IEA
Advanced Motor Fuels Agreement

Annex XVI

Biodegradable Lubricants - Phase 2

Gasoline Type Vehicles

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IEA
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MEK-ET-2004-02
ISBN 87-7475-317-7 **September 2004**

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Abstract

The IEA Advanced Motor Fuels Agreement has initiated this project concerning the application of biodegradable lubricants in diesel and gasoline type vehicles. The member countries: Denmark, Finland, Italy, Japan, Sweden and USA have supported the project financially.

Emission measurements on a chassis dynamometer were carried out. The purpose of these measurements was to compare the emissions of CO, CO_2, NOx, THC, PM, lubricant-SOF and PAH from one diesel and one gasoline type vehicle using biodegradable lubricants and conventional lubricants. This report describes the results of the experiments with the gasoline type vehicles only. In another report [2] the results of the experiments on diesel type vehicles are described. Lubricant consumption and fuel consumption are other important parameters that have been evaluated during the experiments.

Both vehicle types were operated on conventional crude oil based fuels and alternative fuels. The diesel vehicles were operated on conventional diesel fuel from a Danish fuel station and biodiesel, which was bought at a fuel station in Germany. The gasoline vehicles were really FFV's (Flexible Fuel Vehicle), which were operated on gasoline and ethanol respectively.

The driving patterns that were applied in these experiments were the FTP and EU test cycles.

Since the biodegradability of lubricants changes with age, it was necessary to measure this change by driving the vehicles for a number of kilometers in order to obtain a full picture of the environmental impact of implementing biodegradable lubricants. Therefore lubricant samples were taken from the engine crankcase after driving 7500 km on the road. These samples were analyzed in order to evaluate biodegradability of the used lubricant and engine wear.

1. Introduction.

Recently there has been increased interest in extending the use of biodegradable vegetable oils in lubricants, driven mostly by environmental as well as health and safety issues, and also arising from changes in economic and supply factors. There is a plentiful supply of vegetable oils in many parts of the world where mineral oils are expensive and in short supply. Biodegradable synthetic esters are used to a wide extent in outboard two-stroke engines, and also for other more specialized engines.

Biodegradable oils are desirable from many environmentally beneficial aspects, being advantageous from the viewpoint of oil spill or illegal waste and improved working environment in workshops.

Lubricants cause parts of the emissions from vehicle engines. From the viewpoint of emissions, biodegradable lubricants are expected to behave differently from conventional lubricants, particularly with respect to SOF emissions (Soluble Organic Fraction of particulate emissions). Vegetable oils do not contain polycyclic aromatic hydrocarbons, which pose a great risk to human health. Vegetable oils are also low in potential pollutants like sulfur containing compounds. Sulfur containing compounds are in many cases environmentally undesired, and may also cause technical problems in connection with catalytic converters.

Since the application of biodegradable lubricants is rapidly growing, several member countries of the IEA Advanced Motor Fuels Agreement (Denmark, Finland, The Netherlands, Sweden and USA) found it appropriate to be equal to the recent development, also foreseeing an extension of the use of biodegradable lubricants to more conventional automotive applications. It was therefore decided to open an annex that looked into the recent lubricant technology, and evaluated the possible future market in the light of advantages and drawbacks of biodegradable lubricants. The result of this investigation was published in 1999 [1].

The investigation revealed that there was a demand for experimental data concerning the behavior of biodegradable lubricants in automotive applications. It was therefore decided to carry out phase 2 of the annex. The purpose of this project was to investigate experimentally the technical and environmental aspects of the application of biodegradable lubricants. The countries: Denmark, Finland, Italy, Japan, Sweden and USA decided to sponsor the project. The results of phase 2 are reported in this document and in another document [2]. This report describes the results of the experiments with gasoline type vehicles. In [2] the results of the experiments on diesel type vehicles are described.

The project was carried out at The Technical University of Denmark, who is also the operating agent for the project. For more information the following address can be used:

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2. Biodegradable Lubricants Testing – Overview of the Investigation.

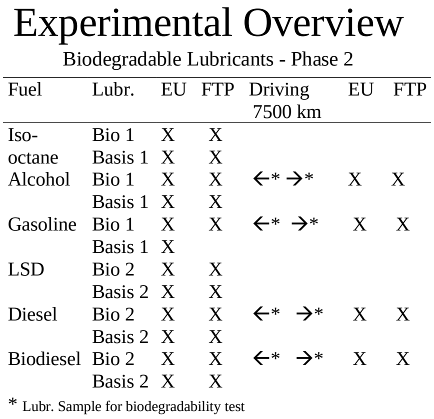
Emission measurements on a chassis dynamometer were carried out. The purpose of these measurements was to compare the emissions of CO, CO_2, NOx, THC, PM, lubricant-SOF and PAH (Polycyclic Aromatic Hydrocarbons) from one diesel and one gasoline vehicle using biodegradable lubricants and conventional lubricants. Lubricant consumption and fuel consumption are other important parameters that have been evaluated during the experiments.

The vehicles were operated on conventional crude oil based fuels and alternative fuels. The diesel vehicle was operated on conventional diesel fuel from a Danish fuel station and biodiesel, which was bought on a fuel station in Germany. The gasoline vehicles were really FFV’s (Flexible Fuel Vehicle), which were operated on gasoline and ethanol.

The driving patterns that were applied in these experiments were the FTP and EU test cycles.

Since the biodegradability of lubricants changes with age, it was necessary to measure this change by driving the vehicles for a number of kilometers in order to obtain a full picture of the environmental impact of implementing biodegradable lubricants. Therefore lubricant samples were taken from the engine crankcase after driving 7500 km on the road.

In the figure below the test matrix is shown:



Experimental Overview

Biodegradable Lubricants - Phase 2

Fuel	Lubr.	EU	FTP	Driving 7500 km	EU	FTP
Iso-octane	Bio 1	X	X			
	Basis 1	X	X			
Alcohol	Bio 1	X	X	←* →*	X	X
	Basis 1	X	X			
Gasoline	Bio 1	X	X	←* →*	X	X
	Basis 1	X				
LSD	Bio 2	X	X			
	Basis 2	X	X			
Diesel	Bio 2	X	X	←* →*	X	X
	Basis 2	X	X			
Biodiesel	Bio 2	X	X	←* →*	X	X
	Basis 2	X	X			

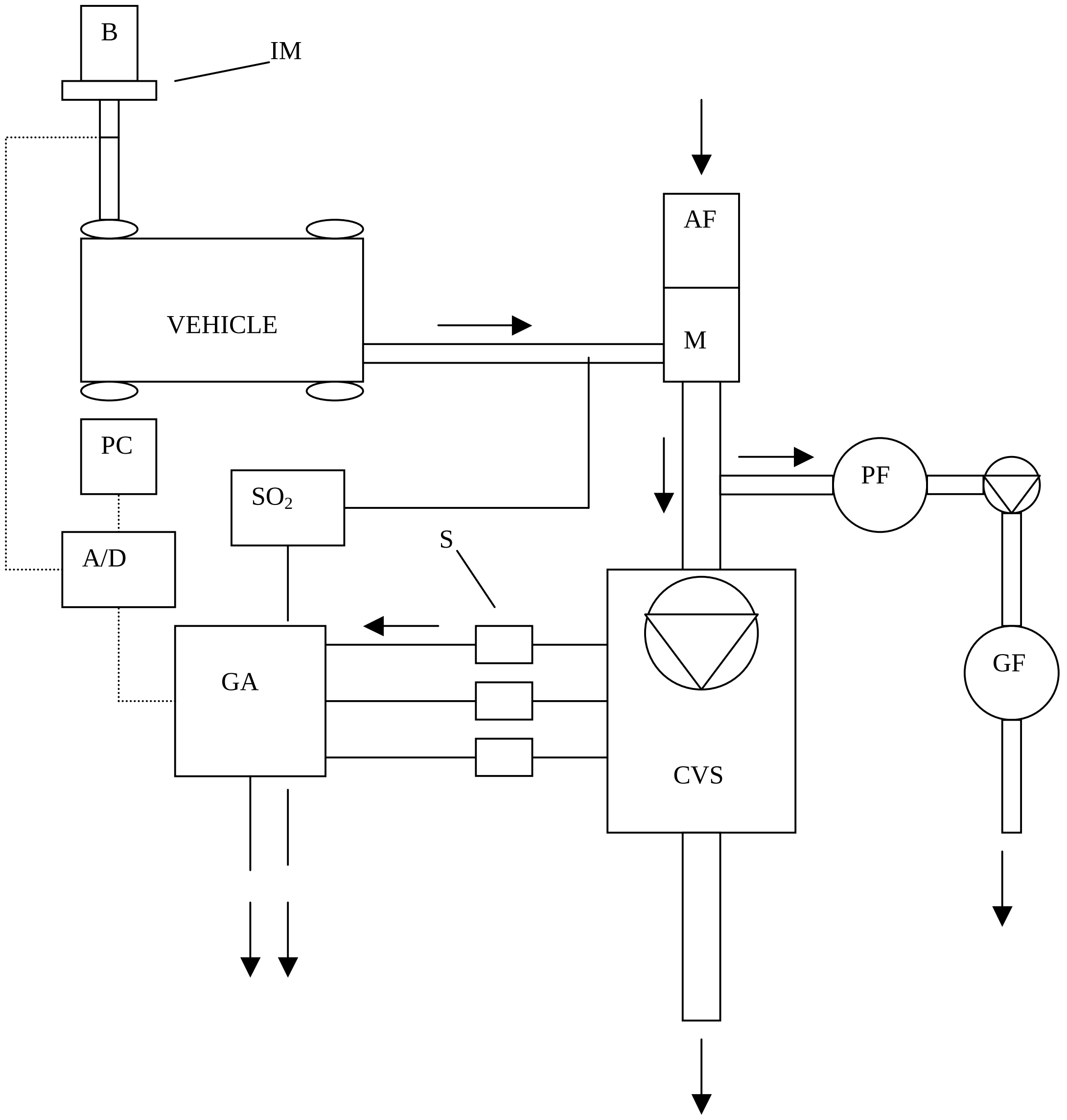
* Lubr. Sample for biodegradability test

For each fuel/lubricant combination the FTP and EU cycle test were carried out. In every case 2 measurements were carried out. Gaseous emissions were measured, and PM samples were taken for SOF analysis and PAH analysis. In order to measure lubricant-SOF emissions, additional tests were carried out on Swedish low sulfur diesel (LSD) and isooctane. A new diesel vehicle was used for testing on LSD, normal diesel and biodiesel, and two new FFV vehicles were borrowed from Sweden to be tested on isooctane, gasoline and alcohol. After the first two FTP and EU tests the vehicles operating on biodegradable lubricants were run for 7500 kilometers on the roads in order to age the lubricant. Before carrying out the FTP and EU tests again, samples of the lubricants were taken in order to measure the biodegradability and wear parameters of the aged lubricants.

3. Test Procedure.

A schematic picture of the experimental procedure is shown below:

(the following abbreviation applies: B: brake, IM: Inertial Mass, AF: Air Filter, M: exhaust/air Mixer, PF: Particulate sampling Filter, PC: Personal Computer for data collection, A/D: A/D converter, S: Sample bags, GF: Gas Flow meter, CVS: Constant Volume Sampler, GA: Gas Analyzers)



The vehicle is placed on a chassis dynamometer. The chassis dynamometer allows one to simulate real driving conditions in a controlled environment. The chassis dynamometer consists of two rollers driven by the wheels of the vehicle and connected to inertia plates and to a power brake. The car is placed with its driving wheels on the rollers while the other two wheels are anchored to the basement of the dynamometer with adjustable chains. The rotating resistance of the rollers simulates friction losses and aerodynamic resistance. Inertial mass has to be added to simulate the weight of the vehicle. The power absorbed by the rollers can be adjusted by regulating the power brake. The power absorbed by the brake was estimated by calculation of the deceleration time of the rollers. A speed sensor was installed giving an analog signal proportional to the speed of the rollers; the signal was converted from analog to digital. The final output is the instantaneous value of the car's velocity in km/h.

The absorbed power is adjusted at 80 km/h as specified in the FTP test procedure, which says that the power should be calculated according to the formula:

$$P = aA + P + tW$$

where:

P_a = the power in kW
a = 4,01
A = the front area of the car
P = a correction factor for projecting parts
t = 0 for vehicles with radial tires and 4,93 x 10^{-4} for other types
W = the reference weight of the vehicle in kg

A short flexible metal hose was attached to the tail pipe of the car and connected to a rigid transfer pipe whose function is to collect the exhaust gases from the diesel car and direct them into the Constant Volume Sampler. The transfer pipe is thermally insulated to minimize the risk of condensation of the water present in the exhaust gas.

In simulating driving conditions on the dynamometer, the volume of the gas emitted from the exhaust pipe of the car is continuously changing with the speed of the engine and of the load. To determine the amount of the emissions a Constant Volume Sampling method was used. The exhaust gas is diluted with a source of filtrated ambient air. The flow is regulated with a constant volume pump. With this system, an increase in exhaust flow means a decrease in the dilution air feed. The dilution ratio can be estimated, knowing the concentration of carbon dioxide before entering and after the tunnel by using the following equation:

$$DR = \frac{CO_{2,exhaust} - CO_{2,air}}{CO_{2,dilutedexhaust} - CO_{2,air}}$$

Where $CO_{2,exhaust}$ is the concentration of CO_2 in the raw exhaust, $CO_{2,air}$ is the concentration of CO_2 in the dilution air and $CO_{2,diluted\ exhaust}$ is the concentration of CO_2 in the diluted exhaust. A constant volume rate of the diluted exhaust gas can be taken and collected in sample bags. The sample bag allows one to collect the gas during different conditions and analyze it later in order to have a mean value of the pollutant concentrations. The bags are always used while running the standard driving patterns. A sufficient ratio of dilution avoids condensation of water that may cause several problems since some compounds can interact with water. Moreover, dilution air inhibits the tendency of exhaust components to react with one another, especially hydrocarbons. With this system ambient air is filtrated before diluting the exhaust. Air flows through a particle filter, an activate carbon filter and a micron filter (d<2μm): this allows one to keep the concentration of hydrocarbons under an acceptable level. A heat exchanger is placed before the pump.

The driving patterns were implemented in a program called OPTIMA 2000. This software was installed in a PC that was placed near the driving position: the driver had the keyboard inside the vehicle and was able to follow the driving patterns looking at the monitor of the PC.

4. Measurements of Gaseous Emissions.

Gases sampled through the heated line were analyzed with a CUSSON P7450 Exhaust Gas Analysis System. The system includes the following instruments:

O_2 Analyzer: Oxygen concentration is measured with a paramagnetic ADC WA 363 analyzer

CO Analyzer: The instrument used to analyze the Carbon monoxide concentration is an ADC Nondispersive Infrared analyzer.

CO_2 Analyzer: Carbon dioxide concentration is measured with a non-dispersive infrared ADC analyzer

Total Hydrocarbon Analyzer: The instrument used to measure the unburned hydrocarbons present in the exhaust is 'Signal' Model 3000 Heated Flame Ionization Detector.

NO/NOx Analyzer: Nitrogen Oxides are measured by a 'Signal' Model 4000 Heated Chemiluminescent Analyzer

Before entering the O_2,CO, CO_2 analyzers, the sample gas is cooled in a refrigerated water bath dryer to remove excess water vapor. An extra connection to the SO_2 Analyzer was made for the experiments from the output of this cold system.

The mass, M_i, of a polluting component, i, in kg/test is determined according to US FTP as:

$$M_i = V_{mix} \cdot \rho_i \cdot k_H \cdot C_i \cdot 10^{-6}$$

where:

V_{mix} = volume of diluted exhaust in norm-m^3/test
ρ_i = the density of component i, expressed as kg/norm-m^3
k_H = NOx correction factor for humidity
C_i = concentration of component i in the diluted exhaust, corrected for the background concentration, expressed in ppm

If the mass is to be expressed in g/km, the above expression has to be divided by the length of the driving pattern in km.

The concentration of component i in the diluted exhaust is calculated according to:

$$Ci = Ce - Cd\,(1 - \frac{1}{DR})$$

where:

C_e = concentration of component i in the diluted exhaust, expressed in ppm
C_d = concentration of component i in the dilution air, expressed in ppm
DR = the dilution ratio

The dilution ratio is estimated according to a standard formula:

$$DR = \frac{13{,}4}{C_{CO2} + C_{THC} + C_{CO}}$$

where:

C_{CO2} = concentration of CO_2 in the diluted exhaust (%)
C_{THC} = concentration of THC in the diluted exhaust (%)
C_{CO} = concentration of CO in the diluted exhaust (%)

This equation is only valid at near stoichiometric combustion, which is not correct for a diesel engine. However, in our case the correction due to background concentration in the dilution air is negligible.

The NOx humidity correction factor was calculated according to:

$$kH = \frac{1}{1 - 0{,}329 \cdot (H - 10{,}71)}$$

where:

$$H = \frac{6{,}211 \cdot R_a \cdot P_d}{P_B - P_d \cdot R_a \cdot 10^{-2}}$$

where:

H = the absolute humidity, expressed as g water per kg dry air
R_a = relative humidity, expressed at atmospheric pressure in %
P_d = the saturation pressure of water at surrounding air temperature, expressed in kPa
P_B = surrounding pressure in kPa

5. PM/SOF and PAH Measurements.

Special filters were used to collect the Particulate Matter. A separate pump carries a constant volume stream of diluted exhaust from the dilution tunnel before the CVS pump through a filter house where the filter is placed. The filter was a circular quartz fiber filter of the type Palflex TXW40HI20WW with a diameter of 293 mm. The filter was conditioned at 50% relative humidity and 20^{o}C before measuring the mass. After sampling the filters were conditioned again at the same condition and weighed in order to estimate the mass of the emitted PM.

The soluble organic fraction (SOF) was obtained by Soxhlet extraction of the filter using dichloromethane as the extracting solvent. After the filters were extracted for 4h, the extracts were concentrated using rotary evaporation with reduced pressure at 45 °C. The mass of the SOF was determined gravimetrically from the concentrated extract.

The SOF was then used to evaluate the lubricant contribution to the emission of particulate matter and to determine the levels of certain PAH compounds.

PM consist of two major groups of material:

1) insoluble material, often just called soot, which mainly consist of solid carbon, water and sulfurous compounds

and

2) soluble material, which is soluble in an organic solvent, and most often just referred to as SOF (Soluble Organic Fraction).

The latter group consists of a wide number of organic compounds, which will have to be separated into individual compounds for identification and quantification. First the group is divided into a certain number of subgroups with similar chemical structure. The number of physical/chemical procedures needed for the grouping of SOF depends on the number of components. One of the groups is the PAH (Poly Aromatic Hydrocarbons) group, which are organic compounds containing several aromatic ring structures. The individual groups are finally separated into individual compounds, in our case by HPLC (High Performance Liquid Chromatography).

The organic compounds of the particulate matter were as earlier mentioned collected in Soxhlet apparatus. The extracted material was divided into 3 fractions by open column chromatography on silica gel. The eluent volumes were:

Fraction I:	7,5 ml hexane
Fraction II:	5 ml hexane/dichloromethane (1/1)
Fraction III:	5 ml dichloromethane

The fractions then consist of: I: Non-polar compounds (aliphatics), II: Aromatics, III: Polar components.

The aromatic fraction was analyzed in order to estimate the content of PAH compounds. These compounds were chosen for their presumed health effects and for the fact that they have been widely reported as diesel exhaust components. The individual PAH components were separated and identified (by comparison to known reference standards) using reverse phase HPLC (high performance liquid chromatography) with a fluorescence detector. The HPLC column was 2mm X 250mm long and contained a polymeric C18, 5-micron particle size stationary phase (Vydac 52TP201).

The mobile phases and the time program with respect to mobile phase flow and concentrations are shown in the following table:

Step	Time (min.)	Flow (ml/min.)	% H_2O	% CH_3CN
1	3	0,4	50	50
2	15	0,4	0	100 1)
3	15	0,4	0	100

1) Linear change in concentrations from step 1 to 2

It is essential for the calibration of the PAH measurements that the calibration standard composition reflects the PAH composition in the exhaust as much as possible. This is a difficult task, since there are hundreds of different PAH compounds in the exhaust. The standard that we chose for the calibration in these experiments was the EPA 610 Polynuclear Aromatic Hydrocarbon Mix, which is often used for this kind of analysis. The content of this standard is shown in the following list:

PAH-compound	Concentration (mg/l)
Acenaphthene	1000
Acenaphthylene	2000
Anthracene	100
Benzo [a] anthracene	100
Benzo [a] pyrene	100
Benzo [b] fluoranthene	200
Benzo [ghi] perylene	200
Benzo [k] fluoranthene	100
Chrysene	100
Dibenz [ah] anthracene	200
Fluoranthene	200
Fluorene	200
Indeno [123-cd] pyrene	100
Naphthalene	1000
Phenanthrene	100
Pyrene	100

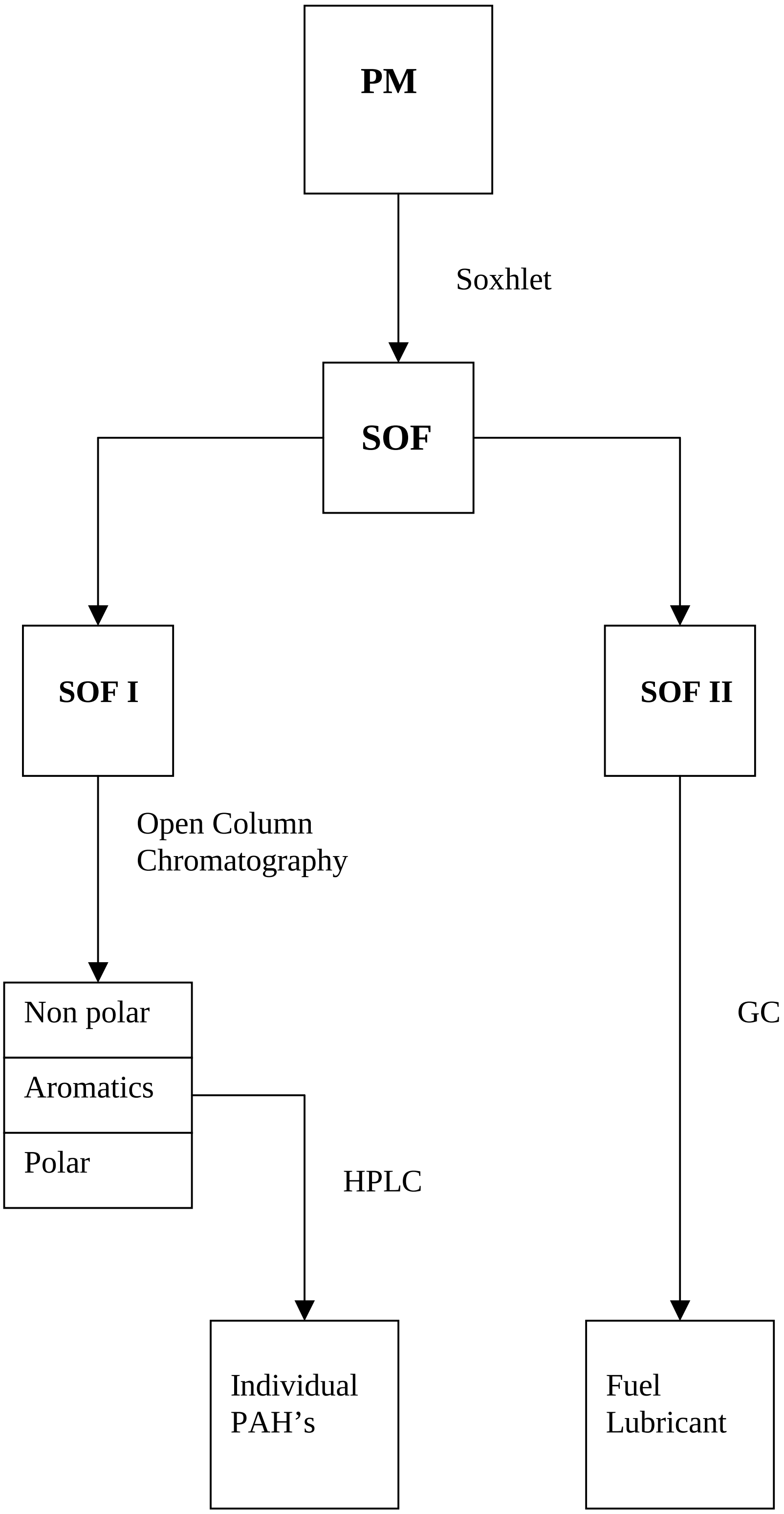
A similar sample of the SOF was used for estimation of lubricant contribution to the particulate matter. In this case the SOF was diluted by dichloromethane and the organic compounds were separated and identified as fuel or lubricant, by comparison to a sample of a mixture of pure fuel and lubricant diluted by dichloromethane, using GC (Gas Chromatography). Capillary columns coated with 100% dimethylpolysiloxane were used. The detector was an FID (Flame Ionization Detector). Helium was used as carrier gas.

The temperature programming are shown in the table below:

Step	Start Time (min.)	End Time (min.)	Start Temp. (^{o}C)	End Temp. (^{o}C)
1	0	3	55	55
2	3	17	55	310 1)
3	17	30	310	310

1) Linear increase in temperature from step 1 to 2.

The total analysis schedule is shown in the figure below:


PM
Soxhlet
SOF
SOF I
SOF II
Open Column Chromatography
Non polar
Aromatics
Polar
HPLC
GC
Individual PAH’s
Fuel Lubricant

6. Lubricant Consumption Measurements.

Drain Weight Method.

Traditionally lubricant consumption is measured by the drain weight method. In this way the amount of lubricant added to the engine of the vehicle is weighted, and after driving a certain distance the engine is drained for lubricant and the drained weight is measured. The difference between the added amount of lubricant and the lubricant that is left over (drained from the engine) is taken as a measure of the consumed lubricant over the driven distance.

This method is only applicable when the vehicle has been driven for a large number of kilometers. Otherwise the method is too uncertain. In our case the measurements could be carried out only in the cases where the vehicles were driven for 7500 km on the roads in connection with the estimation of the biodegradability of the used lubricants (i.e. the biodegradable lubricants only). Therefore we had to adapt another method for comparison between the different lubricants. For this reason we applied the “S-Tracer Method”. However, this method was only applied to the measurements on diesel type vehicles [2].

7. Lubricant Biodegradability Measurements.

Biodegradability tests of the used lubricants in this project were carried out according to the CEC L-33A-93 procedure. This is a method specially developed for measuring biodegradability of lubricants. More information about this method and other methods for biodegradability testing can be obtained from an earlier project report [1].

8. Fuels and Lubricants Applied.

The main purpose of this study was to apply a biodegradable lubricant in a gasoline type vehicle, and investigate the applicability of this, compared to traditional lubricants. Therefore a commonly sold biodegradable lubricant was chosen from the European market. There were only very few products available at the start of this project [2], so the possibilities were very limited. The one chosen was a synthetic based lubricant. The available data on the lubricant are shown in Table 8.1 and denominated “BioLube”.

As a reference we chose a mineral oil based lubricant. This is due to the fact that this type of lubricant represents the traditional type of lubricant and was a very commonly sold lubricant at Danish fuel stations. The available data on this lubricant are shown in Table 8.1 and denominated “Ref.Lube”.

Lubricant		BioLube	Ref.Lube
Base Oil		Synthetic	Mineral Oil
SAE Classification		5W-40	10W-40
Density at 15°C	kg/m^3	925	880
Viscosity at 40°C	mm^2/s	77	99,1
Viscosity at 100°C	mm^2/s	14,0	14,4
Pour Point	°C	-60	-36
Flash Point	°C	205	220
Sulphur	Wt-%	0,39	0,52

Table 8.1. Lubricant data.

Two different fuels were chosen: an ethanol based fuel (E85) and a reference gasoline fuel. The ethanol fuel was chosen because this is an alternative fuel based on biomass. The reference gasoline fuel was the normal gasoline available at Swedish fuel stations at the time. Data for the two different fuels are shown in Table 8.2.

Fuel		Ethanol (E85)	Ref. Gasoline
Density at 15°C	Kg/m^3	780	750
Composition:	(%)		
Ethanol		85	
MTBE		2,1	
"Gasoline"		12,5	100
Boiling Point (final)	°C	210	195
Vapor Pressure	kPa	45-95	45-95
Octane			
Number		98	95
RON		88	85
MON			
Calorific Value	MJ/kg	30,4	44,1
Sulphur	Wt-ppm	<5	<30

Table 8.2. Fuel Data.

9. The Test Vehicles.

The test vehicles were two Ford Focus FFV. Important vehicle/engine data are given in Table 9.1.

Ford Focus FFV	**FFV1**	**FFV2**
Fuel	Ethanol (E85)	Gasoline
Model Year	2002	2002
Emission Class	EURO III	EURO III
Mileage	3000 km (from start)	19000 km (from start)
Engine Size	1596 cc	1596 cc
TWC	Yes	Yes
Maximum Power	74 kW at 6000 rpm	74 kW at 6000 rpm

Table 9.1. Vehicle/Engine Data.

10. Results.

In order to make the report more readable all the figures are shown last in this chapter. All data are presented in tables in appendix 1. In the following presentation the results are shown in figures and tables in order to interpret the result for the reader.

10.1. Lubricant Consumption.

After carrying out EU and FTP emission test on the used biodegradable lubricant the lubricant was drained from the engine. In this way we found that the lubricant consumption had been 76 g pr. 9347 km. The vehicle had been driven on the roads for this distance on ref. gasoline fuel in order to measure biodegradability of used lubricant. This corresponds to an average lubricant consumption of 0,008 g/km. Since the average driving speed was about 40 km/h this corresponds to about 0,32 g/h which is a very low lubricant consumption.

Part of the reason for this low lubricant consumption was that the used lubricant contained some fuel (as the lubricant analysis in Table 10.4 shows). If we correct for this fuel content we find that the lubricant consumption really was 100 g pr. 9347 km, corresponding to a lubricant consumption of 0,011 g/km, or 0,44 g/h.

The measured lubricant consumption was a little lower in the case of driving on ethanol fuel with biodegradable lubricant. Here the lubricant consumption was 35 g pr. 6905 km which corresponds to an average consumption of 0,005 g/km. Assuming again that the average speed was 40 km/h this corresponds to 0,2 g/h.

If we correct for the fuel content of the used lubricant we find that the lubricant consumption really was 55 g pr. 6905 km, corresponding to a lubricant consumption of 0,008 g/km, or 0,32 g/h.

As a conclusion we can say that the lubricant consumption seems to be low when applying the biodegradable lubricant with both fuels. The lubricant consumption for these particular vehicles seems to be much lower than usual. This indicates the need for lubricant consumption measurements on a bigger number of vehicles in order to get a full picture of the lubricant consumption.

10.2. Gaseous Emissions and Energy Consumption.

CO emissions are shown in Figure 10.1.

The vehicles fulfill the requirements of EURO III (2,3 g/km), except for the ethanol vehicle with used biolube. However, the CO emission is close to the limit. Ethanol does, however, generally give a higher CO emission. This is not what is expected with ethanol, but large variations from one vehicle to another is seen in the literature [3]. Probably the engine control is not working ideally. CO emissions are lower with reference lubricant. Explanations for this could be variations in engine load due to a little higher friction with the biolube. Increased lubricant combustion could be another explanation. However, the lubricant consumption does not seem to be very high. Finally variations in measurements from one day to another could count for some variations.

HC emissions are shown in Figure 10.2. In this case the EURO III limit (0,2 g/km) is fulfilled in all situations. There seems to be no significant differences in HC emissions.

NOx emissions are shown in Figure 10.3. In this case the EURO III limit (0,15 g/km) is fulfilled except for the case with gasoline and the FTP test. It seems as if the case with fresh biolube gives lower NOx emissions, compared to the case with used biolube and reference lubricant. This is probably due to an improperly working regulation mechanism in the engine, since measurements indicated changes in emissions measured in autumn 2002 (where the fresh biolube measurements were carried out) to spring 2003 (where the other measurements were carried out). In all cases ethanol gives the lowest emissions compared to gasoline. This is also in agreement with other investigations [3].

CO_2 emissions are shown in Figure 10.4. We notice a small increase in CO_2 (fuel consumption) with biolube, except in the combination "Petrol EU". This would also influence NOx emissions, and we do notice that NOx emissions for the case "Petrol EU" behaves different from the other cases. However, NOx emissions are influenced by other more important factors, as mentioned earlier.

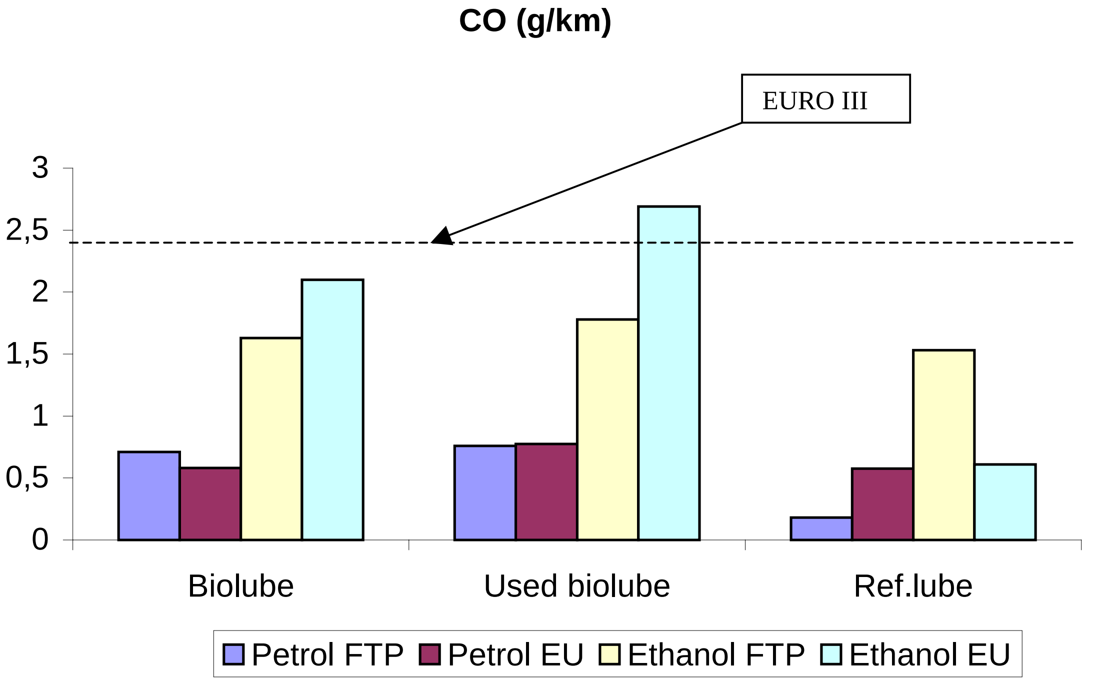


Figure 10.1. CO emissions from the FFV's.

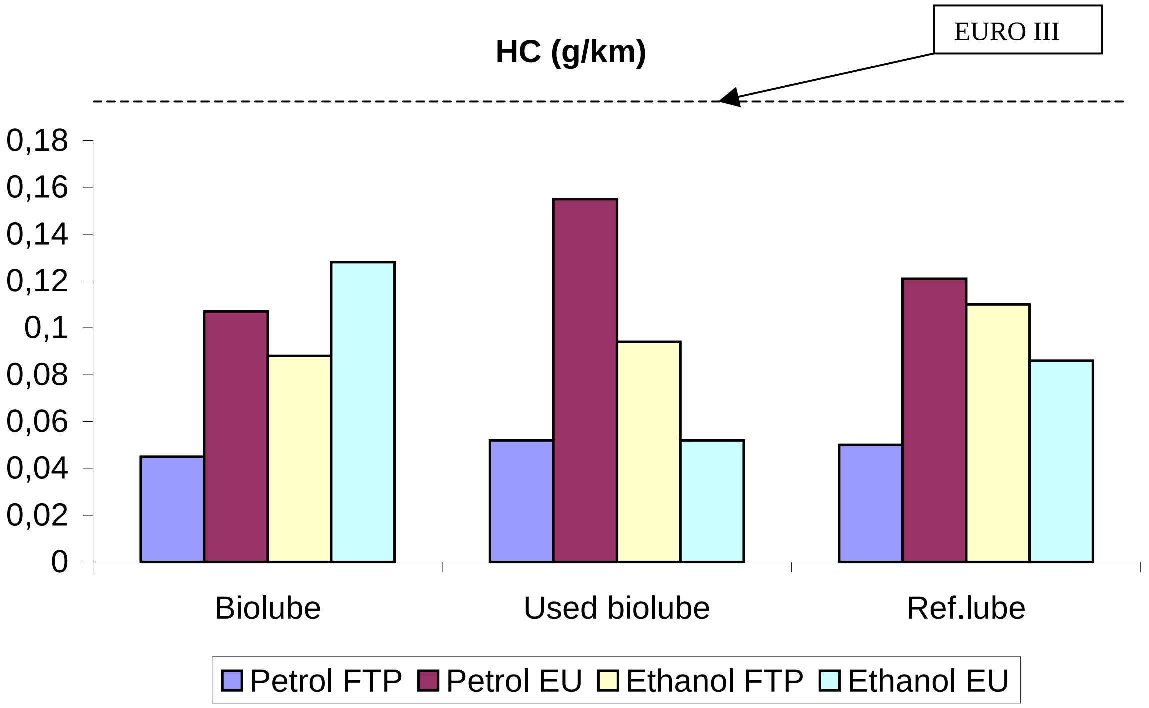


Figure 10.2. HC emissions from the FFV's.

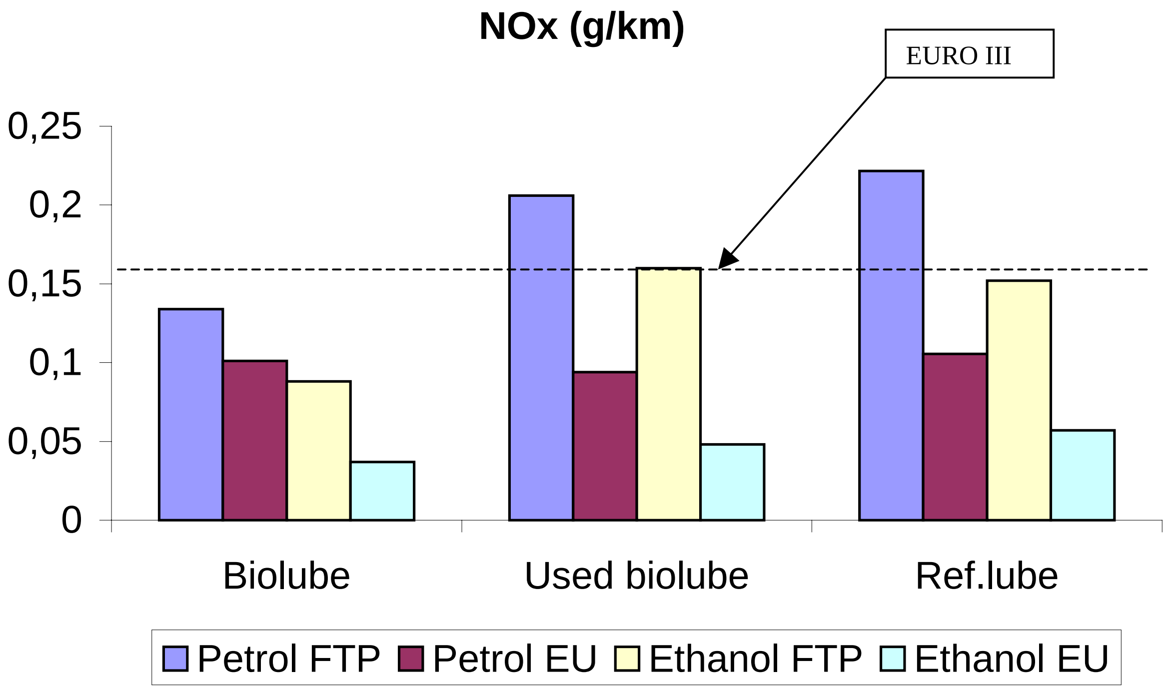


Figure 10.3. NOx emissions from the FFV's.

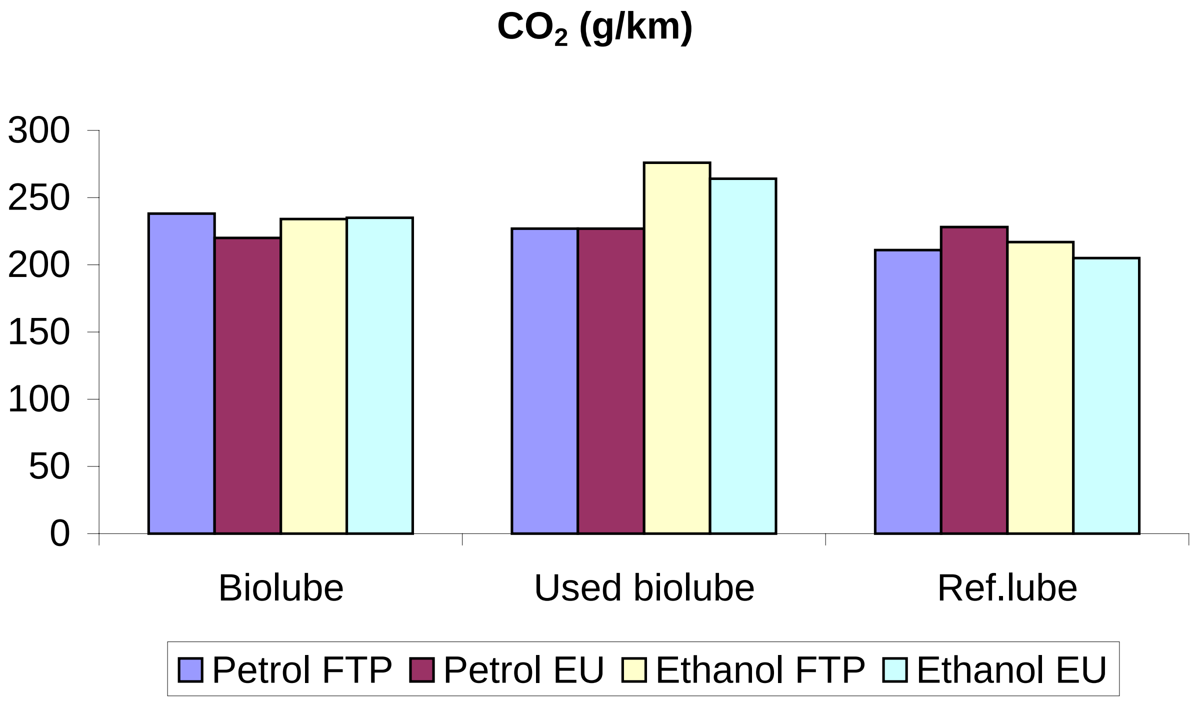


Figure 10.4. CO_2 emissions from the FFV's.

10.3. Particulate Emissions.

Total particulate emissions (PM) are shown in Figure 10.5. The emissions of SOF (Soluble Organic Fraction of particulate matter) are shown in Figure 10.6, and the contributions of SOF to PM in percent are shown in Figure 10.7.

From the PM measurements it is seen that the fresh biolube gave much higher emissions than the used biolube. This is most likely because some components in the lubricant are emitted from the lubricant and burned, or rather partly burned right after the addition of fresh lubricant. After some time these components are no longer present in the lubricant, and the emission level stabilizes. The reason for this behavior is probably that the lubricant is designed for diesel engines rather than gasoline/ethanol engines. If we look away from the results with fresh biolube we notice, that PM emissions with ethanol generally are lower, compared to gasoline. We also notice, that the reference lubricant application results in lower PM emissions, although emissions in all cases are very low (the EURO IV limit is 25 mg/km!). The difference could be a result of differences in load, due to differences in engine friction, caused by the lubricant. This seems to be supported by the fact that PM emissions are lower with biolube in the case of "Petrol EU", an exception that was noticed also for the fuel consumption/CO_2 emission measurements.

The SOF samples were further investigated for fuel and lubricant contributions. In all cases no fuel was found. Furthermore all hydrocarbons in the SOF were found in the range of lubricant hydrocarbons, indicating that all the SOF is made up by lubricant or lubricant combustion products. The relative amounts of lubricant/lubricant combustion products are listed in Figure 10.8. From this figure we notice that the lubricant contribution to SOF emissions with fresh biolube is much higher compared to used biolube. This supports the earlier suspicion about an excess emission of lubricant right after lubricant exchange with the biolube.

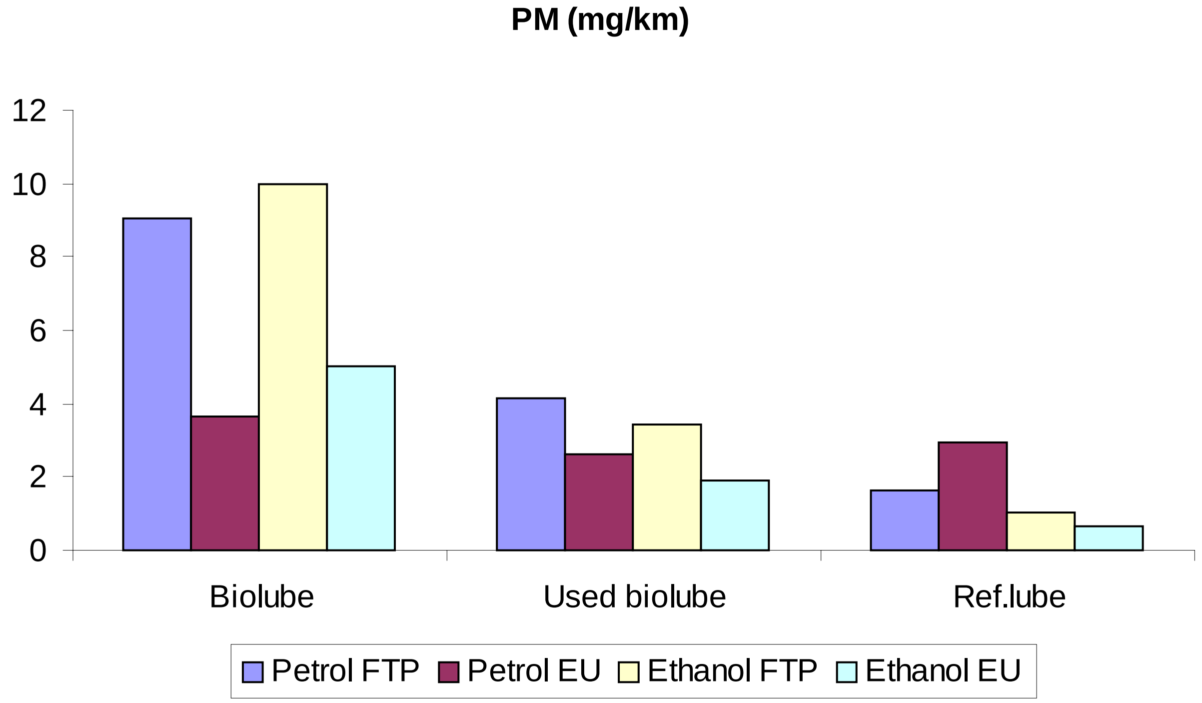


Figure 10.5. PM emissions from the FFV's.

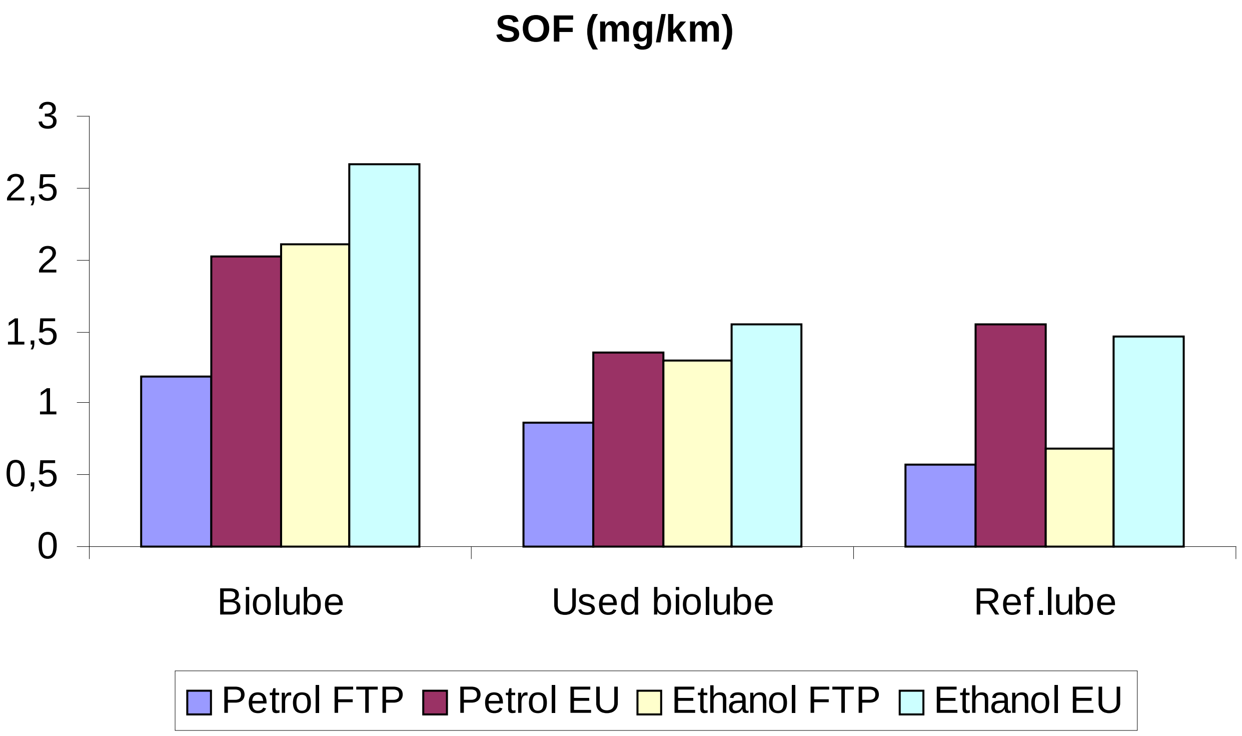


Figure 10.6. SOF emissions from the FFV's.

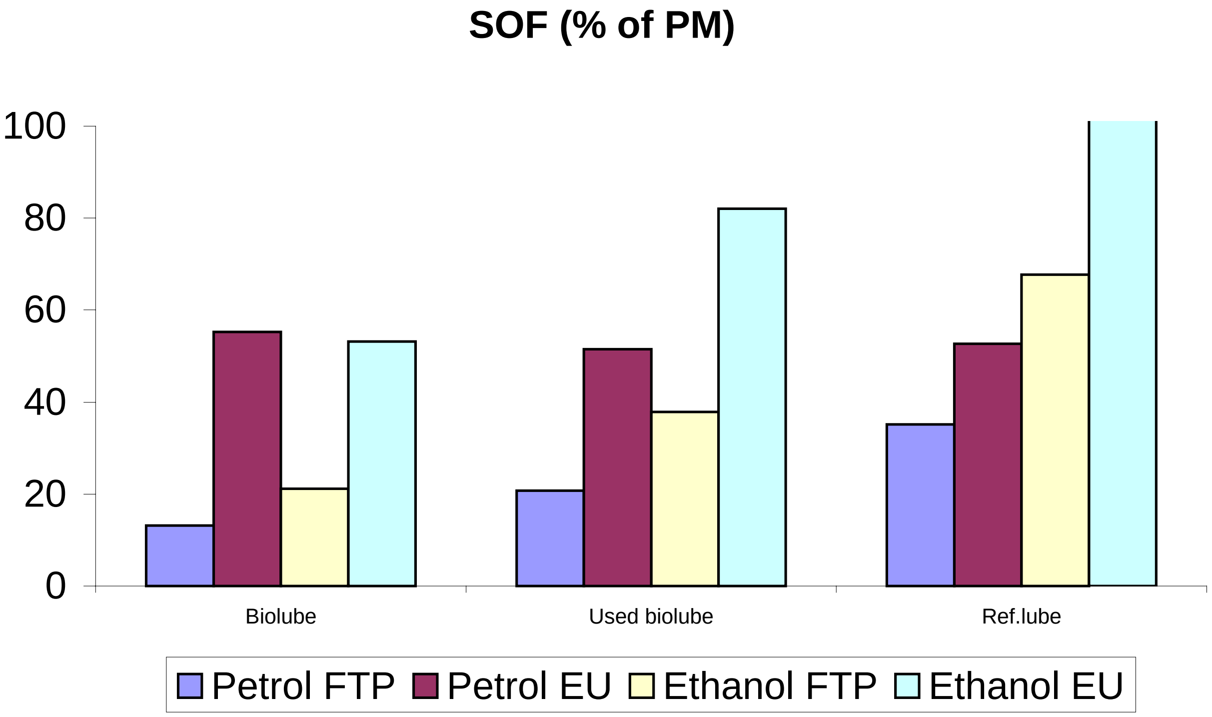


Figure 10.7. SOF emissions in percentage of PM emissions from the FFV's.

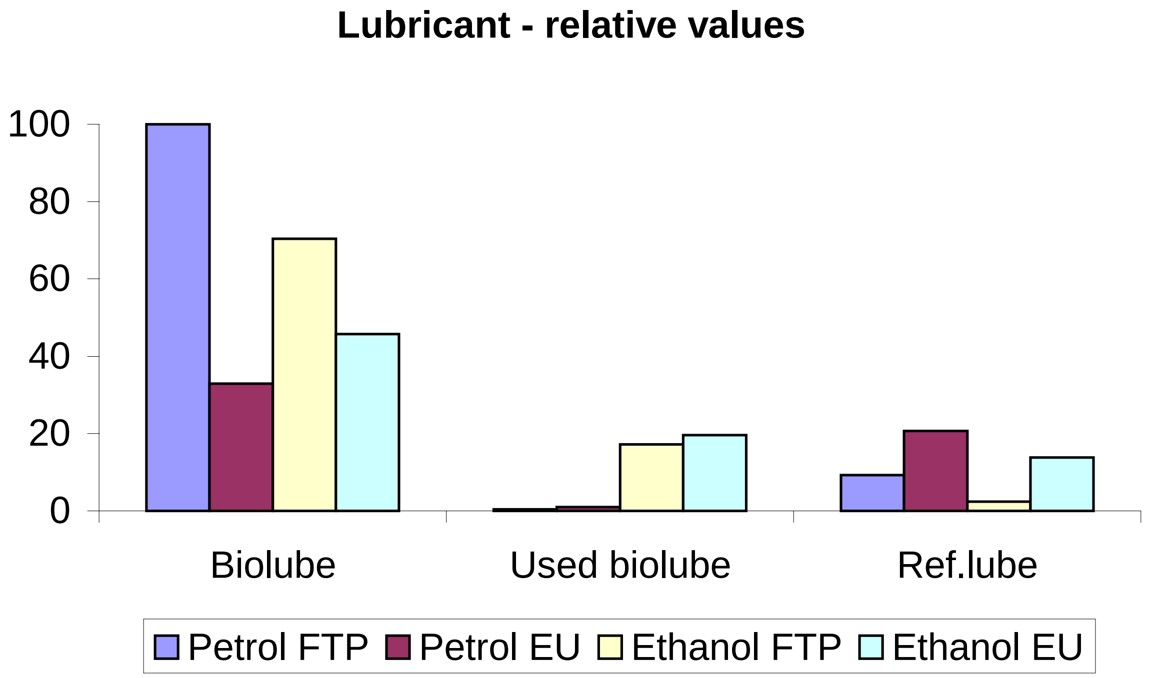


Figure 10.8. Lubricant emissions (relative values), estimated from GC analysis of SOF.

10.3.1. PAH Emissions.

PAH emissions are given in Table 10.1 for PAH's with more than 2 benzene rings. Only PAH compounds with more than 2 rings are shown, because the calibration standard very badly reflected the composition of PAH’s with 2 or less rings, and because this fraction, as the definition says, contain a lot of monoaromatics, which are not really considered as PAH’s. In any case the fraction with more than 2 rings made up the major part of the total PAH, and furthermore the most harmful PAH’s are the heaviest ones.

PAH > 2 rings (ng/km)	**Petrol**		**Ethanol**	
	FTP	EU	FTP	EU
Biolube	15	30	21	26
Used Biolube	17	39	11	7
Ref.lube	7	12	4	2

Table 10.1. PAH emissions in ng/km.

If we compare the result with the similar measurements on diesel vehicle emissions [2] we find a factor 100-1000 more PAH's from diesel vehicles. It is seen that the biodegradable lubricant emits more PAH's than the reference lubricant. This was not expected but could be a result of higher fuel consumption. This was found to control PAH emissions from the diesel vehicles [2]. Finally it is obvious that the ethanol fuel emits less PAH than gasoline.

10.4. Engine Wear.

Engine wear is evaluated based on the analysis of fresh and used biodegradable lubricant. The results of the lubricant analysis are shown in Table 10.2.

Lubricant Analysis

Analysis	**Fresh BioLube**	**BioLube Used 7500 km with Gasoline**	**BioLube Used 7500 km with ethanol (E85)**
Viscosity (CST 40°C)	70,8	62,9	59,2
Flash Point (°C)	192	142	188
Fuel Content (%)	0	0,84	0,50
TBN (mgKOH/g)	12,0	10,7	10,2
Water (%)	<0,1	<0,1	<0,1
Silicon (ppm)	0	6	29
Particulates (%wt)	<0,2	<0,2	<0,2
Fe (ppm)	2	13	14
Al (ppm)	0	0	0,2
Cr (ppm)	0	0	0
Mo (ppm)	5	6	5
Cu (ppm)	0,3	2	9
Pb (ppm)	4	2	0
Ni (ppm)	2	5	4
Mn (ppm)	0	6	6
V (ppm)	0	0	1

Table 10.2. Lubricant Analysis

From the metal analysis it is seen that there is no unusual wear in any of the cases. The most noticeable changes are the low flash point in the gasoline case and the low viscosity in the case with ethanol.

The low flash point with gasoline application indicates that the lubricant contained too much fuel. However, measurements of fuel content only showed 0,84 % fuel. At the same time the viscosity of the used lubricant was lowered quite much, again indicating fuel dilution - or maybe a chemical modification of the lubricant due to the fuel dilution.

In the ethanol case we notice an even larger decrease in viscosity for the used lubricant, indicating that ethanol has a stronger influence on the lubricant viscosity or a stronger modification of the used lubricant.

We notice, that the measurement of viscosity of the fresh lubricant does not show the quite the same value as the manufacturer specifications in Table 8.1. This could be due to differences from the measurement methods. As a general rule the change in viscosity should not be more than ±25 %. It is doubtful whether this is fulfilled, at least in the case of ethanol application.

10.5. Biodegradability of Lubricants.

The classification of a lubricant as biodegradable by the different environmental labels only covers fresh unused engine oils. However, according to different authors e.g. [4] the biodegradability of a lubricant may change considerably after only a few hours of use due to oxidation and thermal and hydrolytic reactions. Accumulation of dust, combustion products, wear particles and especially heavy metals might inhibit biodegradation as well. The amount of investigations done in the past on the biodegradability of used engine oils is very limited, but Boehme et al [5] presented a paper where they had tested the performance of a synthetic ester based biodegradable engine lubricant. Part of the test program was a test of the biodegradability of the oil before and after use, and the results showed that the degradability of the fresh oil was above 90% (CEC L33-T82), and the biodegradability of the used oil was between 70 and 80%.

The results of the tests carried out in this investigation are seen in Table 10.3.

Biodegradability according to CEC L-33A-93 test		
Fresh BioLube	BioLube used 7500 km with Gasoline	BioLube used 7500 km with E85
90%	79%	74%

Table 10.3. Biodegradability test results

This means that after 21 days of biological activity, 90%, 79% and 74% respectively were degraded. As we expected, the biodegradability of used lubricants are not the same as for new one’s. If we assume a linear degradation decrease with time and an average lifetime of a lubricant to be 15.000 km, then the results for the used lubricants in the table reflects the average biodegradability of lubricants in use.

The results agree very well with the earlier reported results [4]. Furthermore, the results show that the fuel is important in this context, since the lubricant used with gasoline is more biodegradable than the lubricant used with ethanol.

One would have expected that a biologically derived fuel like ethanol would result in a more biodegradable lubricant. This does not seem to be the case. In this context we must remember that E85 does contain other components beside ethanol. However, the results do indicate a chemical modification of the used lubricant in the case of ethanol application, since the content of wear particles and heavy metals in the used lubricant is low.

11. Conclusions

The application of a biodegradable lubricant in a Flexible Fuel Vehicle did not result in any unusual wear on the engine, neither when gasoline nor E85 was applied as fuel.

The biodegradability of the used lubricant was dependent on the applied fuel. Application of gasoline resulted in an average biodegradability of the lubricant of 79 % whereas application of E85 resulted in an average biodegradability of 74 %. This should be compared with the biodegradability of the fresh lubricant which was 90 %. The decrease in biodegradability is of the same size order as result from the litterature.

The lubricant consumption was low in both fuel cases.

The viscosity of the used lubricant was quite low, but the lubricant was primarily designed for diesel fuels. E85 had the strongest influence on the viscosity.

NOx emissions were, as expected lower with the E85 fuel. CO emissions were higher with E85, compared to gasoline. This could be explained by improper engine adjustment, which was indicated by a higher fuel consumption from the vehicle when E85 was applied.

The fuel consumption with biodegradable lubricant compared to reference lubricant was dependent on the fuel and the driving cycle.

The emissions of particulate matter when different lubricants were applied were dependent on fuel/driving cycle combination. The SOF of the particulate matter came from the lubricant.

Particulate emissions were lower with E85 than with gasoline.

PAH emissions from E85 was lower than with gasoline. PAH emissions were also lower with reference lubricant compared to the biodegradable lubricant. In all cases PAH emissions were very low compared to diesel vehicle PAH emissions.

12. References

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Acknowledgements

The author would like to gratefully acknowledge the financial support from the organizations of the IEA Advanced Motor Fuels Agreement member countries that made this investigation possible. These where:
DTU (Denmark)
Tekes, VTT (Finland)
EURON (Italy)
LEVO (Japan)
STEM (Sweden)
DOE (USA).

Also thank you very much to VISAB, Malmö, Sweden for lending us the FFV's.

Abbreviations

CO	carbon monoxide
CO_2	carbon dioxide
EU	European test driving cycle
FTP	USA test driving cycle (Federal Test Procedure)
GC	gas chromatography

HPLC	high performance liquid chromatography
LSD	low sulphur diesel
MON	motor octane number
MTBE	methyl-tert-butyl-ether
NOx	nitrogen oxides
PAH	polycyclic aromatic hydrocarbons
PM	total particulate matter
RON	research octane number
THC	total hydrocarbons
TWC	three-way catalyst
SOF	soluble organic fraction

Appendix 1. Data Tables.

CO (g/km)	PETROL		ETHANOL	
	FTP	EU	FTP	EU
Biolube	0,71	0,58	1,63	2,1
Used biolube	0,76	0,774	1,78	2,69
Ref.lube	0,18	0,575	1,53	0,61

HC (g/km)	Petrol		Ethanol	
	FTP	EU	FTP	EU
Biolube	0,045	0,107	0,088	0,128
Used biolube	0,052	0,155	0,094	0,052
Ref.lube	0,05	0,121	0,11	0,086

NOx (g/km)	Petrol		Ethanol	
	FTP	EU	FTP	EU
Biolube	0,134	0,101	0,088	0,037
Used biolube	0,206	0,094	0,16	0,048
Ref.lube	0,2216	0,1056	0,152	0,057

CO2 (g/km)	Petrol		Ethanol	
	FTP	EU	FTP	EU
Biolube	238	220	234	235
Used biolube	227	227	276	264
Ref.lube	211	228	217	205

Particulates (mg/km)	Petrol		Ethanol	
	FTP	EU	FTP	EU
Biolube	9,03	3,67	9,97	5,02
Used biolube	4,16	2,62	3,44	1,89
Ref.lube	1,61	2,94	1,01	0,649

SOF (mg/km)	Petrol		Ethanol	
	FTP	EU	FTP	EU
Biolube	1,19	2,03	2,11	2,67
Used biolube	0,864	1,35	1,302	1,55
Ref.lube	0,566	1,55	0,684	1,46

PAH>2 rings (ng/km)	Petrol		Ethanol	
	FTP	EU	FTP	EU
Biolube	15	30	21	26
Used Biolube	17	39	11	7
Ref.lube	7	12	4	2