The Use of Biofuel in Modern Diesel Engines

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INTRODUCTION

If vegetable oils are to be used as fuels the engine developers above all have to determine the optimum way to pro ceed, that means define the requirements such an alternative fuel system has to meet. *Table 1* lists the requirements which in our view should serve as development guidelines for any alternative fuel system including a system on the basis of vegetable oils.

First of all, it should be possible to use an alternative fuel in already existing engines because:

- vegetable oils can only make a marginal contribution to fuel supply worldwide,
- vegetable oil fuels might only acquire a significant share of the fuel market under limited local conditions (*e.g.* in Malaysia, in some EU countries, in the US) and
- fluctuations of the world market price for vegetable oils make it very difficult to assess the economic viability and the availability of vegetable oil fuels as compared to conventional fuels.

For the above reasons, it seems practically indispensable that existing engines and vehicles can be used in such vegetable oil fuel schemes; also, there would be additional advantages:

- no major investment risk for the operator,
- the overall investment required for fuel production and distribution will increase with the growing amount of vegetable oil available and
- the vehicles remain independent of the new fuel being available (long-distance transport, vehicle sold into a region where the alternative fuel is not available, supply infrastructure can be built up gradually).

Another essential criterion is that if existing vehicles cannot be fully integrated into the scheme, the necessary conversion of existing engines and vehicles should only be minimal; "hardware" changes are acceptable only to a very limited extent (*e.g.* different fuel hose materials). Changes to the engine setting are less critical, involving for example start of delivery, maximum injection amount and/or service fluid system where a certain lubricating oil or modified lubricating oil change intervals might be specified. Of course, all these changes must not preclude or deteriorate the use of conventional diesel fuel; at least, reconversion must be easy to effect. Complete compatibility between alternative and conventional fuels of course continues to be the best solution.

Environmental compatibility of an alternative fuel system is another indispensable criterion for its feasibility; it must not be worse than that of the conventional system. Not only the currently applicable limits on gaseous emission constituents must be taken into account, *i.e.* unburnt hydrocarbons, carbon monoxide, nitrogen oxides and particulate emissions, but - if an investigation is possible with reasonable effort - certain unlimited emissions such as polycyclic aromatic hydrocarbons, aldehydes *etc.* should be included, too. Certain importance should also be attached to the overall emission of "greenhouse gases", in particular carbon dioxide, and to the noise emission.

Apart from that, the additional expense as compared to conventional diesel fuel operation which is to be borne by the operator should be kept to a minimum, in particular reductions in engine service life, ease of maintenance, operational reliability *etc.* or increased cost of the fuel, of other service products such as lubricating oil, or increased maintenance and/or repair effort and others.

Finally, it must be ensured that a sufficient quantity of fuel is available, a condition which is of course met if diesel fuel and alternative fuel can be used alternately; in this context it is decisive that the new fuel offered is always of the same good quality.

From today's point of view, the best possibility of adapting vegetable oils to the demands of existing diesel engines is transesterification to vegetable oil fatty acid esters, usually with methanol to vegetable oil fatty acid m-ethyl esters. The resulting vegetable oil methyl esters can basically be used in all existing diesel engines even though their use necessitates modifications to the engine or the vehicle (*e.g.* to some elastomer materials, sometimes to the fuel tank coating *etc.*) or to some adjustment parameters.

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TABLE 1. DEVELOPMENT GUIDELINES FOR ALTERNATIVE FUELS SYSTEMS

Applicability to existing engines

- no unreasonable investment risk to the user
- no impediment to the market introduction
- investment required for fuel production grows with the quantity of vegetable oil
- no dependence on alternative fuel availability (long distance traffic, vehicle sale etc.)

Modification of existing engines to a marginal extent only, if at all

- Hardware modifications easy and cheap to realise (e.g. fuel lines)
- hardware modifications should not affect the use of conventional diesel fuel; at least, re-modification should be very easy
- engine parameter modifications less critical (e.g. fuel injection volumes, start of delivery, type of lubricating oil, oil change interval etc.)
- best of all: complete compatibility between conventional and alternative fuel

Environmental compatibility at least as favourable as with conventional diesel fuel, and that concerning;

- the limited emissions (HC, CO, NOx, PM)
- important non-limited emissions (e.g. benzene, PAH, aldehydes etc.)
- the overall greenhouse gas emissions
- perhaps the noise emission

Additional costs to the engine user as low as possible

- engine lifetime, long term reliability, operational availability, ease of maintenance, safety etc.
- costs for the alternative fuel itself, for other materials, for maintenance or repairs etc.

Alternative fuel availability at a constant good quality

TABLE 2. PROPERTIES OF VARIOUS VEGETABLE OIL FATTY METHYL ESTERS, DIESEL FUEL PROPERTIES FOR COMPARISON

Methyl esters of the fatty acids of	Number of double bonds	Formula			Composition [% by mass]			Molecular weight [g/mole]
		C	H	O	C	H	O	
coconut oil	0.08	13.4	26.7	2	73.3	12.2	14.5	220.4
palm kernel oil	0.13	13.9	27.7	2	73.7	12.3	14.1	227.6
palm oil	**0.59**	**18.0**	**34.9**	**2**	**76.3**	**12.4**	**11.3**	**283.7**
peanut oil	1.10	19.0	35.0	2	77.0	12.2	10.8	296.3
cotton seed oil	1.20	18.5	34.6	2	76.9	12.1	11.1	289.2
rapeseed oil (erucic)	1.25	21.0	39.5	2	77.8	12.3	9.9	324.2
rapeseed oil (non-erucic)	**1.33**	**19.0**	**35.4**	**2**	**77.2**	**12.0**	**10.8**	**296.0**
sunflower oil	1.49	18.9	34.8	2	77.2	11.9	10.9	294.1
soya bean oil	1.51	18.8	34.6	2	77.2	11.9	10.9	293.0
linseed	2.12	18.9	33.6	2	77.5	11.6	10.9	292.1
typical diesel fuel	**-**	**1**	**1.85**	**0**	**86.6**	**13.4**	**0**	**120-320**

Methyl esters of the fatty acids of	Iodine number	Density at 15 °C [g/l]	Lower heating value		Viscosity at 40 °C [mm²/s]	Cetane number
			MJ/kg	MJ/l		
coconut oil	10	872	35.3	30.8	2.7	62.7
palm kernel oil	15		5.5			
palm oil	**52**	**872-877**	**37.0**	**32.4**	**4.3-4.5**	**64.3-70.0**
peanut oil	94		37.2			
cotton seed oil	105		37.0			
rapeseed oil (erucic)	98		37.7			
rapeseed oil (non-erucic)	**114**	**882**	**37.2**	**32.8**	**4.2**	**51.0-59.7**
sunflower oil	129	885	37.1	32.8	4.0	61.2
soya bean oil	131		37.1			56
linseed	183	891	37.0	33.0	3.7	52.5
typical diesel fuel	**-**	**830-840**	**42.7**	**35.5**	**2-3.5**	**51**

I hope that with my comprehensive introduction I succeeded in explaining to you why Mercedes-Benz AG decided to opt for the use of vegetable oil esters.

CHARACTERISTICS OF VEGETABLE OIL FATTY ACID METHYL ESTERS

In the following section, I would like to dwell on the fuel-relevant characteristics of vegetable oil esters. *Figure 1* shows a simplified presentation of the transesterification process which is important to understand the properties of esters. As can be seen from this figure, the vegetable oil molecules are triglycerides, huge molecules which are split up into three much smaller ester molecules and one glycerol molecule through reaction with three methanol molecules.

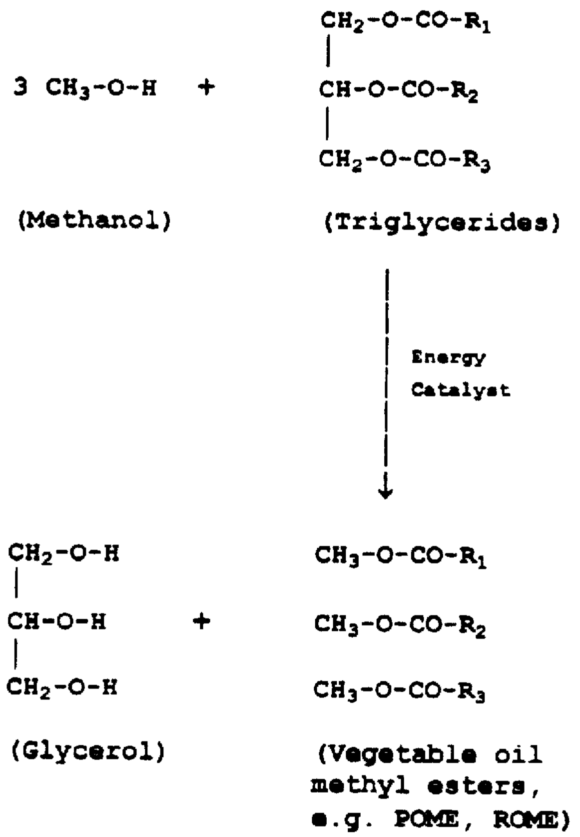
The fatty acid radicals R_1, R_2 and R_3 feature carbon chains of different length and a differing number of double bonds. Of course, the transesterification shown in an idealised way in *Figure 1* may not only result in the main products vegetable oil ester and glycerol but also in a number of other products or leave impurities in the end product which had been introduced before. *Figure 2* shows a number of such by-products which in some cases bear considerable effect on the fuel-relevant properties of the main product vegetable oil ester. Apart from the desired main product, the following products occur: reaction products from incomplete transesterification, namely mono-, di- and triglycerides; free fatty acids through hydrolysis (for example prior to transesterification) which are left unchanged by the usual alkaline transesterification; methanol due to the surplus methanol required for the reaction; also glycerol, catalyst residues, water, possibly slimy substances etc. All these undesirable by-products should be removed to the largest extent possible in order to produce a high-quality fuel. This point will be dealt with at greater detail within the context of product specification. These by-products interfere to a greater or smaller extent with the in-engine behaviour: tri- and diglycerides will behave in a similar way as the vegetable oil esters in terms of coking and deposits, all glycerides and the free glycerol will be unfavourable for the formation of , for example, acrolein in the exhaust gas; furthermore, the free fatty acids and glycerol have a highly corrosive effect on some non-ferrous metals and their alloys, methanol residues do not have an unfavourable effect on the engine but they do lower the flash point of the product considerably, thus possibly resulting in a different dangerous materials class, and catalyst residues usually lead to the formation of ashes and deposits in and wear of the engine.

Table 2 shows fuel-relevant properties of some vegetable oil methyl esters. The esters of palm oil and of rapeseed oil which is low in erucic acid are highlighted since they are of particular interest in this paper; the values of typical diesel fuel which have been added in the last line for comparison purposes have also been highlighted. In addition, Mercedes-Benz AG performed a more thorough investigation of soya bean oil ester whose in-engine behaviour will be expanded on later within the appropriate context.

When we have a look at the properties of vegetable oil methyl esters it first strikes the eye that they all feature a certain unsaturation; the corresponding number of double bonds in a statistic average molecule was chosen as order criterion. A distinction can be made between the almost saturated esters including palm oil ester, the moderately unsaturated ones including rapeseed oil ester, the more highly unsaturated esters of sunflower oil and soya bean oil and the highly unsaturated esters of drying vegetable oils such as linseed oil. According to our experience, soya bean oil ester as compared to rapeseed oil ester or particularly to palm oil ester causes much more problems due to a chemical reaction in the lubricating oil (polymerisation?); *e.g.* the comparison of a direct-injection commercial vehicle diesel engine after comparable continuous operation with rapeseed oil methyl ester and soya bean oil methyl ester respectively shows that the deposits formed under the cylinder head cover are much more marked with the soya bean oil ester fuel. Therefore, a fuel specification must include the iodine value as a parameter.

During the following section on the in-engine behaviour of vegetable oil esters I will limit my remarks mainly to the ester of palm oil highlighted in *Table 2*, which is of major economic significance here in Malaysia and available in large quantities, and to the ester of rapeseed oil because of its importance in Germany and in Europe. We conducted particularly thorough investigations of these two vegetable oil esters.

When comparing the properties of these two vegetable oil esters and of diesel fuel the first thing that strikes the eye is that with their mean mole mass they are within the spectrum of diesel fuel but at the upper end, which means they are much less volatile than diesel fuel, resulting in an entirely different boiling behaviour which is not covered by DIN EN 590 (which is the binding diesel fuel standard for the CEN states). In this context, it should be noted at this point that an alternative fuel need not necessarily comply with the specifications of existing fuels because these mainly aim at defining a permanent reliable quality, but that the in-engine behaviour is of decisive importance. For this reason, I have not included DIN EN 590 in this table nor should the values of typical



R_1, R_2, R_3: Different fatty acid chains, e.g.
$C_{17}H_{35}$ (Stearic acid)
$(CH_2)_7$-CH=CH-$(CH_2)_7$-CH_3 (Oleic acid)
$(CH_2)_7$-CH=CH-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH_3 (Linolenic acid)

Figure 1. Transesterification of a Vegetable Oil to the Respective Methyl Ester

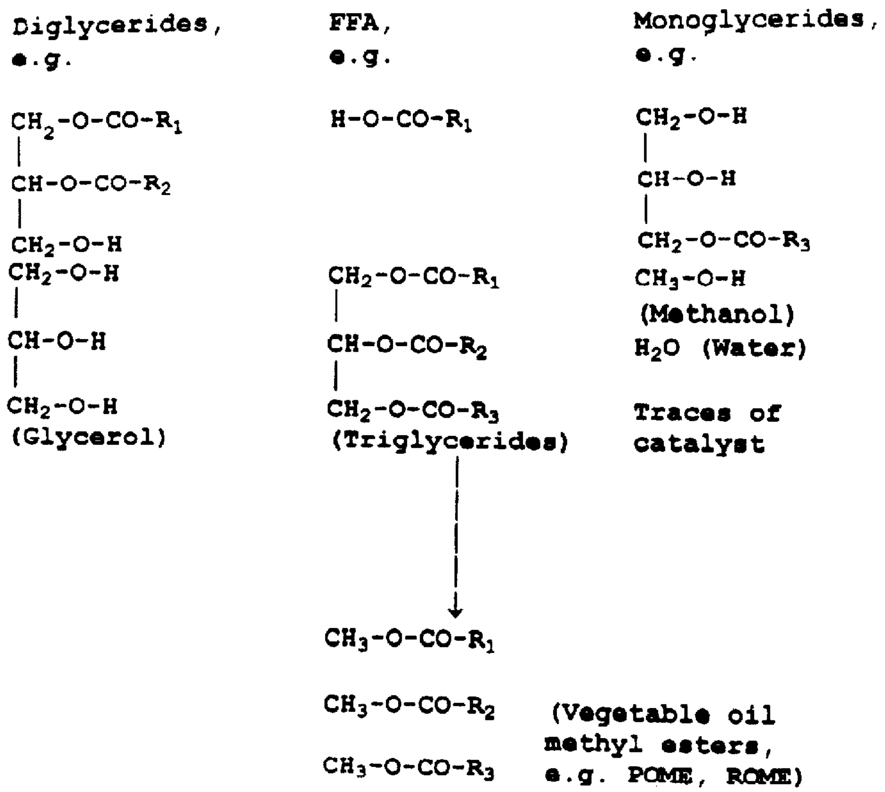


Figure 2. Possible Impurities of Vegetable Oil Esters

diesel fuel listed for comparison be seen as development objectives for an alternative fuel.

The density values of vegetable oil esters are very similar to each other and clearly higher than those of conventional fuel; the same holds true for the net calorific value which is approx. 13% lower per unit of weight for esters than for diesel fuel, but only approx. 8% lower per unit of volume because of the higher density. The viscosities differ only negligibly from those of the crude oil middle distillate while the cetane rating of rapeseed oil ester with measured values between 51 and almost 60 is on average much higher than the 51 which are common today. The ignition quality of palm oil ester with a cetane rating between 64 and 70 is at values which today are entirely unknown for diesel fuel.

The properties which influence a fuel's low-temperature behaviour have been deliberately left out of *Table 2*. They are listed exclusively for rapeseed oil ester in *Table 3* since the low-temperature behaviour plays hardly any role at all for palm oil ester because in Malaysia temperatures are sufficiently high throughout the year including the nights so that it did not seem necessary to analyse the low-temperature behaviour of palm oil ester. For rapeseed oil methyl ester, the cold filter plugging point, that is the temperature at which the fuel filter starts to clog, is approx. -7 °C, the cloud point is approx. -3 °C, and the pour point, a measure of the setting point, is approx. -16 ° C. The CFPP is of importance for practical operation; with -7 °C it is too high for Germany with its cold winters.

As shown in the upper part of *Table 3*, we tried to influence the CFPP by admixing methanol which up to 30% by mass does not impair in-engine use but on the contrary has a favourable influence on soot and nitrogen oxide emissions but would, on the other hand, require an adjustment of the injection amount due to the calorific value; however, as can be seen, our efforts have not been successful. With the help of an additive which was provided to us for testing purposes and was already dissolved in rapeseed oil ester so that the amount of active substance added could certainly be reduced by another 90%, it is possible to exert considerable influence on the CFPP which is important for winter operation and on the already sufficiently low pour point. As a result, values can be achieved we can normally live with in moderate climatic regions. CFPP values of -18 °C and less are reached with the ROME qualities currently sold in Germany. If these values are not sufficient because the ambient temperatures are too low, diesel fuel would have to be used instead of rapeseed oil ester during the cold months, which is yet another reason why it should be possible to alternately use vegetable oil fuel and diesel fuel in existing engines.

As a summary it can be said that the fuel-relevant properties of vegetable oil methyl esters should allow use in an unmodified diesel engine; actually, this was mainly the result of engine testing which will be outlined in the following.

ENGINE INVESTIGATIONS

Engine tests of alternative fuels in the commercial vehicle division usually comprise the phases;

- single-cylinder engine tests,
- multi-cylinder engine tests and
- vehicle field tests.

The choice of engines to be tested is, among other factors, geared towards the expected size of the vehicle fleet.

Several types of engines were included in the investigations into rapeseed oil methyl ester; I would like to limit my remarks to one engine which is widely used by our customers who are interested in rapeseed oil fuel and who have this engine installed for example in MB-tracs and Unimogs, the OM 314 A. The palm oil ester tests were mainly conducted with the OM 352 engine which is widely used in Malaysia. The characteristic data of these two engines are as follows:

		OM314A	**OM352**
Number of cylinders		4	6
Bore	(mm)	97	97
Stroke	(mm)	128	128
Swept volume	(ml)	3784	5675
Rated output	(KW)	63	96
Rated speed	(rpm)	2400	2800
Compression ratio		17:1	17:1
Air intake		Turbocharged Engine	Natural aspirated Engine

The rapeseed oil methyl ester was supplied by Henkel, Düsseldorf, with the tradenames "Edenor MESU" and "-Edenor MESU DS" respectively, DS meaning diesel substitute. The product contained less than 0.2% by weight of free fatty acids and a maximum of 0.1% by weight of glycerides; all metals - to the extent they could be determined at all - were all below 1 ppm by weight. Some of the palm oil ester was supplied by Henkel, too, the other part had been imported from Malaysia. The content of free fatty acids in the imported product was between 0.17 and 0.21% by weight, the content of glycerides was between 1 and 2.5% by weight; this became noticeable in continuous

TABLE 3. COLD FLOW PROPERTIES OF RAPESEED OIL METHYL ESTER

Rapeseed oil methyl ester ROME [% by mass]	Methanol [% by mass]	Cold filter plugging point (CFPP) [°C]
100	0	-7
90	10	-8
80	20	-8
70	30	-6 / -7

Rapeseed oil methyl ester ROME [% by mass]	Additive [% by mass]	Cloud Point (CP) [°C]	Pour point [°C]	Cold filter plugging point (CFPP) [°C]
100	0	-3	-16	-7
99.5	0.5	-10	-39	-9
99	1	-10	-40	-14
98	2	-11	-40	-18

TABLE 4. FEW IMPORTANT RESULTS OF LONG-TERM ENGINE TEST ON VEGETABLE OIL ESTERS

- Lubricating oil composition is very important for long-term engine behaviour
- No sludging apparent with suitable lubricating oil
- Oil dilution within relatively tight limits; no serious effects on relevant lubricating oil characteristics
- Inlet valves show a slight tendeny to coke when the content of glycerides in the ester is too high
- The cylinder gap has a slight tendeny to burn
- The fuel injection system can remain unchanged; no nozzle coking if adequate fuel quality is applied; too high glyceride content causes nozzle coking
- Some elastomeric materials (e.g. some fuel lines) are not sufficiently resistent to vegetable oil esters; these materials have to be exchanged!
- The unusual exhaust gas smelling ("French fries") is troublesome; an oxidation catalyst significantly diminishes the respective inconvinience

operation in the form of slight coking I will speak about later. No significant amount of metals or catalyst residues was found in this ester either.

SINGLE-CYLINDER ENGINE TESTS

The single-cylinder engines were single-cylinder versions of the multi-cylinder engines mentioned above; output, specific fuel consumption and pollutant emissions were the main variables measured. Investigations of the combustion process and injection rate did not reveal any essential differences as compared to the use of diesel which might indicate subsequent operating problems, nor was any need established to modify the engine or its setting. It will therefore suffice to outline the essential results of these single-cylinder investigations; the results of both rapeseed oil ester and palm oil ester have been deliberately plotted in the same figures, mainly to show the far-ranging similarity of the in-engine behaviour of these two fuels (and thus of the larger number of other vegetable oil methyl esters). In all cases, the results are referred to the corresponding values of operation with conventional diesel fuel to allow joint presentation of the two different engines.

Figure 3 shows the maximum attainable engine output for rapeseed oil ester which in the figures is abbreviated by "ROME" and symbolised by black dots, and the value for palm oil ester, abbreviated by "POME" and shown in the form of empty symbols, plotted against the engine speed. You can see that in both cases the attainable engine output is below that for diesel engine operation which is set 100% and shown here and in the following illustrations as a highlighted bar. The lower engine output can be easily explained by the fact the volumetric net calorific value of the two fuels is approx. 8% lower which means that per working cycle approx. 8% less energy can be released with the same injection amount as for diesel fuel. Seen from this angle, the measured values are higher than expected, which means the efficiency is a little bit higher with vegetable oil ester combustion.

This is confirmed by *Figure 4* which shows the specific fuel consumption, that is to say the fuel consumption reflecting the energy consumption taking the different calorific values into account; it should remain the same with unchanged engine efficiency but it improves by 1-2% when you have a look at the focus of the measurements. The measurements which are shown here for the two fuels are usually taken at rated speed (2400 rpm for the OM 314 A and 2800 rpm for the OM 352), at the engine speed with maximum torque and during idling, and the values are plotted against brake mean effective pressure. At rated speed (the two rhombs in *Figure 4*) and thus at rated output and usually at medium speed, the specific consumption figures are always a little better than for diesel fuel.

The smoke number shown in *Figure 5* depicts a very satisfying situation for the two alternative fuels: for rapeseed oil ester it is always lower than for diesel fuel operation, usually by approx. 60%; the same holds true for palm oil ester with the exception of one outlier value of 150% and with higher overall fluctuations.

Figure 6 shows the NOx emissions and constitutes the bitter point for emission characteristics because the nitrogen oxide emissions with rapeseed oil ester operation are generally higher than with diesel fuel, and NOx emissions are also the same or higher with palm oil ester. As we will see later when we have a look at the 13-mode test results, the higher NOx emissions might be compensated for by retarding the start of delivery by 2 degrees crank angle; this would always be a reasonable thing to do if the engine can be operated for a major period of time with vegetable oil esters only.

The carbon monoxide emission plotted in *Figure 7* looks more dramatic than it actually is: it tends to be lower with palm oil ester anyway, and with rapeseed oil ester it is higher than for diesel fuel in some map points but this is of no importance in view of the absolute emissions of a diesel engine.

Emissions of unburnt hydrocarbons as shown in *Figure 8* are very satisfying: throughout, they are much lower than with diesel fuel operation, on average by a dramatic 50% apart from the two outliers plotted for palm oil ester.

Figure 9 shows the 13-mode test results of the two alternative fuels as compared to diesel fuel operation. The 13-mode test in accordance with ECE R49 is an emission limit which is binding for the EU and tries to combine in the best possible way a commercial vehicle load/engine speed spectrum which is typical of European conditions. The upper part of the graphical illustration shows various values for palm oil ester fuels: in the middle, the values for pure palm oil ester operation are plotted for standard start of delivery, to the left a 50/50 mixture of pure palm oil ester and conventional diesel fuel which was tested because the use of such a fuel is deemed likely in Malaysia; in this case the start of delivery was retarded by 2 degrees crank angle to reduce the Nox emissions as I explained before. As you can see this retarded start of delivery reduces NOx by approx. 15% but there is no deterioration of fuel economy which is usually the consequence in diesel fuel operation nor is there a change in hydrocarbon emisssion, and the carbon monoxide and soot emissions decrease, too.

TABLE 5. GERMAN BIODIESEL STANDARD DIN V 516606

Properties	Units	Testing procedure	Limits min.	Limits max.
Density at 15 °C	g/ml	ISO 3675	0.875	0.900
Kinematic Viscosity at 40 °C	mm²/s	ISO 3104	3.5	5.0
Flash Point (Pensky-Martens)	°C	ISO 2719	100	
CFPP	°C	DIN EN 116		
April 15 - September 30.				0
October 01. - November 15.				-10
November 16.- February 28.				-20
March 01. - April 14.				-10
Sulphur Content	% by mass	ISO 4260		0.01
Carbon Residue (10% distillation)	% by mass	ISO 10370		0.30
Cetane Number		ISO 5165	49	
Ash	% by mass	ISO 6245		0.01
Water	mg/kg	ASTM D 1744		300
Total dirt	mg/kg	DIN 51419		20
Copper Corrosion (3 h at 50 °C)		ISO 2160		1
Neutralization Number	mg KOH/g	DIN 51558 Part 1		0.5
Methanol	% by mass	to be agreed		0.3
Monoglycerides	% by mass	to be agreed		0.8
Diglycerides				0.1
Triglycerides				0.1
Free Glycerol				0.02
Total Glycerol				0.25
Iodine Number	g Iodine/100 g	DIN 53241 Part 1		115
Phosphorous	mg/kg	to be agreed		10

TABLE 6. ADVANTAGES IN USING VEGETABLE OIL ESTERS AS ALTERNATIVE FUELS

- The conventional DI commercial vehicle CI engine can be used in almost unmodified form; no investments and/or operational disadvantages to the user
- Vegetable oil esters can be used in pure form or mixed with conventional diesel fuel
- Vegetable oil esters are non-toxic, easy and safe to handle, biologically degradable (water conservation areas)
- The energetic fuel consumption is at least as good as for diesel fuel
- The power output is almost unchanged; the lower maximum power output caused by the smaller volumetric heating value is unnoticeable in the most cases
- The maximum torque curve is practically the same as with diesel fuel, i.e. the drive train can remain unchanged
- No evaporation of low-boiling fuel components
- The exhaust gas is practically free from sulfur dioxide, lead, halogens
- The exhaust gas is much better than that at diesel fuel operation with respect to soot, unburned hydrocarbons, and CO (after oxidation catalyst); the Nox emission rises slightly with unchanged engine setting
- The good auto-ignition quality of the esters means smooth engine running
- Vegetable oil esters are based on renewable raw meterials and so there use constitutes a step in the rigth direction with reference to the greenhouse effect
- Energy farming could contribute to the reduction of agricultural surpluses and to the creation and/or preservation of agricultural jobs

TABLE 7. MB SERVBICE INFORMATION REGARDING THE USE OF ROME IN COMMERCIAL VEHICLES

- **Mercedes-Benz trucks produced since 1988 with series 300 and 400 engines (DI CI) can be fuelled with ROME.**
- **The leak fuel lines of the injection nozzles on series 400 engines have to be replaced by an ROME-resistant version and connected to the fuel feed line.**
- **If ROME is used in older vehicles, there is a risk that hoses and seals impaired by many years' contact with diesel fuel will be attacked by ROME and thus become leaky.**
- **Mercedes-Benz does not provide warranty coverage for damage caused by using ROME of inferior quality or by non-observance of the instructions for ROME operation.**
- **The lubricating oil change intervals should be halved since oil dilution is likely to occur.**
- **For specific vehicle models and application profiles, disagreeable odour emission can be reduced by installing an oxidation catalyst.**
- **ROME is a very effective solvent. Therefore contact with paint should be avoided. We bear no liability for paint damage which has been caused by contact with ROME.**

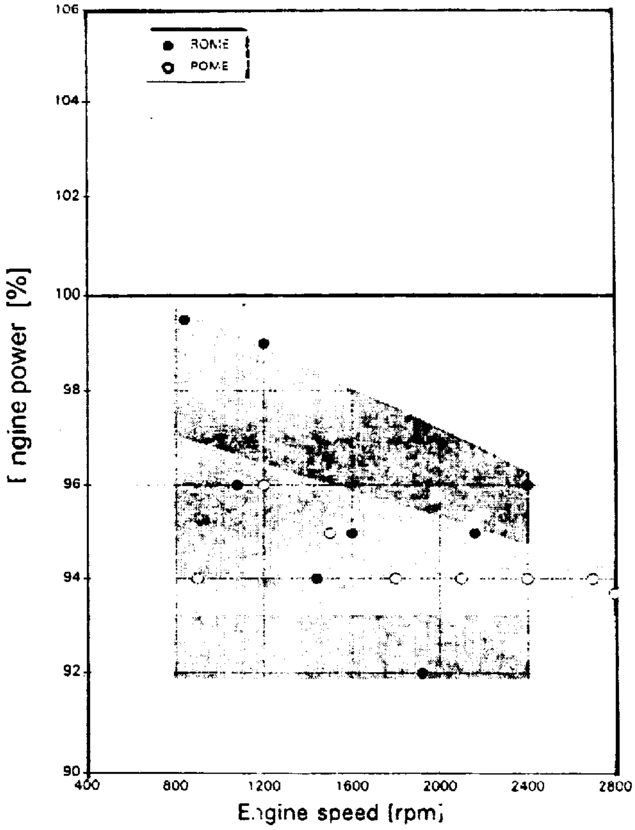


Figure 3. Engine Power at Vegetable Oil Ester Operation Related to the of DF Operation

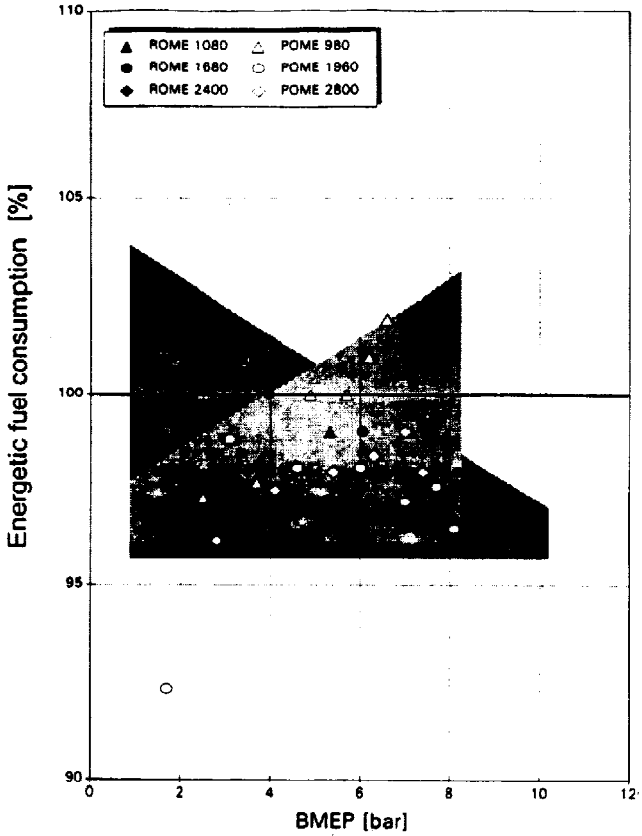


Figure 4. Energetic Fuel Consumption at Vegetable Oil Ester Operation Related to the of DF Operation

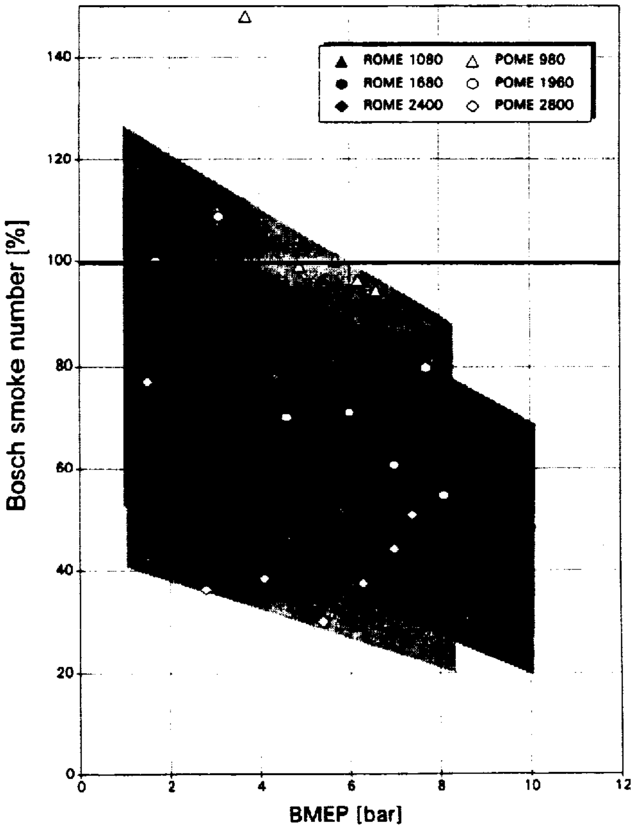


Figure 5. Bosch Smoke Number at Vegetable Oil Ester Operation Related to the at DF Operation

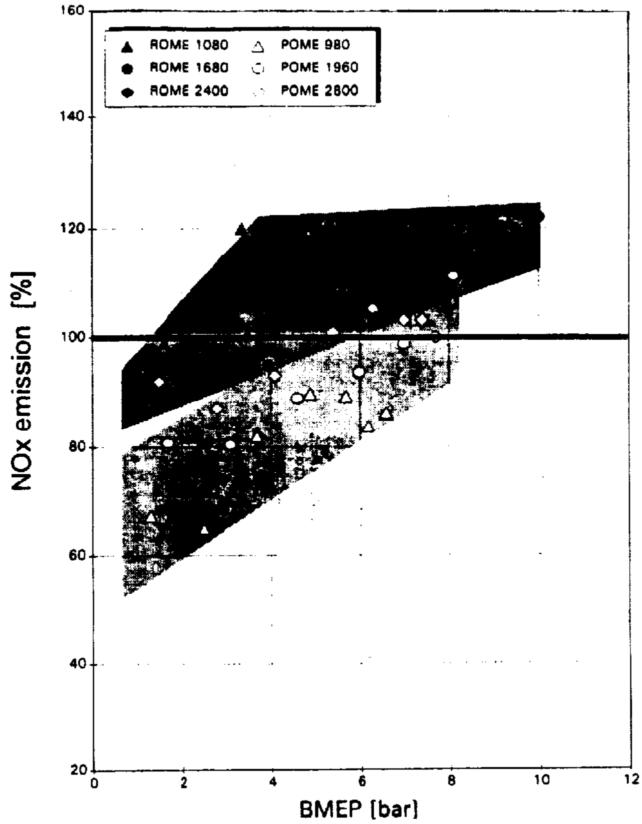


Figure 6. NOx Emission at Vegetable Oil Ester Operation Related to that at DF Operation

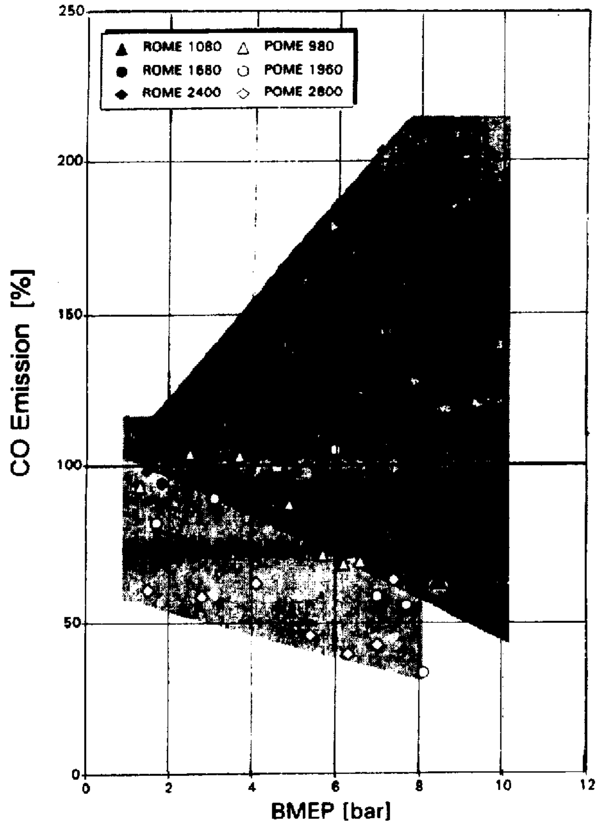


Figure 7. CO Emission at Vegetable Oil Ester Operation Related to that at DF Operation

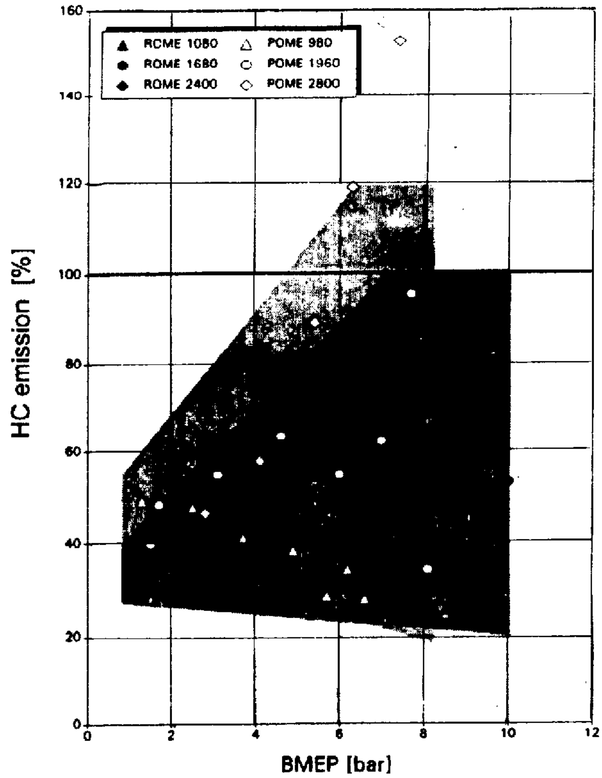


Figure 8. HC Emission at Vegetable Oil Ester Operation Related to that at DF Operation

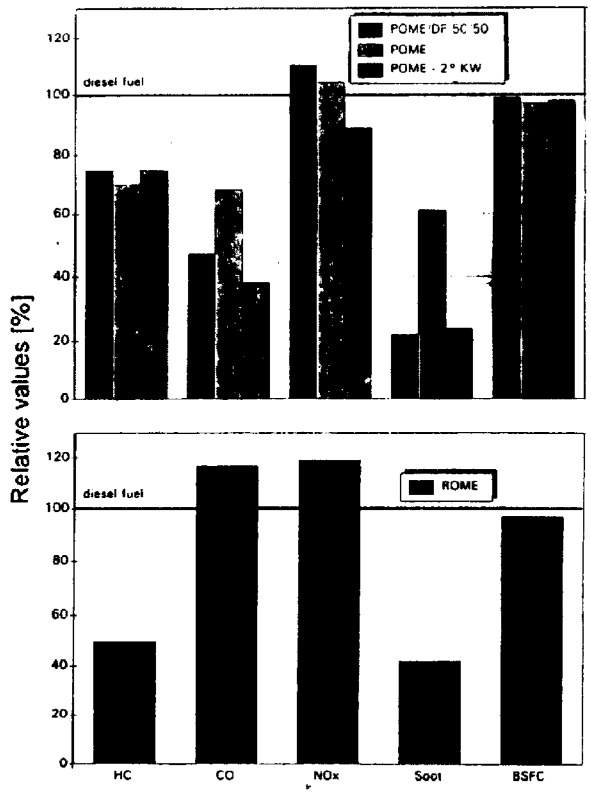


Figure 9. 13 - Mode Test Emissions at Vegetable Oil Ester Operation Related to those at DF Operation

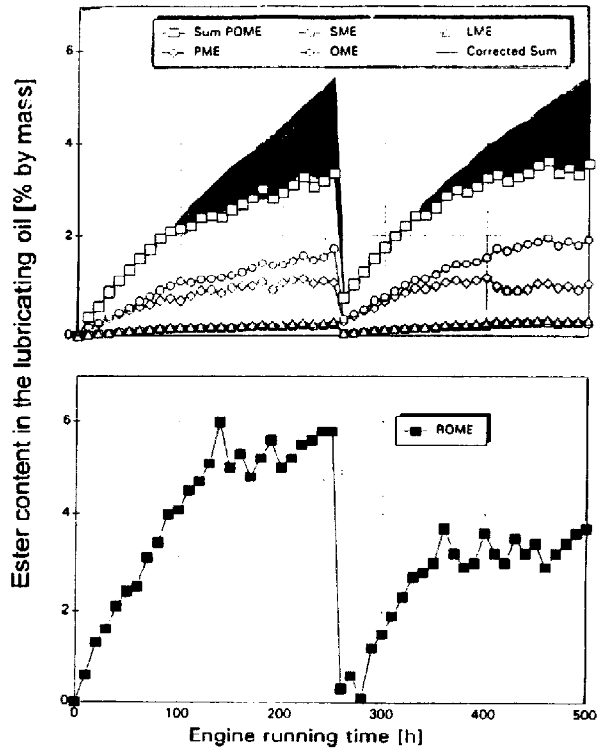


Figure 10. Ester Content in Lubricating Oil Versus Engine Running Time

The situation for rapeseed oil ester is shown in the lower part; it is similar to that of palm oil ester (central bar in the upper diagram): here, we have an increase in NOx emissions by approx. 20% with unchanged start of delivery, slightly increased CO emissions in contrary to palm oil ester which are, however, without significance due to the small amount of CO emissions of diesel engines as compared to those of petrol engines; the specific consumption is at least as good as that of diesel engines but has clearcut advantages as compared to the latter in terms of unburnt hydrocarbon emissions and soot emissions which decrease by almost 60%.

MULTI-CYLINDER ENGINE TESTS

Multi-cylinder engine tests serve the purpose of confirming the data determined with single-cylinder tests and investigating the behaviour in continuous operation.

The engines were unmodified standard production engines, and the standard start of delivery and full-load quantity limits were maintained.

No dramatic difficulties were expected from the investigation into the long-term behaviour of commercial vehicle diesel engines with regard to wear, the formation of deposits and coking etc. because of the relatively large similarity between the two vegetable oil esters and diesel fuel. On the other hand, special attention had to be paid to the lubricating oil behaviour because in the operation of any engine unburnt fuel constituents or the products of their incomplete combustion enter the lubricating oil along the piston rings and dilute it. This lubricating oil dilution is negligible in the case of conventional diesel fuel combustion whose molecules are mainly pure hydrocarbons without reactive functional groups since the highly volatile fuel components are discharged via the crankcase ventilation and the less volatile components are very similar to the base stock of the lubricating oil. If the molecules of vegetable oil esters cause lubricating oil dilution these substances remain to a large extent in the lubricating oil because they are not very volatile; here, because of the permanently high temperatures in the oil, they enter into chemical combinations with each other by means of their functional groups; this holds especially true for polymerisation of unsaturated ester molecules via their C=C double bonds to polymolecular products which after an initial decrease in viscosity (dilution) can lead to a renewed increase in viscosity (polymer products) and to sludging of the oil chamber.

250-hour bench endurance tests were performed to investigate the lubricating oil behaviour. *Figure 10* outlines the tests.

- The first run with rapeseed oil ester (lower part of *Figure 10*) was a special in-house alternating-load programme, the second run involved a new engine in a programme whose load and engine speed points reflect the typical application of an MB-trac. Mobil Delvac 1300 single-grade oil with SAE 30 viscosity grade was used for both runs.

- Many runs were conducted for palm oil ester with different lubricating oils. The upper part of *Figure 10* only shows a 250-hour endurance test with Shell Rimula X, SAE 30 and its immediate reproduction after oil change at 250 hours; practically, this is a 500-hour test. These runs, too, followed our in-house alternating-load programme which we always carry out for such tests.

Every 10 hours, a lubricating oil sample was taken to determine, among other variables,

- the ester content
- viscosity at 40 °C
- the alkali reserve ("total base number", TBN)
- the pH value and
- in some cases also the distribution of the various fatty acid radicals which is also shown for palm oil ester in the upper part of *Figure 10*.

The endurance runs were usually conducted without major problems providing the usual values on fuel and lubricating oil consumption; interim results were to prevent the (unlikely) event of engine damage, and at the end of the tests the engines were completely disassembled and inspected without determining severe damages or complaints (with one exception though: one special Malaysian lubricating oil proved to be so incompatible with the palm oil fuel that severe wear occurred; this oil was excluded from further examinations).

Figures 10 to *12* summarise the main results of the lubricating oil investigations.

Figure 10 shows the ester content over the operating time. You can see in the lower part of the illustration that lubricating oil dilution through rapeseed oil ester continuously increases up to values between 4 and 6% by mass during the 250 hours representing an ordinary oil change interval. The upper part of the figure shows a somewhat more detailed analysis for the palm oil product: the values of the individual fatty accid methyl esters (SME=stearic acid methyl ester, LME=linoleic acid methyl ester, PME=palmitic acid methyl ester and OME=oleic acid methyl ester) indicate that in this only slightly unsaturated product the distribution is roughly the same as in the fuel itself and that there is no major change in the distribution during the long-term thermal load up to the end of the endurance test. This finding constitutes a certain contrast to our experience with soya bean fatty acid methyl ester whose high degree of unsaturation becomes obvious over a major period of thermal load in the lubricating oil: here, oligomerisation of at least the esters of the poly-unsaturated fatty acids (linoleic acid and linolenic acid) to products with higher molecular masses occurs which means that these esters disappear from the ester/lubricating oil mixture. With palm oil ester, reproduction of the first 250 hours leads to a similar pattern, namely an ester content of roughly 3% by mass in the lubricating oil in both runs. The hatched area in both palm oil ester runs is the difference between the measured ester content (large squares) and the theoretical dilution which would result from the measured values and the measured lubricating oil consumption if the esters contained in the lubricating oil were not used up at the same time as the oil: as you can see, dilution of the lubricating oil through the ester fuel would theoretically increase linear to the operating time.

The alkali reserve plotted in *Figure 11* (TBN="total base number") is a measure of the ability of the lubricating oil to neutralise acid combustion products, thus preventing possible corrosion. It is measured in mg KOH per gramme of oil and is to provide information on the still sufficient detergent effect and on corrosion protection. As you can see, only a negligible amount of less than three units are degraded with both fuels during the course of one oil change interval which can be mainly explained by the fuels being free of sulphur and thus free of acid sulphur dioxide.

The change in viscosity during the operating time is always of special interest with regard to lubricating oil (*Figure 12*): as you can see, the lubricating oil viscosity of the two rapeseed oil endurance runs determined at 40°C continuously decreases during the first 100 to 150 hours to then increase again considerably. This is quite an astonishing effect in view of the further increasing ester content and the much lower viscosity of this ester. As shown by an analysis of the distribution of fatty acid radicals during the operating time, this effect can probably not be explained by a polymerisation of the double bonds because here the polyunsaturated molecules do not disappear. It might be explained by another chemical reaction which exerts considerable influence on viscosity. As can be seen from the upper part of the figure, this reaction should not occur at all or only to a small extent when using palm oil ester because here we have a practically monotonous decrease in viscosity which can be reproduced and which is confirmed by additional measurements at 100 °C. It must therefore be assumed that the degree of unsaturation which is more than twice as high for the rapeseed oil product than for the palm oil product does play a dominating role: perhaps polymerisation of the double bonds does not take place to such an extent that this would become manifest in a changed fatty acid distribution but the reaction products do increase the mixture's viscosity considerably.

The following is a summary of the results of the endurance tests of vegetable oil esters (*Table 4*) with the results surely being applicable to both vegetable oil esters in a similar way:

- The composition of the lubricating oil was shown to be of major importance for the long-term behaviour; obviously a lubricating oil which behaves inconspicuously in diesel fuel operation may well lead to major complaints (wear) in vegetable oil ester operation.
- No sludging occurs with suitable lubricating oils.
- Oil dilution remained within a relatively small band and had no major influence on relevant lubricating oil data (*e.g.* viscosity, TBN).
- The inlet valves displayed a slight tendency to coke which is probably due to the glyceride content which in some cases was 2.5 times higher than the rapeseed oil ester values. Unreacted triglycerides alone accounted for far more than 1% by weight which is a content of non-transesterified vegetable oil which may already impair continuous operation.
- The cylinder gap displays a slight tendency to burn; a remedy may be the compression rings made of different materials which are installed in more modern engines anyway.
- The injection system can be left unchanged; no unusual coking occur on the injection nozzles as long as a sufficiently high fuel quality is used with a low glyceride content in particular. A content of 2% by mass of glyceride which was occasionally observed does lead to considerable coking of the nozzles.

VEHICLE TESTS

Since the characteristics of alternative fuels proved to be favourable in standard production engines, both single-cylinder and multi-cylinder versions, it seemed sensible to conduct vehicle tests which in the final analysis are decisive for a system's practical feasibility.

Numerous ROME field tests were conducted in Germany, for example:

- An MB-trac 900 fitted with an OM 314 A engine was operated from October 1987 until the beginning of

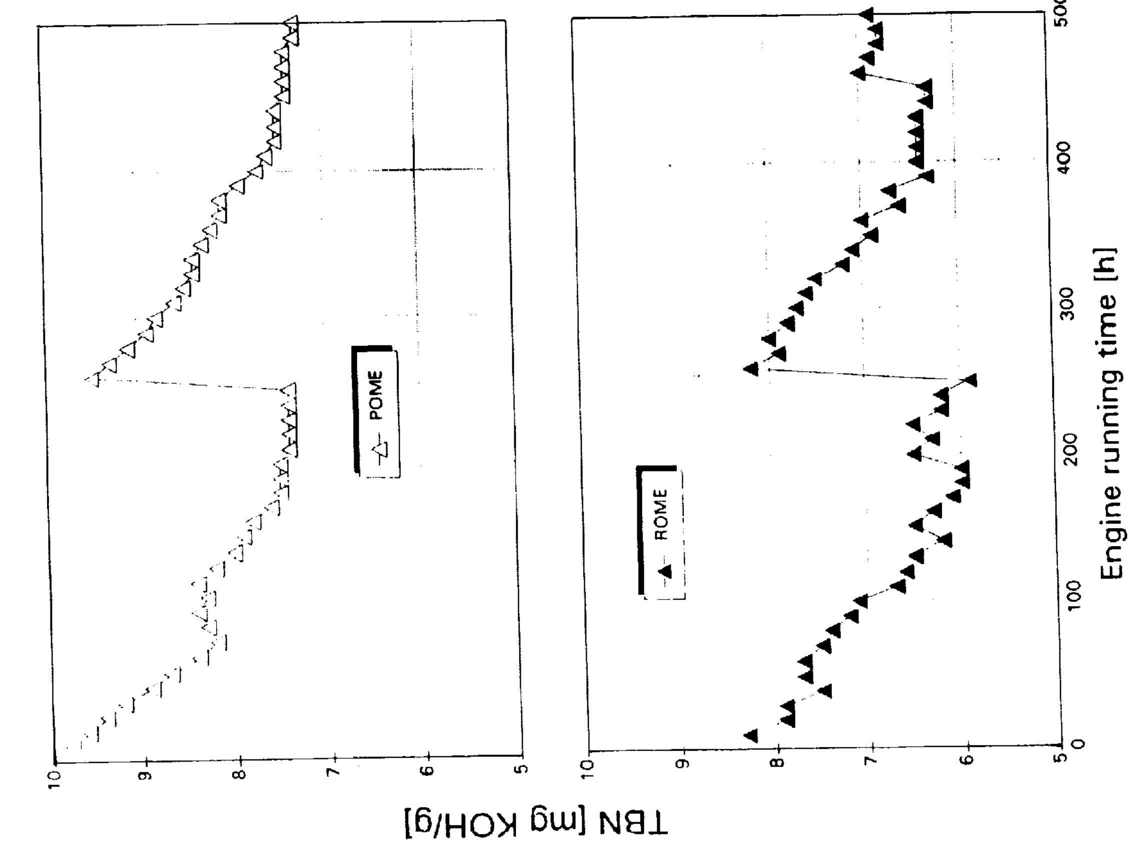


Figure 11. Total Base Number (TBN) of the Lubricating Oil Versus Engine Running Time

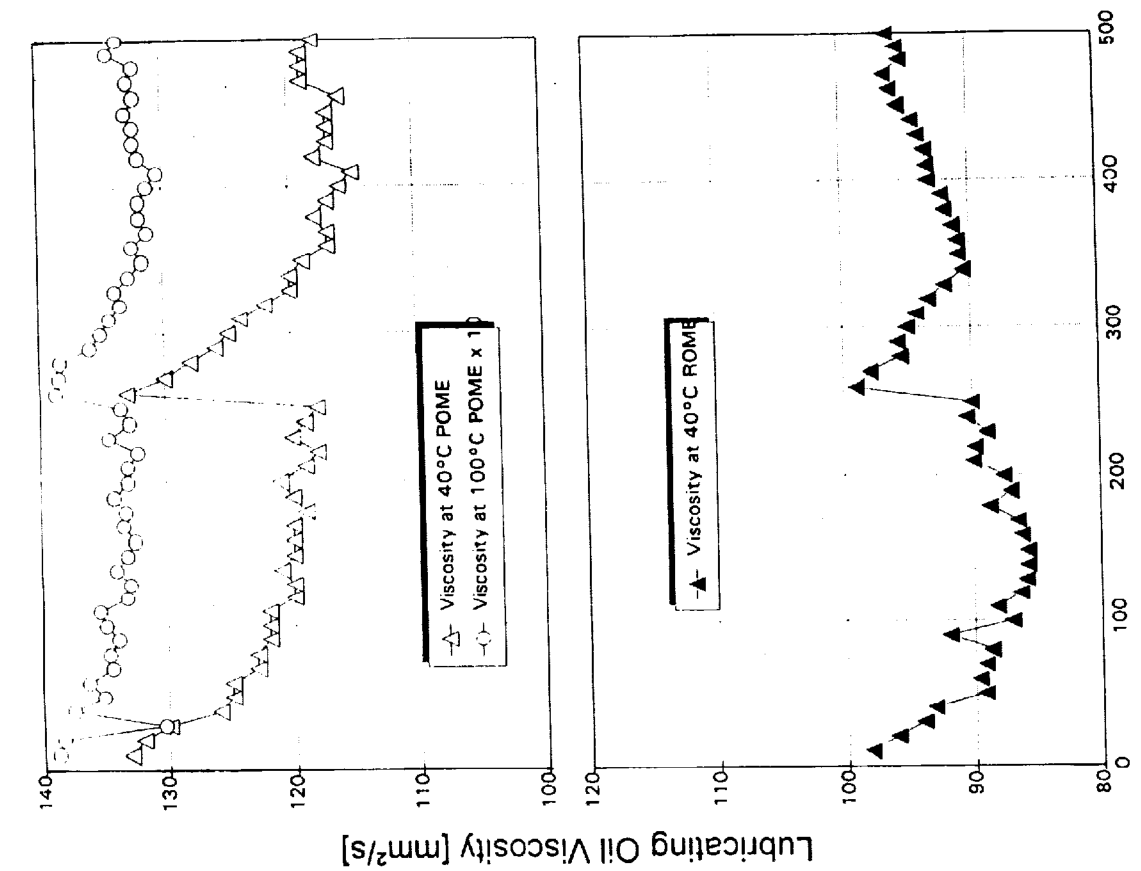


Figure 12. Lubricating Oil Vis-Cosity Versus Engine Running Time

1991 at the Agricultural Academy of Upper Franconia in Bayreuth. The vehicle was used to do all the necessary agricultural jobs and was run for more than 2500 operating hours without problem. Lubricating oil samples (Mobil Delvac 1300 with the adequate viscosity for the time of year) were taken every 20 hours during the entire operating time and analysed with regard to the ester content and viscosity; as in the bench tests, the ester did not change over the operating time; for safety reasons the lubricating oil interval was reduced from 250 to 1-00 hours. The results allow the conclusion to be drawn that such a large reduction in the lubricating oil change interval is not required; however, no sufficient data to answer this question is available yet.

- A fleet test with numerous city buses, trucks and taxis from January 1991 to October 1992 in Fulda.

The results obtained in these fleet tests are encouraging: specific fuel consumption and lubricating oil consumption do not differ from the values obtained during diesel fuel operation, the drivers were very satisfied with the vehicle behaviour, the slightly lower rated output due to the calorific value and the increased volumetric fuel consumption only rarely led to complaints.

However, a number of more or less serious problems was determined requiring a solution, for example:

- The unpleasant odours of the exhaust gas (smelling like French fries)
- The most essential problem since it concerns safety: the insufficient stability of the elastomer materials which are used as standard for fuel hoses, seals etc.
- The auxiliary heaters installed in the vehicle which must also be operated with rapeseed oil ester usually do not work without problem *etc.*

A few words on the unpleasant odours emitted during ROME combustion:
Since it is a well-known fact that an oxidation catalyst can reduce the emission of unburnt hydrocarbons and the odorous constituents of the exhaust gas almost exclusively comprise the elements C, H and O, it offered itself to try and reduce the unpleasant "French fries" smell with the help of such a catalyst. Smell being a very subjective sensation, it is not possible to measure it on the engine test bench but what is possible is to measure the effect an oxidation catalyst has on emissions. *Figure 13* shows the effect of a downstream oxidation catalyst on the 13-mode test emissions of conventional diesel fuel on the one hand and on ROME exhaust gas on the other hand. The figure shows the limited gaseous CO, HC and NOx and soot emissions (not particulates though because PM measurements require tremendous effort and are negligible to preassess the odour-reducing effect of the catalyst). Operation without oxidation catalyst and with conventional diesel fuel was taken as reference. With CO it becomes evident that the oxidation catalyst brings about the same reduction for both exhaust gases as was to be expected. With HC, however, there is a clearly better effect achieved for ROME exhaust gas (approx. 60% of the HC substances are oxidised) than for diesel fuel exhaust gas which probably has to do with the structure of the organic substances. As expected, the oxidation catalyst does not influence NOx emissions but it was shown that another engine (in this case a turbocharged Mercedes-Benz OM 366 A without intercooler) did not feature the NOx disadvantage of ROME of 5-20% which is so often found so that the general statement claiming that "use of ROME in a direct-injection engine without changing the engine's setting will increase NOx emissions" rather describes a trend. The black smoke emission (soot) did not change either, as was also expected, following the installation of a downstream oxidation catalyst. Bench testing gave rise to the expectation that the application of oxidation catalysts would clearly reduce the odorous emissions of ROME vehicles as had been observed before on diesel cars with exhaust gas recirculation and oxidation catalyst. However, the issue can only be resolved through field tests and (subjective) reactions of people coming into contact with ROME vehicles. During the fleet tests, we fitted a total of 7 buses at 4 sites with oxidation catalysts. The feedback was unanimously positive, quite obviously the smell of French fries during operation is "completely" eliminated. This does not - and cannot - apply to the cold start and warming up phase during which the oxidation catalyst has not yet reached the temperature level required for conversion.

The second point on the above list of problems refers to the stability of certain elastomers in contact with vegetable oil esters. Until the use of ROME in city buses, our long years of experience with ROME and other esters had not provided us with any indication at all that the stability of elastomers used in vehicles might turn out to be a problem. Only the use of ROME in buses with obviously much higher engine compartment temperatures led to a combination of thermal load and solvent attack which destroyed some materials, especially fuel hoses made of nitrile rubber. Extensive laboratory investigations which I can only briefly touch upon in this context have revealed that nitrile rubbers actually are much less resistant to ROME attacks than fluorinated rubbers. *Figure 14* shows the changes in elongation at tear and tensile strength of nitrile rubber (NBR) which is normally used to produce bus fuel hoses as compared to two different fluorinated rubbers (FPM1 is a terpolymer, FPM2 a copolymer) after 1000 hours' storage in ROME at 100 °C. *Figure 15* shows a similar comparison for the

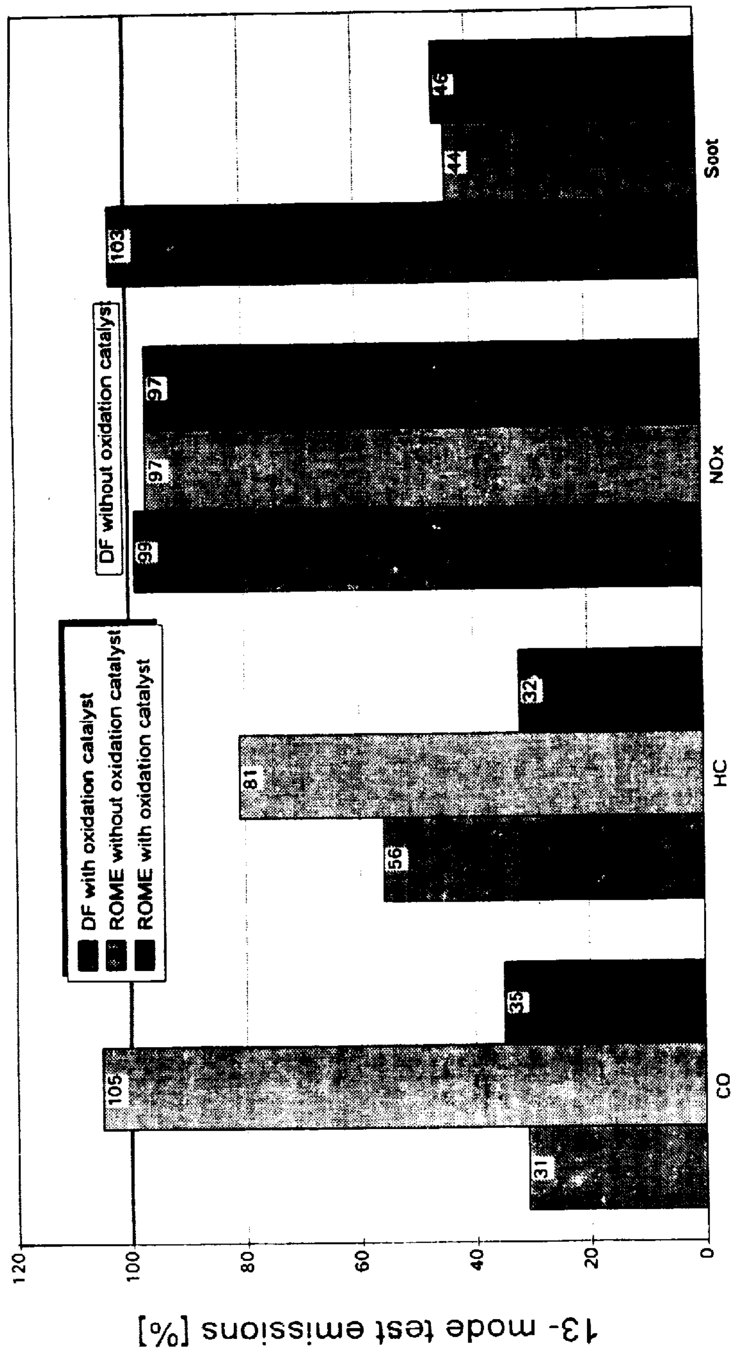


Figure 13. 13-Mode Test Emissions According to ECE R 49 at ROME Operation Related to those at DF Operation

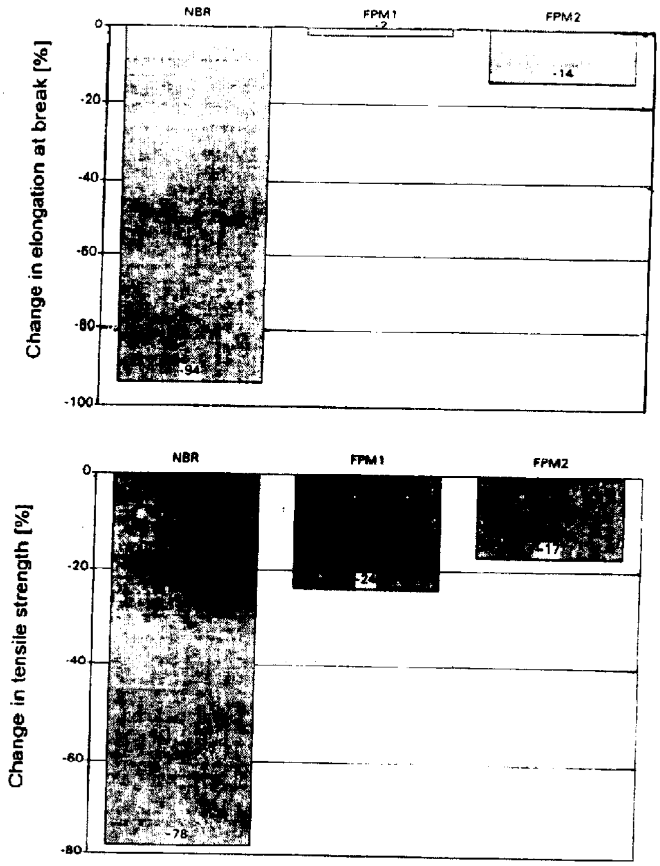


Figure 14. Mechanical Properties Retention of Elastomers After 1000 hours ROME Exposure at 100°C

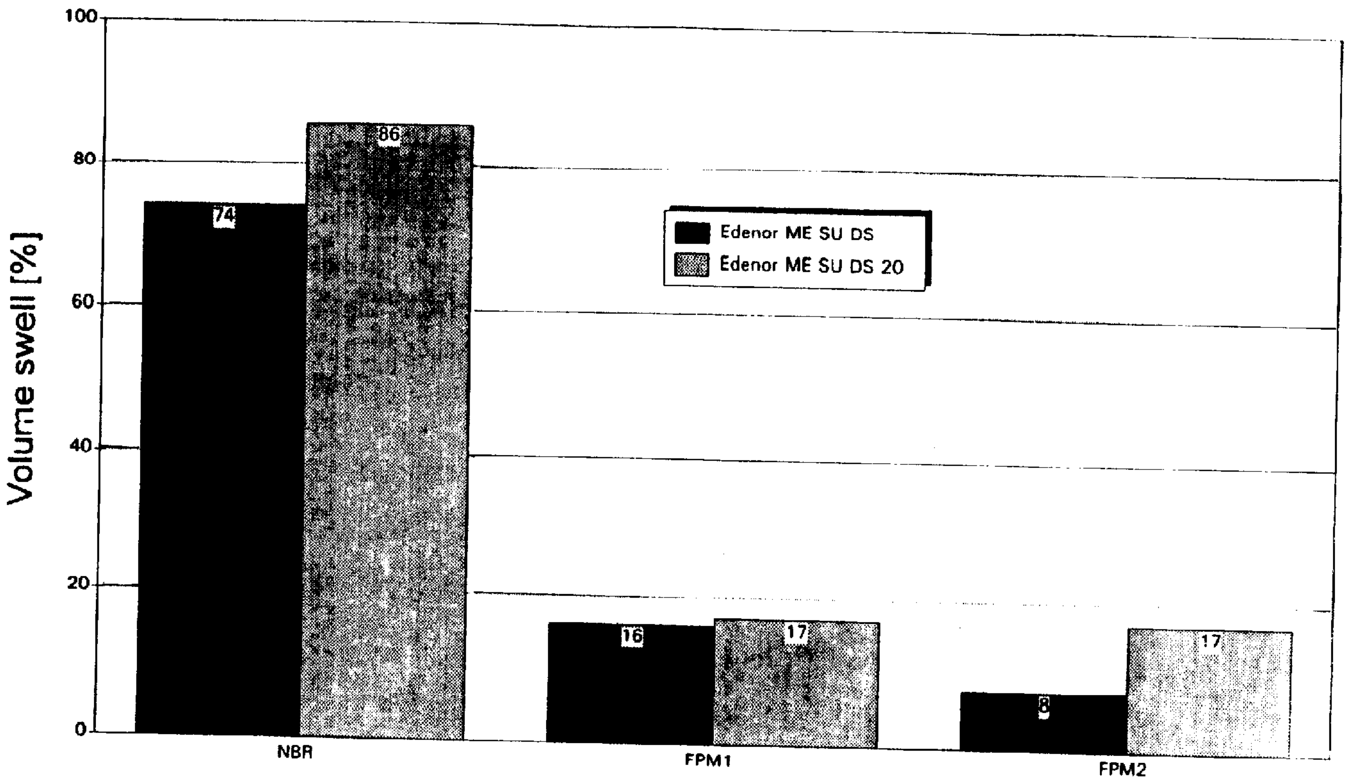


Figure 15. Volume Swell of Elastomers after 1000 hours ROME Exposure at 100°C

swelling behaviour; in this context, the influence of shorter-chain methyl esters was investigated which are included to the amount of 20% in the "Edenor ME SU DS 20" product from Henkel, Düsseldorf, in order to ensure a sufficiently low CFPP for winter operation. Both figures show that fluorinated rubber elastomers are much more suited to ROME operation with a clear leading edge for the ROME "summer grade", that is "Edenor ME SU DS". For safety reasons, the fuel hoses in all buses concerned must be replaced by hoses with an FPM interior lining.

For field testing of palm oil ester, we are currently performing a fleet test with 30 buses here in Malaysia in close co-operation with the "Palm Oil Research Institute of Malaysia (PORIM)" which began at the end of 1991. For reference purposes, 10 buses are operated with conventional diesel fuel, 10 are operated with pure palm oil ester and 10 with a 50/50 mixture of these two fuels. A test period of two to a maximum of three years was aimed at; each bus is to cover approx. 300,000 km during this period. Oil samples are taken from each bus every 2500 km and analysed (a total of approx. 3600 samples). The test has almost come to an end, we expect it to be concluded by the middle of 1995. This means we are not yet able to present final results and test details. They will be published in due time in agreement with our co-operation partners PORIM and Cycle&Carriage Bintang Berhad.

ASSESSMENT

When trying to assess the practical feasibility of vegetable oil esters as alternative fuels, the problems mentioned several time before must of course be taken up again for which a solution must be found and implemented. These problems are in particular;

- the insufficient resistance of standard elastomer materials,
- the lubricating oil behaviour (type of lubricating oil, oil change intervals *etc.*),
- the exhaust gas odours,
- the slight increase in NOx with unchanged engine setting and
- the fuel quality. Especially as regards the last point, we think that the vegetable oil ester quality must be specified at a high level; in this respect, the DIN V 51606 standard has become applicable in Germany (*Table 5*).

Despite the problems and questions mentioned above, the overall scenario is very positive so allow me to conclude with a list included in *Table 6* of the advantages of using vegetable oil esters (at least ROME, the POME testing is not yet finished and assessed) as alternative diesel engine fuels. This list also includes some remarks which are self-explanatory and which have not been dealt with before:

- The conventional direct-injection commercial vehicle diesel engine can be used without essential modifications, this means no investment must be made nor must the operator accept operational disadvantages
- Vegetable oil esters are non-toxic and can be handled by anybody without special safety measures, there is no danger of explosive air/fuel mixtures forming, and they are fully biodegradable (ground water preservation areas).
- Consumption is at least as good as for diesel fuel in terms of energy, and volumetric consumption is even some percentage points better.
- Performance is almost unchanged; with the same injection amount, the marginally lower output due to the calorific value is in most cases negligible.
- There is no evaporation of fuel components with low boiling point.
- No additional measures on the vehicle to warm up or liquefy the fuel are required.
- The exhaust gas is practically free of sulphure dioxide, lead, halogens.
- The exhaust gas is much better than with diesel fuel operation in terms of soot and unburnt hydrocarbon emissions and hardly differs in terms of CO emissions. The NOx emissions increase slightly with unchanged engine setting which can be easily compensated for without disadvantage by somewhat retarding the start of delivery when frequently using vegetable oil esters.
- The good ignition quality of vegetable oil esters provides for smooth running characteristics of the engine.
- Vegetable oil esters are successive products of vegetable oils and thus biofuels. As far as the greenhouse effect is concerned (increase of carbon dioxides in the atmosphere caused by burning fossil resources), their use therefore constitutes a step in the right direction.
- Since vegetable oil esters are based on agriculturally produced resources, their use as fuels might make a contribution to using up excess crops and to creating and maintaining jobs in agriculture.

Since vegetable oil ester systems will surely increase in importance in future and promise success technology-wise, Mercedes-Benz AG has decided on the basis of its experience with ROME (no other vegetable oil ester so far) to approve this alternative fuel under certain conditions for commercial vehicles; the relevant conditions have been listed in a Service Information

Bulletin which has been sent to all Mercedes-Benz dealers, branches, workshops and so on and which is also available in English. In conclusion, I would like to summarise some major points of this Service Information Bulletin (*Table 7*):

- Mercedes-Benz commercial vehicles of the LK/MK/SK ranges and Unimogs as of the year of construction 1988 fitted with series 300 and 400 engines can be operated with ROME.
- Commercial vehicles with series 600 engines cannot be operated with ROME.
- The leak fuel lines of the injection nozzles on series 400 engines must be replaced by an ROME-resistant version and connected to the fuel feed line.
- If ROME is used on older vehicles there is a danger of hoses and seals which have aged through long years' contact with diesel fuel being attacked by ROME and becoming leaky.
- The fuel must comply with DIN V 51606.
- No warranty if ROME of a lower quality is used or if our regulations for ROME operation are not complied with.
- Operation with a lower-quality fuel can lead to malfunctions and engine damage. Mixed-fuel operation with ROME and diesel fuel has not been approved.
- The oil change intervals must be halved because oil dilution must be expected.
- The typical smell of ROME exhaust gas ("French fries") is occasionally felt to be a nuisance, especially during long idling periods or operation at low loads. Fitting an oxidation catalyst can reduce the unpleasant odours for certain vehicle models and applications.
- ROME is a very efficient solvent, therefore contact with the paintwork must be avoided. No warranty for paint damage caused by ROME.

The evaluation of the vehicle tests which will come to an end during the next few months and which involved co-operation between Mercedes-Benz AG, the Palm Oil Research Institute of Malaysia and Cycle & Carriage Bintang Berhad, the Mercedes-Benz distributor here in Malaysia will show if and to what extent approval can be granted for this ester; results available to date have been very promising.