

Biodiesel

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Introduction

Crude oil and natural gas are the most important fossil raw materials today. Many things we use everyday are made from them such as plastics, coatings, paints, synthetic fibres, pharmaceuticals and fuels. Common fuels like petrol, diesel fuel and aviation fuel are produced from crude oil. Natural gas is used mainly for producing heat energy in furnaces.

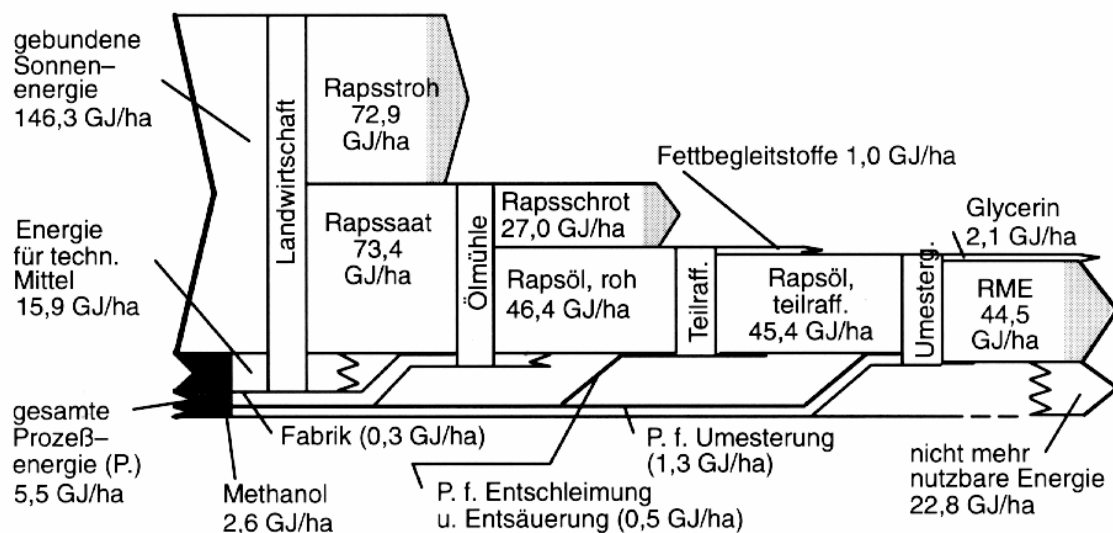
There are numerous disadvantages of fossil raw materials. Their supply is limited, and they are distributed unevenly in the world. This results in long transport routes and possible risks of accidents that could lead to environmental damage, economic and political dependence on the producing countries and, finally, to the release of combustion products like carbon dioxide which affect climate by heating up the atmosphere and contributing to the greenhouse effect.

Ecological aspects, the finite amount of fossil resources and need to fully utilize agriculture are the motives for using regenerative raw materials. The use of rapeseed oil as an alternative fuel has been examined in Germany since the seventies. In 1981 systematic studies showed that pure rapeseed oil was unsuited for long-term use in conventional diesel engines because of possible serious motor damage.

Nevertheless, to use rapeseed oil as a fuel, either the engine has to be changed or the fuel. Rapeseed oil can be employed as a liquid fuel either by constructing special engines or by transesterifying it – mostly to rapeseed oil methyl ester (RME or biodiesel).

In agriculture, the growing of rapeseed makes good ecological sense in that it regenerates the soil and serves as a long-term soil cover. Moreover, because rapeseed oil and biodiesel are biodegradable, they are better for the environment than diesel fuel in the event that accidental spills occur. Like all regenerative raw materials, rapeseed is also found in a mostly closed cycle. However, the dioxide cycle is not completely closed, because fossil fuels are still needed in agriculture, industrial oil production and the conversion of rapeseed oil to RME. Nevertheless, by considering the whole process, the use of rapeseed oil helps to considerably reduce the emission of gases that may affect the climate.

Figure 1 shows the energy flow in rapeseed oil and biodiesel production. About 1.2 tonnes of rapeseed oil with an energy content of 49.6 GJ in the raw oil or 47.8 GJ in biodiesel are harvested per hectare. In order to plant the rapeseed, fertilize it and protect it from pests, there is an energy input for fuel, fertilizer and pesticides. This is also summarized as 'technical means' by considering production and transport linked with the fraction of energy expended for making agricultural machines and constructing buildings. The process energy needed for pressing oil, cleaning and transesterification as well as the energy found in methanol should also be considered. Thus, without including the energy of the shaft and the straw, there is an energy expenditure-to-use ratio of about one to two.



Labels: gebundene Sonnen-energie = bound Sun energy; Energie für techn. mittel = energy for technical means; gesamte Prozeß-energie = total process energy; Landwirtschaft = agriculture; Rapsstroh = rapeseed straw; Rapssaad = rapeseed; Rapsschrot = oil mill, rapeseed grist; Rapsöl, roh = rapeseed oil, raw; Rapsöl, teilraff. = partially refined rapeseed; Fettbegleitstoffe = fat-accompanying substances; Umesterung = transesterification; Entschleimng u. Entsäuerung = desliming and deacidification; nicht mehr nutzbare Energie = no longer usable energy; Glycerin = propane-1, 2, 3-triol (glycerol)

Figure 1 Energy flow diagram for rapeseed oil and biodiesel

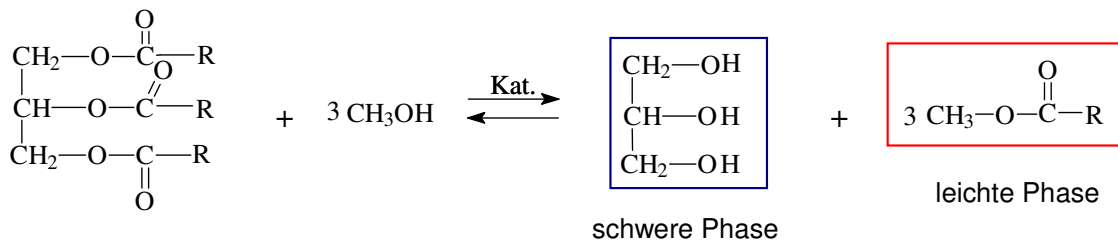
Rapeseed can still substitute only a small part of the diesel fuel consumed in Germany. Currently, the cultivation of rapeseed on a maximum of 20 % of the field area is seen to be ecologically acceptable. Based on the agriculture of Federal Republic of Germany, this would correspond to a rapeseed oil production of 2640 kt (Table 1). However, since rapeseed oil is traditionally employed in the food, chemical and pharmaceutical industries, a potential of 6.4 % of the entire diesel fuel consumption is the maximum by considering its somewhat lesser energy content compared to diesel fuel. Consequently, rapeseed fuels from domestic production can contribute somewhat towards protecting fossil resources.

Fraction of rapeseed grown on crop area	10 %	15 %	20 %
Possible rapeseed production / kt	1320	1980	2640
- Traditional use / kt	870	870	870
- Usable for fuel / kt	450	1110	1770
- Replacing diesel fuel / kt	390	970	1540
Fraction of diesel fuel consumption	1.6 %	4.1 %	6.4 %

Table 1 Possible substitution of diesel fuel by RME in Germany by assuming various percentages of rapeseed cultivation of crop area

What is biodiesel?

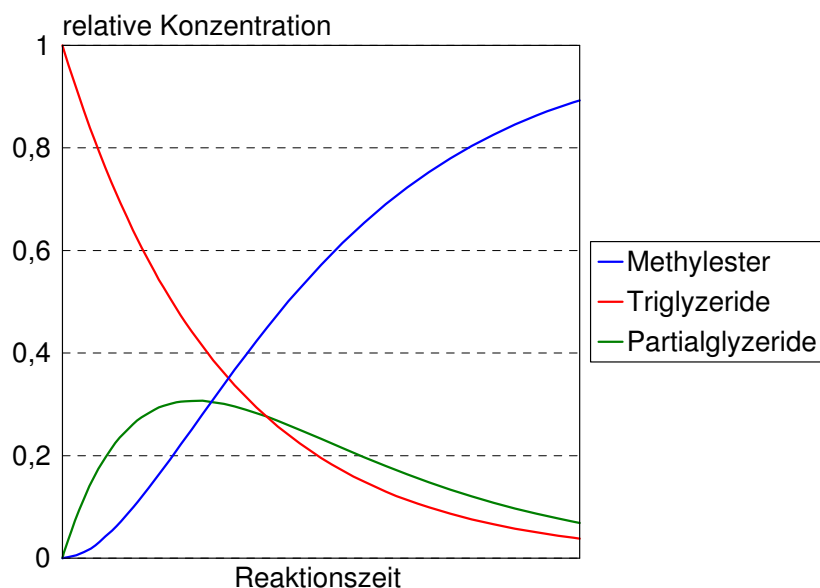
At first sight, the answer looks easy: biodiesel is a mixture of fatty acid methyl esters obtained from transesterification of the triglyceride rapeseed oil with methanol. The corresponding reaction is shown in Figure 2 below.



Labels: Kat. = catalyst; schwere Phase = heavy phase; leichte Phase = light phase

Fig. 2 Reaction route in the transesterification of the triglyceride rapeseed oil

The Fatty acid methyl ester (light phase) and propane-1, 2, 3-triol (glycerol) (heavy phase) are formed from the triglyceride in a typically base-catalyzed equilibrium reaction via partial glycerides as intermediate products. The reaction is a typical steady state reaction; *ie* at a particular reaction conversion, the rates of the forward and backward reaction (methyl ester formation and methyl ester decomposition) are the same. The reaction can progress further only by removing the reaction products or adding reactants in excess. The kinetics of this reaction are of the 2nd order (Figure 3).



Labels: relative Konzentration = relative concentration; Reaktionszeit = reaction time, Methylester = methyl esters; Triglyzeride = triglycerides; Partialglyzeride = partial glycerides

Figure 3 Kinetics of the reactions for forming fatty acid methyl esters from triglycerides.

The altered rapeseed oil acquires properties which closely correspond to those of diesel fuel based on mineral oil. That is why RME is also called biodiesel. In particular the viscosity and the ignition properties resemble that of commercial diesel

to the extent that a mixing or a replacement is possible without changing the engine settings (Table 2).

	Biodiesel (RME)	Diesel Fuel
Cetane rating	> 51	> 51
Heat value / MJ kg⁻¹	37	40-44
Kinetic viscosity at 288 K / mm²s⁻¹	3.5-5	2.0-4.5
Density at 288 K / gcm⁻³	0.875-0.900	< 0.845
Sulfur content / % w/w	< 0.01	0.035

Table 2 Properties of rapeseed methyl ester and diesel fuel

Long-term studies have shown that typical diesel engines can be operated in cars, trucks, agricultural machines and stationary units without having to change the engine or engine settings and without deviations in wear and engine contamination. Thus, many automobile producers have permitted the use of biodiesel in their models without restrictions. Trucks have been allowed to do this with the oil-change intervals being halved. Consequently, biodiesel is an alternative fuel with the special advantage of it neither requiring complicated structural changes of the engine, nor special infrastructures for filling. Nonetheless, plastics that are non-resistant to biodiesel have been built into some vehicles. Thus, the manufacturer has to be consulted regarding the tolerance of its vehicles to biodiesel fuel.

What are the requirements of a modern biofuel to be a diesel substitute?

The large-scale conversion of rapeseed oil to RME is quite simple. It is also suitable for smaller local units. Thus, projects have already been carried out in which the conversion took place on site at the rapeseed producer. Moreover, this process yields propane-1, 2, 3-triol (glycerol) which can be marketed, for pharmaceutical and cosmetic applications, for example,. In addition, the remaining production wastes can be used as solid fuels in heating plants or as protein-rich additives to animal feed.

Consequently, one could mistakenly conclude that producing biodiesel is an easy low-tech affair which only requires elementary knowledge in chemistry to produce a biodiesel that meets the specifications. On the contrary, at the smaller RME units, distillates are obtained that have dubious qualities which may lead to damage to fuel-injectors. In reality, several specifications are placed on a modern biofuel before it can be used at all to substitute diesel. The following lists a few of the most important specifications of an alternative fuel:

- applicability in commonly marketed engines / fuel-injection systems;
- oxidation- and storage-resistance comparable to that of mineral oil-based fuels;
- no mixing gaps with typical diesel fuel (possibility of mixed operation ;
- maintaining emission declarations made for conventional fuels;
- standardization of the fuels and setting of minimal specifications;
- acceptance by the automobile industry;
- proof of ecological sustainability (eg CO₂ and energy balance); and
- acceptable price and sufficient availability.

Each of these aspects raises several other questions which decide the future of a fuel. At the moment alternative fuels will always compete with conventional mineral oil-based fuels that currently dominate the market. In this light, the price of the alternative product and its sufficient availability are very important.

Raw materials for RME: what are the special merits of rapeseed oil?

Besides rapeseed oil, other plant oils like sunflower oil, for example, can be used for manufacturing biodiesel. However, the iodine count of sunflower oil (number of double bonds in the fatty acid molecule) is too high which is why it can only be used as a mixture with rapeseed oil. In comparison, rapeseed oil shows these advantages making it ideal for producing biodiesel:

- its fatty acid composition approaches the optimum for obtaining a good cetane rating;
- with correct pre-processing, it contains only few free fatty acids and few hetero-elements (phosphorus and sulfur);
- it inherently contains a considerable fraction of antioxidants (eg β -carotene);
- it has a low level of contamination;
- a large number of developed technologies are available for transesterifying rapeseed oil; and
- it is a commonly grown and marketed crop.

However, rapeseed oil is hardly uniform. Depending on the type and – within a given type – depending on climatic effects, the composition of fatty acids may differ from one another. Table 3 shows typical fatty acid profiles of different varieties of rapeseed. The conversion of such rapeseed oils into biodiesel would yield differing products.

Oil Type	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C22:1
Rapeseed oil "00"			4,9	1.7	65.6	17.3	7.2	traces
Rapeseed oil, erucate-rich			3.9	1.5	25.3	19.1	9.2	32.5
Rapeseed oil, laurate-rich	36.7	3.9	3.1	1.3	33.2	11.9	7.4	traces

Table 3 Fatty acid profile of common varieties of rapeseed (data in %)

Aside from these plant-related differences, the by-products of the raw substance for biodiesel production will noticeably differ through the type of oil production and the subsequent cleaning process. Thus, the standardization of the fuels and the setting of minimum specifications are the most important for its acceptance by the automobile industry and the consumer.

Environmental and health effects caused by exhaust gas components of biodiesel

The use of rapeseed as fuel was initially triggered by the energy crisis in the early 1970s. Today's prime motivation for the use of RME is environmental protection. The decision to use an alternative fuel is not only a question of technical practicability. The exhaust gas emissions and their effects on the environment and human health have also to be taken into consideration.

Diesel engine exhaust (DEE) has been classified as carcinogenic to experimental animals and as a probable carcinogenic agent to humans by the International Agency for Research on Cancer. Several studies reported a relative risk of approximately 1.5 for incidence of lung cancer after a long-term exposure to DEE. The carcinogenic effect of diesel exhaust exposure is mainly ascribed to the inhalation of carbon black particles. Many known or suspected mutagens and carcinogens, eg polycyclic aromatic hydrocarbons (PAH,) are adsorbed onto the surfaces of carbon cores of DEE particulate matter as an organic phase.

For particulate matter, the mass is the controlled value. However, recently it became evident that the particle number and size distribution may be more important than its mass alone. One 1 μm diameter particle has the same mass as 1000 particles of 0.1 μm . Furthermore, small particles reach pulmonary alveoli and deposit there, while larger particles are deposited in the upper airways and eliminated by its ciliated epithelium. Thus, small particles, especially those ultrafine particles under 100 nm, are considered critical in their effect on human health. Therefore, the particulate matter emissions from diesel fuel (DF) and from biodiesel are compared not only regarding masses, but also their particle sizes and number distributions. In order to estimate the physiological effects of DF and RME particulate matter, the determination of their mutagenic potencies was also carried out.

Additionally, the potentials of both fuels to form ozone were calculated. Therefore, several substantial ozone precursors (eg ethene and methanal (formaldehyde)) were determined comparatively. Furthermore, the regulated, and some important non-regulated, exhaust gas constituents (eg benzene and dinitrogen oxide (nitrous oxide)) were determined using different blends of both fuels.

The engine type (direct or indirect fuel injection) as well as the test cycle employed affect the relative emissions of biodiesel compared to DF. For cars, the stationary tests FTP-75 and MVEG-A (formerly ECE-15) are commonly used. In the EU, trucks are examined according to the stationary 13-point test. For tractors, the stationary 5-step test (though not yet legislated) is often used. However, it reflects the real emission of tractors. In the future, the 8-step test according to the ISO-Norm 8178 C1 will be applied.

To estimate the actual emissions of an engine, in many places engine test techniques have been developed which allow the real-operation simulation at the engine testing site. At the Federal Research Agency for Agriculture in Braunschweig, Germany, tractors are loaded in the 5-point test at the testing site. Figure 4 illustrates the test setup. For sampling, suitable probes are installed in the exhaust pipes of the test vehicles. By means of these, defined exhaust streams can be removed through heated pipes and analyzed.

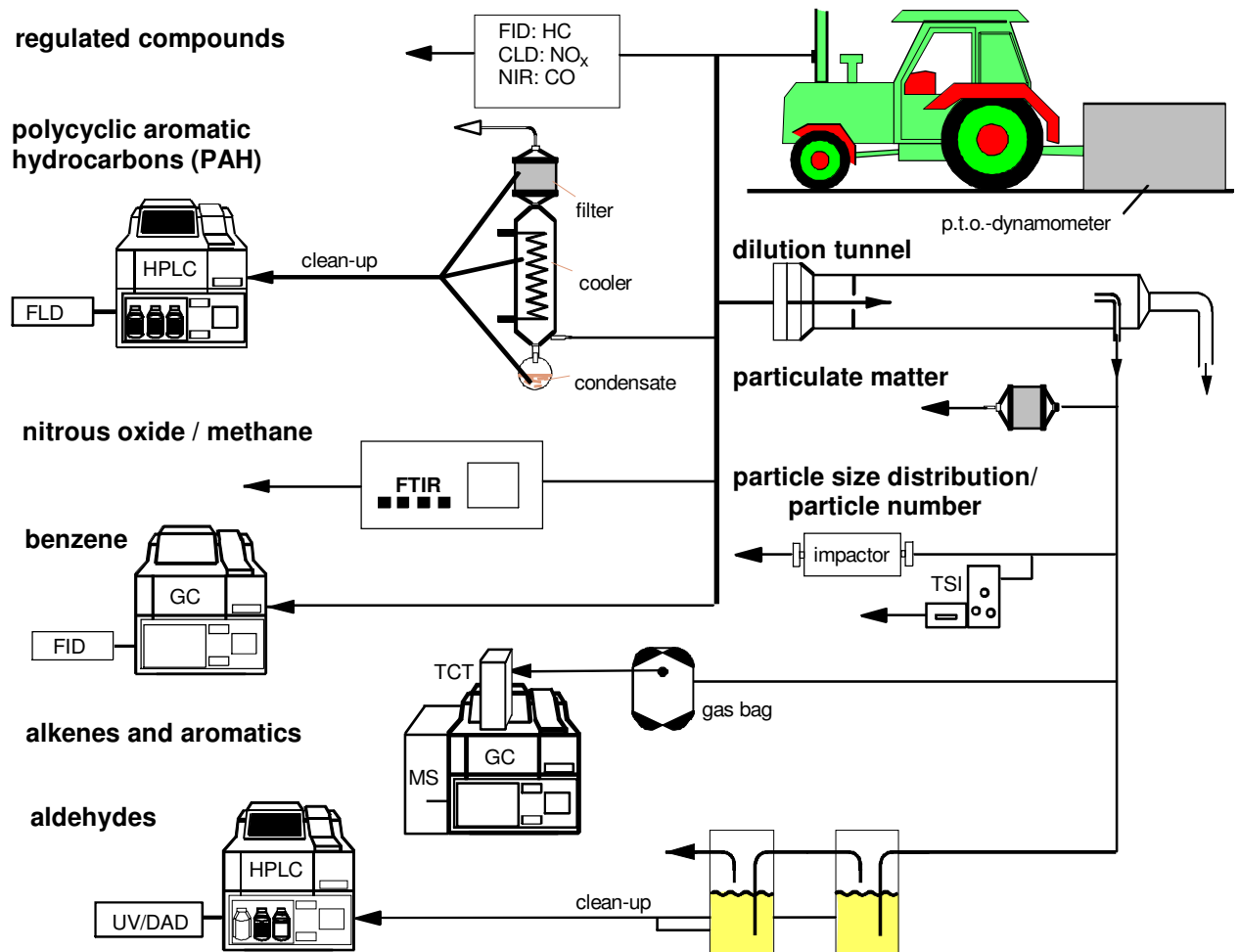
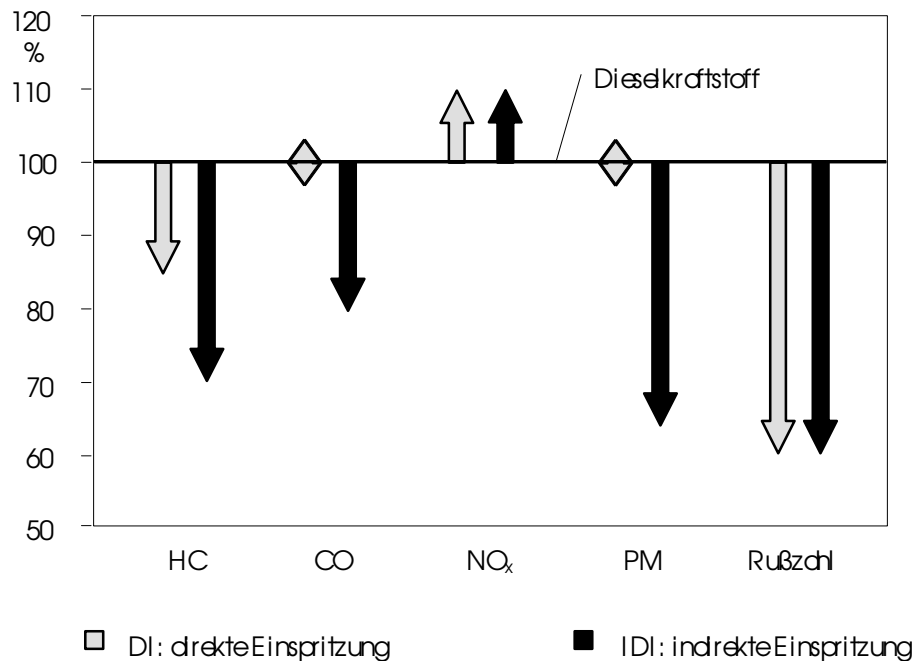


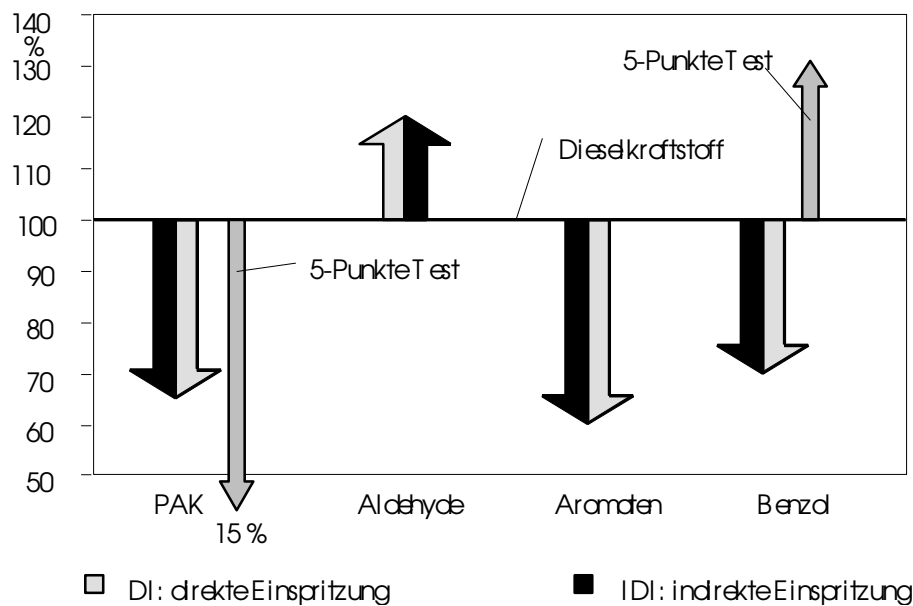
Figure 4 Schematic overview on the exhaust gas constituents and the analytical equipment.

Figures 5 and 6 summarize the trends shown from the various studies without showing the number of relevant measurement values or their accuracy. After evaluation of the available data and comparison to diesel fuel, biodiesel shows decreased emissions of hydrocarbons, carbon black and polyaromatic hydrocarbons (PAH) but also increased emissions of NO_x and aldehydes. In particular, it is found that the type considerably affects the changes in the emissions of hydrocarbons, carbon monoxide and particulate matter. In contrast to other test cycles, in the agricultural 5-point test a drastic reduction or an obvious increase was observed for the unrestricted components PAH and benzene. Initial results of a current research project at the Technical University in Coburg confirm the tendency for slightly increased benzene emissions from biodiesel combustion.



Labels: Dieselkraftstoff = diesel fuel; DI direkte Einspritzung = direct fuel injection; IDI indirekte Einspritzung= indirect fuel injection; Rußzahl = carbon black count

Figure 5 Relative emission values of the restricted components and of the carbon black particles from engine operation with DF and biodiesel (DF = 100 %)



Labels: PAH = polyaromatic hydrocarbons; Aromaten = aromatics; Benzol = benzene; 5-Punkte test = 5-point test; Dieselkraftstoff = diesel fuel; DI direkte Einspritzung = direct fuel injection; IDI indirekte Einspritzung = indirect fuel injection

Figure 6 Relative emission values of the unrestricted components from engine operation with DF and biodiesel (DF = 100 %)

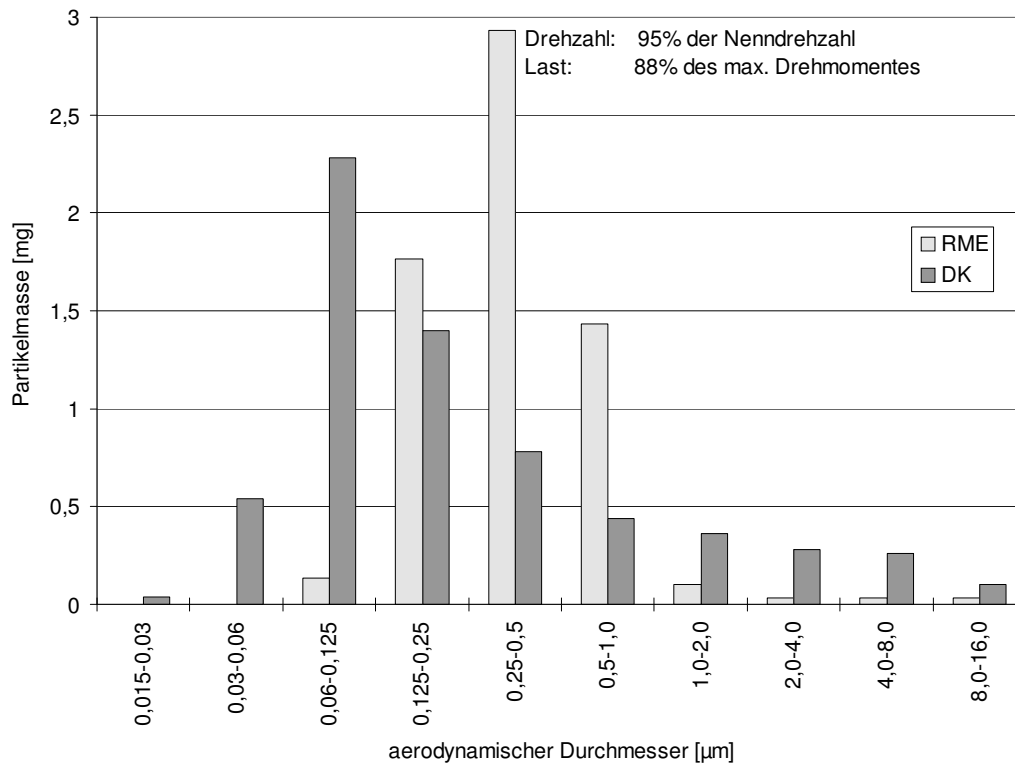
Genotoxicity of diesel engine emissions

Based on unequivocal *in vitro* and *in vivo* studies on animals, diesel engine emissions (DEE) were classified in 1987 in Germany as being carcinogenic substances in Group III A2 of the MAK list, although a transfer of these results to carcinogenicity in humans could not be derived from the epidemiological studies existing at that time. The International Agency for Research on Cancer of the WHO (IARC, 1989) confirmed the validity of the evidence of carcinogenicity in animals tests (sufficient evidence) and classified the carcinogenicity in humans as being likely (limited evidence), where the results of epidemiological studies were also considered. Based on other recently published studies, there seems to be a one- to 1.5-fold increase in the risk of contracting lung cancer after long-term exposure to the exhaust gases from diesel engines. However, these studies were also criticized. For example, the effect of smoking habits was disregarded in these studies. Nonetheless, the genotoxic effects of DEE are mainly attributed to particulate matter (carbon black) and to the combustion products adsorbed to these particles (primarily PAH and their nitro-derivatives). Newer studies also showed that carbon black itself already has carcinogenic properties which are accentuated with the simultaneous action of PAH and carbon black. The mutagenic properties of RME were described for the very first time in 1978 in the Ames test (*Salmonella* microsome test) and were later confirmed by further comprehensive studies. However, the respective data regarding the combustion of biodiesel are missing as yet. Thus, initial studies on the genotoxicity of biodiesel exhaust gases using the Ames test was taken up by the Center for Environmental and Occupational Medicine (Zentrum für Umwelt- und Arbeitsmedizin) of the University of Göttingen.

In the tests conducted so far, the filter extracts from biodiesel operation were clearly less mutagenic than the DF-extracts in all load classes and driving cycles and despite a higher absolute mass. This is probably due to the lower PAH-concentration in the exhaust gas from biodiesel operation. If it is confirmed that biodiesel exhaust gases show a lower mutagenic potential than DK exhaust gases, consideration should be given to substituting DF with biodiesel in the operation of diesel vehicles in particularly critical workplaces, (eg in warehouses and underground sites) and other high risk places (eg for taxis and buses in city centers).

Particulate-size distribution for DF- and biodiesel emissions

To obtain indications of a possible alteration in particulate size of the emissions from engines operated with DF compared with those operated with biodiesel, the mass distribution of the particulates in DF and biodiesel operation was determined at high load and rotational speed by means of a 10-step low-pressure cascade impactor. Figure 7 illustrates the mass distribution of the particulates as a function of the aerodynamic diameter. For both fuels, over 80 % of the collected particulate mass is under 1 μm . The particulate mass in biodiesel operation is essentially distributed amongst the diameter range from 0.125 to 1.0 μm . Notable here is that a shifting of the particulate size to smaller particulate diameters occurs in DF-operation. 44 % of the total particulate mass collected in the impactor has a diameter of less than 0.125 μm , while in the biodiesel operation only 2 % of the particulate mass falls in this range. Accordingly, in the study of a biodiesel engine operated at high load, the fraction of very small particulates is clearly lower. However, further systematic studies are necessary for clarifying the question on whether this statement can be made for biodiesel operation in general or whether the result specifically depends on the particular engine or load.



Labels: Drehzahl = Rotational speed; 95% der Nenndrehzahl = 95 % of the nominal rotational speed; Last = Load; 88 % des max. Drehmomentes = 88% of the max. torque; RME = Rape Methyl Ester; DK = diesel fuel; Partikelmasse = particulate mass; aerodynamischer Durchmesser = aerodynamic diameter

Figure 7 Mass distribution of the particulates in the exhaust of a tractor (Fendt Farmer 306 LSA) in operation point A of the 5-point test

Summary and outlook

The use of biodiesel should be promoted from an energy viewpoint, since only about 50 % of its energy content has to be expended for producing it. Nonetheless, biodiesel cannot be seen as a comprehensive alternative to fossil diesel fuel, because a maximum of 6-7 % of the DF-consumption could currently be substituted in Germany. Hence, biodiesel remains a so-called 'niche' fuel, having the particular advantage of requiring neither complicated engine conversion measures nor the building of special infrastructures for filling. Nevertheless, some cars have plastics which are not resistant to biodiesel. In case of doubt, the manufacturers should be asked about the biodiesel tolerance of their vehicles.

In the result of comparing DF-emissions to biodiesel emissions, various trends are recognizable depending on the engine types and the motor test technique applied. Irrespective of all peripheral conditions, the biogenic fuel shows increased aldehyde emissions and decreased carbon black emissions compared to DF. Moreover, biodiesel exhibits decreased hydrocarbon and PAH-emissions as well as slightly increased NO_x emissions. Since exhaust gases cannot be evaluated based on the spectrum of their single components alone, supplementary studies were conducted on the mutagenicity of biodiesel and DF. In summary, there is a noticeable advantage of biodiesel over DF. Initial results of the comparison of the particulate size distribution of DF and biodiesel using the result of a tractor test at full load likewise infer a slight advantage of the alternative fuel over diesel fuel. However, this preliminary result does not mean that this is absolutely characteristic for biodiesel

operation. To clarify any open questions, systematic studies must be done on the genotoxicity and on the particulate mass and number distributions.

School experiments on the topic biodiesel *versus* diesel fuel

The following presents a selection of school experiments which allow the production and a comparison of the properties of biodiesel RME with commonly used diesel fuel from petroleum.

Experiment 1: biodiesel production in school

Each group of students will need

- Eye protection
- One 400 cm³ beaker
- Three large test tubes
- One-hole stoppers with fitted with glass tube (40 cm)
- Thermometer
- Magnetic stirrer with heating plate
- Stirrer bead
- 50 cm³ pipette
- Rubber bulb pipette filler
- Rapeseed oil
- Methanol Highly flammable, toxic by inhalation, if swallowed and by skin absorption
- Sodium hydroxide causes severe burns, very dangerous to eyes and skin
- Hydrochloric acid 0.05 mol dm⁻³

Safety

- Wear eye protection
- Methanol is flammable and poisonous
- Sodium hydroxide is corrosive

Method

The beaker is filled halfway with water and heated to 75 °C. 0.3 g sodium hydroxide is dissolved in 100 cm³ of methanol. 8 cm³ of this solution and 4 cm³ rapeseed oil are put in a dry test tube and the stirrer bead added. After the glass tube has been attached as a reflux condenser, the mixture is heated with vigorous stirring in a water bath. Upon stirring, a milky emulsion forms and, after about another 5 minutes reaction time, a clear solution. After the stirrer has been turned off, the contents of the test tube are transferred without cooling to another test tube filled about $\frac{3}{4}$ full with water. Two phases appear. After brief shaking, the phases are allowed to separate, and then the upper phase is pipetted into the third test tube.

Rapeseed oil and sodium hydroxide are hardly miscible either at room temperature or at 75 °C. The transesterification of the rapeseed oil takes place by reaction with methanolate ions, whereby a mixture of fatty acid methyl ester and propane-1, 2, 3-triol (glycerol) is formed. These substances are soluble in heated methanol. If one mixes the reaction solution with water, the sodium methanolate partially reacts to

sodium hydroxide and methanol. Methanol, propane-1, 2, 3- triol (glycerol), sodium hydroxide and sodium methanolate dissolve in water. However, the various fatty acid methyl esters remain in the non-aqueous phase.

Experiment 2 viscosity of RME and diesel fuel using a falling ball viscometer

Each group of students will need

- Eye protection
- Two 100 cm³ measuring cylinders
- Porcelain marbles (about 0.7-1 cm)
- Diesel oil
- Rapeseed oil

Safety

- Wear eye protection

Method

Two measuring cylinders are filled with diesel oil and rapeseed oil, respectively. Then, a porcelain marble is put into each cylinder simultaneously, and the sinking of the marble is observed. The time it takes for each marble to reach the bottom is determined.

Result

The marble in the cylinder with rapeseed oil needs about two to three times longer to reach the bottom. Other ways in comparing the viscosity are also feasible such as timing the flow of samples down an inclined glass plate, which likewise takes longer with rapeseed oil.

Experiment 3: determination of the flash point of rapeseed oil, diesel fuel and RME

Each group of students will need

- Eye protection
- Magnetic stirrer with heating plate
- Stirrer bead
- Porcelain dishes with a shallow bottom
- Wooden splints
- Diesel oil
- Rapeseed oil
- RME

Safety

- Wear eye protection

Method

Samples of rapeseed oil, diesel fuel and RME are heated in shallow dishes on a magnetic stirrer plate. At regular intervals, one tries to ignite the samples with a burning wooden splint. Continue to heat until the fuel ignites or a temperature of 250 °C is reached.

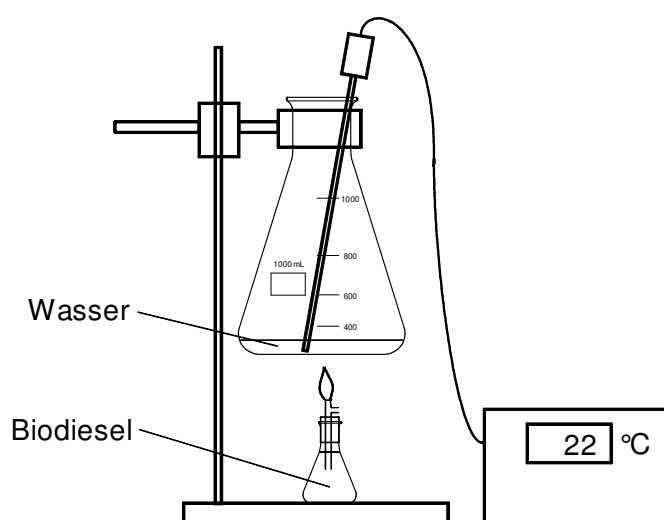
Result

The sample of diesel fuel ignites at temperatures above 80 °C. Rapeseed oil cannot be ignited even at 250 °C. The flash point of RME is reduced from 250 °C to about 170 °C by transesterification of rapeseed oil. However, it is still clearly above that of diesel fuel. Nonetheless, this decrease in the flash point is enough for biodiesel to be used in diesel-operated vehicles without having to alter the engine.

Experiment 4: comparison of the heat values of RME and diesel fuel

Each group of students will need

- Eye protection
- One 1 dm³ Erlenmeyer flask
- One 50 cm³ Erlenmeyer flask
- Stoppers fitted with a short length of glass tube and wick
- Digital thermometer
- Clock
- RME and diesel fuel



Labels: Wasser = water

Figure 8 Apparatus for determining the heat value of RME and of diesel fuel

Method

The experiment is set up according to Figure 8. The upper large Erlenmeyer flask is filled with 200 g water. The mass of the small Erlenmeyer flask (filled with RME or diesel fuel (DF) and equipped with a stopper and glass tube) is determined precisely

and the initial temperature determined. Then, the RME or DF is ignited at the wick and burned until the temperature of the water has increased by exactly 10 °C. By pulling the wick in or pushing it out, the flame is adjusted so that it does not cause soot. Especially good results are obtained when the wick is placed in a T-piece (as shown) instead of a glass tube and when some air is directed into the side arm by using, for example, an aquarium pump. This makes the DF burn more completely. After the temperature has increased by exactly 10 °C, the mass of the RME or DF that has burned is determined by weighing the flask again.

Result

One obtains, for example, the values cited in Table 4 which show that for heating water, a larger mass of RME must be burned in comparison with DF.

Measurement	RME	Diesel fuel
1	0.335 g	0.291 g
2	0.310 g	0.294 g
3	0.315 g	0.295 g
<i>Mean</i>	<i>0.320 g</i>	<i>0.293 g</i>

Table 4 Typical results of the reduction of the mass upon combustion of RME and DF after the heating of the same portions of water by 10 °C