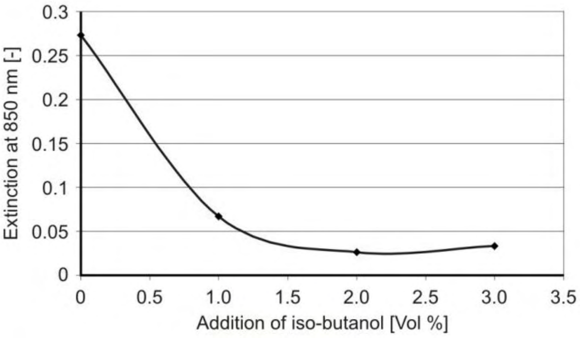

Figure 4: Dissolution of sediments by addition of iso-butanol

Opportunities to overcome the problems

In our research, we found some measures which are, in principle, suitable to overcome the sedimentation problems with blends. A first solution lies in the addition of fresh RME to the blend. This leads to a re-dissolution of the precipitates and the anti-oxidants are detectable in the spectrum again (not shown here). However, the amount of RME needed to perform this procedure ends up with about 30% overall RME content, which is pretty outside of the diesel fuel standard EN 590.

Another measure is the addition of alcohols. Figure 4 demonstrates that by adding of relatively small amounts of iso-butanol the extinction comes down. In further experiments (not shown here) we could demonstrate that the same result can be obtained by addition of ethanol. Thus it could be shown that by addition of further biogenic components the sedimentation of polymers or oxidized products can be prevented. However, the resulting fuel has a very low flashpoint, such that it does not meet the EN 590 requirements and must be treated and stored like gasoline. Also the question whether this blend constitutes a sufficiently stable fuel must be researched further. Another positive effect is shown in Figure 5: The blend of 20% oxidized RME with 78% fossil diesel fuel and addition of 2% ethanol (B20agdE2) exhibits a relatively low NO_x emission.

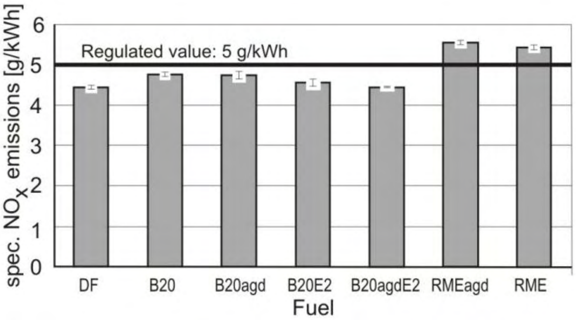

Figure 5: Specific NO$_x$ emissions of various fuels and blends

With respect to neat RME, requirements were formulated during the 2007 Wuhan IRC Congress and were subsequently published in Krahl et al., 2007. According to these findings, chain lengths of 12 to 16 carbon atoms are desirable in order to move the boiling line closer to fossil diesel fuel. For a low melting point it needs unsaturated fatty acids. However, for more than two double bonds in the molecule the polymerization becomes a critical parameter. This means that C12:1 to C16:2 are the desirable fatty acids. It is highly questionable whether it ever will be possible to fulfill this requirement through conventional plant breeding or genetical engineering methods. A further opportunity to shorten the chain lengths of unsaturated fatty acid methyl esters (FAME) is provided by the olefin metathesis, a chemical reaction that is also known in the field of oleochemistry (Rybak et al., 2008). Whether this type of reaction can also be successfully applied to FAME is currently investigated in a research project. In this project, the cross-metathesis reaction with short-length alkenes has been, for the first time, applied to a biofuel. A schematic diagram of possible reactions is shown in Figure 6.

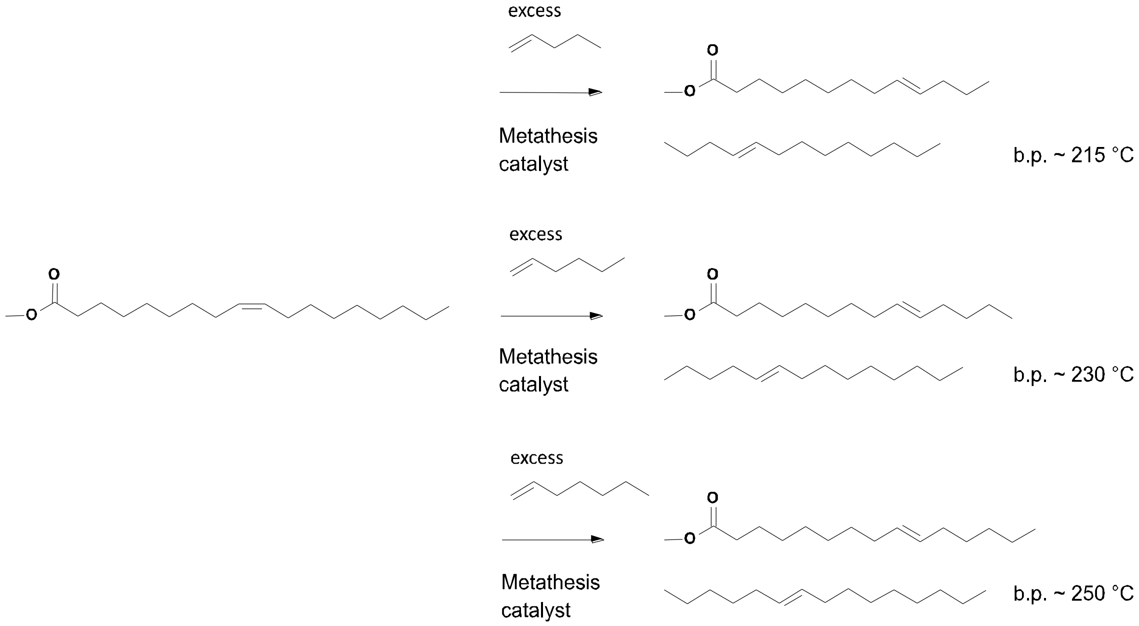

Figure 6: Schematic diagram of a cross-metathesis reaction of biodiesel with alkenes

Acknowledgement

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