Property Demands on Future Biodiesel[1]

Jürgen Krahl[2,3], Axel Munack[3] and Dieter Bockey[4]

Abstract

Rapeseed oil methyl ester (RME) is currently not suitable for diesel particulate filters. The boiling characteristic of RME is an additional problem that presumably limits its further usability in Euro VI engines.

Currently, hydrogenated vegetable oil (HVO) is in the state of obtaining acceptance as alternative fuel in the German legislation and is in the focus of discussions worldwide. HVO has physical and chemical advantages versus RME. In case RME should continue to be an appropriate fuel its molecule structure must be designed - probably by means of plant breeding. It is important to lower the boiling line by achieving chain lengths between 12 and 16 carbon atoms and to have in mind the oxidation stability by focussing the number and the position of double bonds.

Moreover, aspects of emissions and health effects must be kept in mind.

Besides plant breeding, research should focus on highly efficient biotechnical transesterification, producing simultaneously shorter chain lengths. The phosphorus and metal contents of future biodiesel must become significantly lower than the specification limits that are valid at present.

Keywords: biodiesel, hydrogenated vegetable oil, diesel fuel, fuel design, boiling curves

Zusammenfassung

Anforderungen an die Eigenschaften zukünftigen Biodiesels[1]

Rapsölmethylester (RME) kann derzeit in PKWs mit Dieselpartikelfiltern nicht eingesetzt werden. Die Siedekurve von RME stellt darüber hinaus ein Problem dar, das dessen zukünftige Verwendung in Euro-VI-Fahrzeugen in Frage stellt.

Demgegenüber hat hydriertes Pflanzenöl (Hydrogenated Vegetable Oil; HVO) beim Gesetzgeber in Deutschland schon eine gewisse Akzeptanz erlangt und wird weltweit als biogener Dieselkraftstoff diskutiert. HVO weist chemische und physikalische Vorteile gegenüber RME auf. Falls RME auch zukünftig als ein geeigneter Kraftstoff für Verbrennungskraftmaschinen gelten soll, müsste seine Struktur verändert werden, zum Beispiel durch Züchtung. Dabei ist es besonders wichtig, die Siedelinie herabzusetzen, indem Kettenlängen von 12 bis 16 C-Atomen angestrebt werden, wobei die Oxidationsstabilität durch entsprechende geringe Anzahl von Doppelbindungen und deren geeigneter Position zu wahren ist.

Darüber hinaus muss man auch die Emissionen und Gesundheitswirkungen der Abgase beachten. Neben der Pflanzenzüchtung sollte sich die Forschung auch effizienten biotechnischen Umesterungsverfahren widmen, die gleichzeitig kürzere Kettenlängen hervorbringen. Schließlich muss auch der Phosphor- und Metallgehalt des Kraftstoffs deutlich unter die jetzt geltenden Spezifikationen der Biodiesel-Norm gesenkt werden, um zukünftige Abgasreinigungssysteme langzeitstabil einsetzen zu können.

Schlüsselwörter: Biodiesel, HVO, Dieselkraftstoff, Kraftstoffdesign, Siedekurven

---

1 Results of the Workshop „Biodiesel“ on March 29, 2007, at the 12th International Rapeseed Congress in Wuhan, China.

2 University of Applied Sciences Coburg, Friedrich-Streib-Str. 2, 96450 Coburg/Germany; Email: Krahl@hs-coburg.de

3 Federal Agricultural Research Center (FAL), Institute of Technology and Biosystems Engineering, Bundesallee 50, 38116 Braunschweig/Germany

4 Union for the Promotion of Oil and Protein Plants (UFOP e.V.), 10117 Berlin/Germany

1 Introduction

The use of biodiesel - fatty acid methyl ester (FAME); in Germany mainly rapeseed oil methyl ester - became indirectly mandatory in Germany due to the biofuel quota act (Biokraftstoffquotengesetz, 2006). This law prescribes an energetically measured admixture of 4.4 % of biodiesel to all fossil diesel fuel sold.

The biodiesel production capacity increased during this decade. In detail, the capacity may reach approx. five million tons at the end of 2007 (Bockey, 2007). The actual German agricultural rapeseed oil production cannot meet the biodiesel producers' mass requirements.

So the question of feedstock remains as most important for both, the biodiesel producers and the engine manufacturers.

This article deals with the question of a chemically optimised future biodiesel or biodiesel blend components based on rapeseed oil with special regard to the molecule design of triglycerides. Facing Euro VI exhaust gas regulations in 2014, the need of high-tech engines in combination with sophisticated fossil and bio-based fuels becomes obvious. Presumably the biodiesel of today, consisting mainly of rapeseed oil methyl ester, is not appropriate for this challenge. This was one of the issues of the Workshop "Biodiesel", which was held during the 12th International Rapeseed Congress in Wuhan, China. Some of the results are communicated in this article.

However, even today biodiesel cannot be used as B100 (100 % biodiesel) for passenger cars with diesel particulate filters. Since the extensive and quasimandatory use of diesel particulate filters all passenger car manufacturers have withdrawn their releases for B100. So, in the future, neat biodiesel will probably be a product for trucks. This holds in case that there will not arise analogous problems --- it is not proven that Euro VI trucks can be fuelled trouble-free with today's biodiesel.

The passenger car market may only be served with blends; actually not higher than 5 % (v/v) biodiesel - according to EN 590. Figure 1 shows and anticipates the tendencies on the German biofuel share for the diesel market with regard to the passenger car release withdraw and the probable and slow increase of 2nd generation biofuels like BTL (Biomass-to-Liquid fuel). So biodiesel will be used at least as blend and probably as truck fuel. It must urgently be optimised to ensure its usability in the long-term.

2 Challenge

The main problems of today's biodiesel are the boiling behaviour, the oxida-tion stability due to double bonds and the engine oil dilution. The latter is more or less initially a technical challenge. Figure 2 shows the boiling curves of different fatty acid methyl esters in comparison with diesel

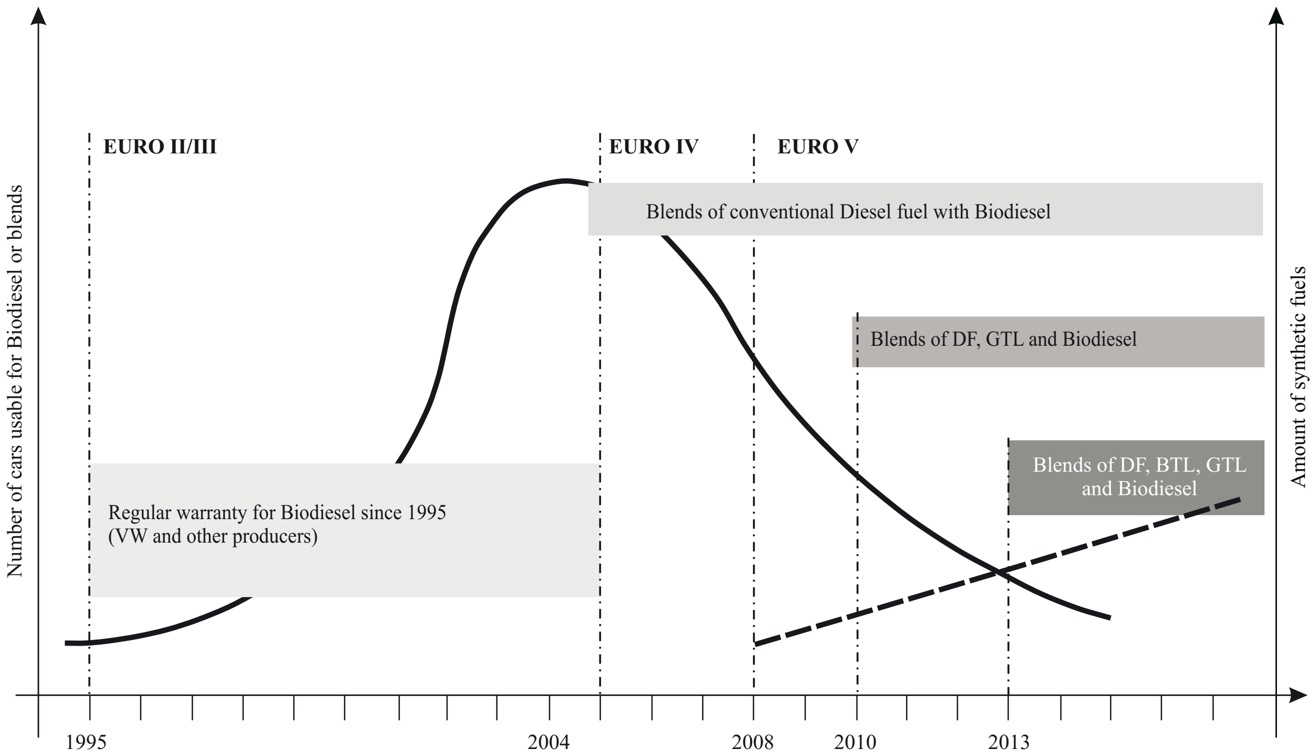

Figure 1:
Future use of biodiesel and biogenic compounds in passenger cars (Bockey and Haupt, 2003)

fuel and table 1 informs about different FAMEs regarding their chain lengths, number of double bonds and melting and boiling points.

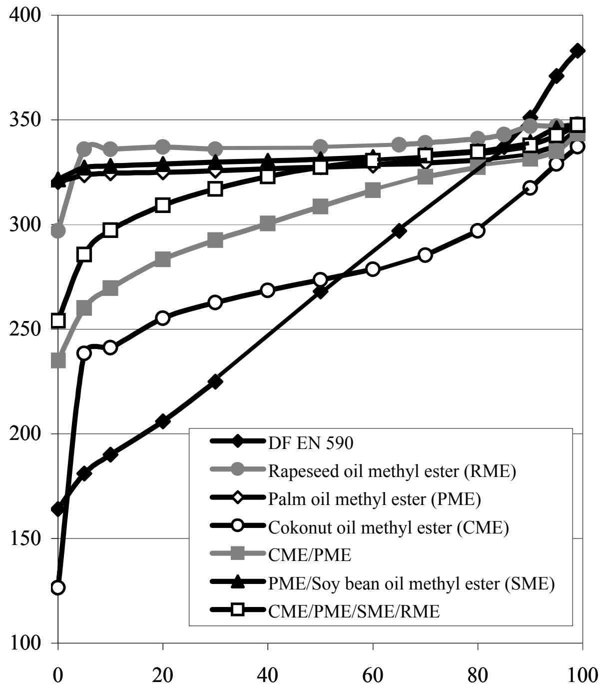

Figure 2:

Boiling curves of different fatty acid methyl esters in comparison to diesel fuel (Fischer, 2007)

Table 1:
Characteristics of different fatty acid methyl esters; data taken from Knothe (2005)

Fatty acid methyl esters	Symbol	Melting Point °C	Boiling Point °C
Lauric acid methyl ester	C12:0	+5,2	+249
Myristic acid methyl ester	C14:0	+19,0	+276
Palmitic acid methyl ester	C16:0	+30,0	+299
Stearic acid methyl ester	C18:0	+39,1	+323
Oleic acid methyl ester	C18:1	-19,9	+318
Linolic acid methyl ester	C18:2	-35,0	+317
Linolenic acid methyl ester	C18:3	-46,0	+318
Erucic acid methyl ester	C22:1	-1,2	+222*

* at 666 Pa

When comparing diesel fuel (DF) with RME, the disadvantage of RME becomes obvious: RME has almost one boiling point, not a well rising boiling curve. An increasing boiling curve is beneficial for a good fuel ignition and combustion in the cylinder. Therefore RME may not be considered as an optimal prospective fuel.

Future engines tend to have lower compression ratios and a more homogeneous fuel-air charging. So the boiling line of future biofuels should be adapted.

The example of coconut methyl ester indicates the general possibility for vegetable oil to lower the boiling line - at the expense of shorter chain lengths. Of course this is a tremendous goal, but future engines may demand fuels with boiling characteristics even between diesel fuel and gasoline (Dorenkamp et al., 2002).

However, the production of biodiesel does not seem to be absolutely necessary in order to fulfil the German biofuel quota act (2006), because rapeseed oil can be hydrotreated in mineral oil refineries to aliphatic compounds. Some experience exists in Germany with the so-called hydrogenated vegetable oil (HVO) (Baldauf and Balfanz, 1994). Moreover, the conversion of vegetable oils to alkanes by NExBTL-processing can be an option to produce a fuel with excellent boiling characteristics versus RME (Rantanen et al., 2005).

In Germany the blending of diesel fuel with approx. 7 % biodiesel content and 3 % HVO is presumably the forthcoming directive for a future quota, cf. Roadmap Biokraftstoffe, 2007. From the point of view of the engine manufacturers HVO is the product of choice.

So the improvement of RME should be considered an urgently needed action. It must be pointed out that the solution can be found by means of plant breeding. It is primarily not a biodiesel quality problem, but one of the molecule structures.

The main requirement for future RME design is to follow the European specification EN 14214 for biodiesel. The maximum phosphorus and metals contents must be specified significantly lower than today. In particular, it has been demonstrated in a 1000 hrs endurance test of a heavy-duty diesel engine with SCR exhaust gas aftertreatment that phosphorus poisons the catalyst (Munack et al., 2006; Krahl et al., 2006).

The number of double bounds shall not induce an iodine number higher than 120. Shorter chain lengths (12 to 16) would lower the boiling line but could increase simultaneously the iodine number, because the iodine number is calculated gravimetrically and not from the total amount of double bonds. In any case, more than two double bonds per molecule FAME should not be exceeded and the position(s) in the molecule must be well chosen.

Moreover the future biodiesel should lead to a clean combustion within the Euro VI exhaust regulations. Hazardous non-regulated effects like ozone (summer smog) formation or increased mutagenicity and cytotoxicity must be kept on a very low level, cf. e.g. Munack et al. (2007).

Further demands on research are highly efficient biotechnical transesterification methods resulting in shorter chain lengths and alternative pathways for utilization of glycerol.

3 Conclusion

Rapeseed oil methyl ester (RME) is currently not suitable for diesel particulate filters. The boiling characteristic of RME is an additional problem that presumably limits its further usability in Euro VI engines.

Currently, hydrogenated vegetable oil (HVO) is in the state of obtaining acceptance as alternative fuel in the German legislation and is in the focus of discussions worldwide. HVO has physical and chemical advantages versus RME. In case RME should continue to be an appropriate fuel its molecule structure must be designed - probably by means of plant breeding. It is important to lower the boiling line by achieving chain lengths between 12 and 16 carbon atoms and to have in mind the oxidation stability by focussing the number and the position of double bonds.

Moreover, aspects of emissions and health effects must be kept in mind.

Besides plant breeding, research should focus on highly efficient biotechnical transesterification, producing simultaneously shorter chain lengths. The phosphorus and metal contents of future biodiesel must become significantly lower than the specification limits that are valid at present.

References

Baldauf W, Balfanz U (1994) Verarbeitung von Rapsöl zu Kraftstoffen in Mineralöl-Raffinerieprozessen. VDI Berichte 1126:153-166

Biokraftstoffquotengesetz – BioKraftQuG: Gesetz zur Einführung einer Biokraftstoffquote durch Änderung des Bundes-Immissionsschutzgesetzes und zur Änderung energie- und stromsteuerrechtlicher Vorschriften vom 18. Dezember 2006.

Bockey D (2007) Biodiesel – ein Sachstandsbericht und Ausblick. Raps 25:144-147

Bockey D, Haupt J (2003) Perspectives and challenges for the market introduction and promotion of biodiesel. 4th European Motor Fuels Forum, November 24-26, 2003

Dorenkamp R, Garbe T, Ohlendorf G (2003) Biodiesel im Zielkonflikt mit Anforderungen an den Dieselmotor. Landbauforsch Völkenrode SH 239:57-62

EN 14214: Automotive fuels - Fatty acid methyl esters (FAME) for diesel engines - Requirements and test methods.

Fischer J (2007) Personal communication.

Grope N, Ruschel Y, Schröder O, Ruschel Y, Munack A [Projektltg], Krahl J [Projektltg] (2007) Messung ultrafeiner Partikel im Abgas von Dieselmotoren beim Betrieb mit Biodiesel : Abschlussbericht zum Forschungsvorhaben ; Projektlaufzeit: 01.03.2005-30.06.2007. Braunschweig : FAL, 108 p, Förderkennzeichen: 22007404 (04NR074)(FNR), Projektnummer: 530/044 (UFOP), Projektnummer: 2-TA-VDB (VDB)

Knothe G (2005) Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. Fuel Processing Technology 86:1059-1070

Krahl J, Munack A, Ruschel Y, Schröder O, Schwarz S, Hofmann L, Bünger J (2006) Influence of the phosphorus content in rapeseed oil methyl esters during a 1000 hours endurance test on the function of a SCR-system measured by exhaust gas emissions and health effects. SAE technical papers 3282

Rantanen L, Linnaila R, Aakko P, Harju T (2005) NExBTL : biofuel for the second generation. SAE Technical Paper 2005-01-3771

Roadmap Biokraftstoffe (2007) Gemeinsame Strategie von BMU/BMELV, VDA, MWV, IG und DBV, Juli 2007

Ruschel Y, Schwarz S, Bünger J, Krahl J, Munack A [Projektleitung] (2006) Abschlussbericht zum Forschungsvorhaben ‚Bestimmung der Emissionen und der Partikelgrößenverteilung (Feinstaub) im Abgas eines modernen Euro-4-Nutzfahrzeugmotors mit SCR-Abgasreinigung im Betrieb mit Biodiesel‘. Braunschweig : FAL