Diesel Fuel Derived from Vegetable Oils, III. Emission Tests Using Methyl Esters of Used Frying Oil

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The preparation of methyl esters of used frying oil, available as waste from restaurants and households, is described. Fuel specifications of this fuel are given, and values for gaseous (HC, CO, NO_x) and particulate emissions, measured with a vehicle powered by a turbocharged, direct injection diesel engine, are shown. The ester fuel shows slightly lower HC and CO emissions but increased NO_x values compared with reference US-2D fuel. The particulate emissions, however, are significantly lower with used frying oil. Preliminary results of an engine road test are described.

The use of straight or modified vegetable oils as fuel in diesel engines has been described recently in many papers (1-8). Especially the methyl and ethyl esters of fatty acids obtained by alcoholysis of triglycerides seem to be an excellent fuel. However, the usage of vegetable oils as diesel fuel depends on world market prices for mineral products and is therefore of special interest at present only for countries with a large excess of vegetable oil production.

A very cheap and useful alternative would be used frying oil-available as waste from restaurants and households. So far only a very small percentage of used frying oil has been collected and processed on to soap; most of the used oil is still waste material and usually a burden to waste water. A similar work dealing with alcoholysis of used frying oil (9) prompted us to publish our own research on the preparation of methyl esters from used frying oil, its properties and especially the emissions of diesel engines operated with such a fuel compared with those of rapeseed oil methyl esters and reference US-2D diesel fuel.

EXPERIMENTAL

Preparation of methyl esters. About 200 kg of used frying oil were collected from different households and restaurants over a period of one year. The consistency of this oil varied from liquid to solid due to the use of nonhydrogenated and partly hydrogenated oil. The oil was heavily polluted with pieces of food and cooking residues. Methanol for alcoholysis is preferred because of the low costs and the best yield of all alcohols. Alcoholysis was carried out in a 50-l glass vessel equipped with a mechanical stirrer and an outlet stopcock at the bottom. The vegetable oil was used directly without any further purification. A solution of 450 g of potassium hydroxide in eight l of absolute methanol was added to 40 kg of vegetable oil while stirring. After 20 min of stirring the mixture, which slowly became clear and less viscous, was allowed to rest for five hr. The dark glycerol layer, which separated and contained most of the impurities, could be removed. The bright yellowish ester layer was washed several times with 10 l of water at 40 C until neutral reaction of the aqueous layer. The separation of the aqueous layer may take several hr because of the formation of soaps. The organic layer was then dried with four kg of anhydrous sodium sulfate and filtered properly. The clear yellowish solution was used in the engine tests without further purification.

The fuel specifications of the ester fuel compared with those of US-2D fuel are listed in Table 1.

Engine and exhaust gas sampling system. The emission tests were carried out according to a previous paper dealing with the emissions of rape oil methyl ester (10). The measurement technique and the gas sampling system are described in (11, 12). All tests were carried out with a vehicle of 1360 kg inertia weight powered by a 2.3 l turbocharged four-cylinder, four-stroke, direct-injection diesel engine with exhaust gas recirculation (EGR), under transient operating conditions on a chassis dynamometer. The vehicle was tested under the US Federal Test Procedure (US-FTP) and in the High-Way-Fuel-Economy-Test (HWFET) as described in the Federal Register (13), and the test results were compared

TABLE 1

Fuel Specifications

	US-2D	Used frying oil methyl ester			
	05-20				
Density at 15 C (kg/m ³)	0.849	0.888			
Initial boiling point $(^{\circ}C)^{a}$	189	307 (1%)			
10%	220	319			
20%	234	328			
50%	263	333			
70%	286	335			
80%	299	337			
90%	317	340			
Final boiling point (°C)	349	342 (95%)			
Aromatics $(\%, v/v)^b$	31.5	-			
Analysis					
Carbon (%)	86.0	77.4			
Hydrogen (%)	13.4	12.0			
Oxygen (%)	0.0	11.2			
Sulphur (%)	0.3	0.03			
Cetane index c	46.1	44.6			
Cetane number d	46.2	50.8			
HC ratio ^e	1.81	3.62^{f}			
Net calorific value (MJ/kg)	42.30	37.50			

^aASTM D-86 correlation for ASTM D-2887 analysis.

 b ASTM D-1019, olefinic plus aromatic hydrocarbons in petroleum distillates.

^cThis index estimates the cetane number from API gravity and 50% mid boiling point of distillate fuels, ASTM method D-976.

 $d{\rm The}$ cetane number describes the ignition quality of diesel fuels, ASTM method D-613.

^eHC ratio describes the number of H atoms/C atom, on average. fCarbon balance factor calculated by %C, %H and %O.

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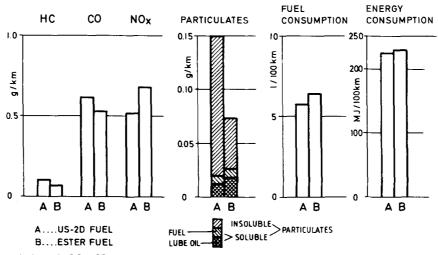


FIG. 1. HC, CO, NO_x and particulate emissions. Fuel consumption US-FTP 72 test (four-cylinder, four-stroke, DI/TC diesel engine with EGR, 2.3 l displacement, 1360 kg inertia weight).

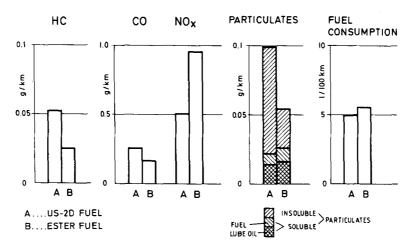


FIG. 2. HC, CO, NO_x and particulate emissions. Fuel consumption HWFET test (four-cylinder, four-stroke, DI/TC diesel engine with EGR, 2.3 l displacement, 1360 kg inertia weight).

with those obtained with a US-2D reference fuel. Deviating from (13) only hot start tests were run, designated as FTP 72 in the following sections.

RESULTS AND DISCUSSION

HC, CO, NO_x and particulate emissions, energy consumption. Emissions of HC, CO, NO_x and particulates as well as fuel consumption are shown in Figures 1 and 2 for the FTP 72 and the HWFET, respectively.

The ester fuel, compared with the US-2D fuel, shows slightly lower HC and CO emissions but increased NO_x values under the US-FTP 72 (Fig. 1) and almost doubled NO_x values under the HWFET Test (Fig. 2). Surprisingly, the particulate emissions are significantly reduced with the ester fuel under both tests, especially the insoluble portion of particulates. Compared with previous investigations (10) the particulate emissions from rapeseed oil methyl ester are also reduced under HWFET Test conditions, but not under FTP 72 conditions. The reduction of the particulate emissions using ester fuels can be explained by their oxygen content thus providing more oxygen for combustion and soot oxidation. Because of the increased oxygen availability of the ester fuel the combustion temperature is higher, which explains the higher NO_x values and lower smoke emissions. The higher volumetric fuel consumption of the ester fuel is due to its lower net calorific value. Rated power of the engine with the two fuels could not be determined accurately because the engine was installed in a vehicle for all tests performed. Engine power with ester fuel relative to US-2D fuel, however, may be estimated by the ratio of energy input (EI) times the ratio of energy efficiency. This calculation is justified, because the engine's fuel injection pump operates on the volume metering principle, and no change to the pump was made during the tests.

The energy input ratio (by volume) is calculated from the density and energy data (Table 1) as follows:

$$\frac{\mathbf{E} \mathbf{I}_{ester}}{\mathbf{E} \mathbf{I}_{US-2D}} = \frac{\mathbf{E}_{ester} [MJ/kg]}{\mathbf{E}_{US-2D} [MJ/kg]} \times \frac{\mathbf{Density}_{ester} [kg/l]}{\mathbf{Density}_{US-2D} [kg/l]} = 0.9174 \quad [1]$$

The efficiency ratio is calculated from the energy consumption data of Figure 1 (energy required to move the vehicle through a defined driving schedule with defined work per test) as in Eqn. [2].

$\frac{\text{Efficiency}_{\text{ester}}}{\text{Efficiency}_{\text{US-2D}}} =$	Work Energy cons	Ester \div	Work Energy cons	$US-2D = \frac{Energy \ cons_{US-2D}}{Energy \ cons_{ester}}$	= 0.9760	[2]
00.12	LJ			65101		

Thus, engine power of the ester fuel relative to US-2D fuel is $0.9174 \times 0.976 = 0.8954$. About 10% power loss with ester fuel can be expected with unchanged fuel delivery of the injection pump. However, in view of the fact that particulate emissions are halved when using ester fuel (organic insolubles are even lower, i.e. one-third of those of US-2D fuel), a higher fuel input for the ester fuel may be tolerated by the engine without excessive full load smoke. So the engine power may become comparable to both fuels without any deteriorating effects on emissions.

Emissions of polycyclic aromatic hydrocarbons (PAH). The PAH emissions were measured under FTP 72 test conditions, according to a previous paper (10). The following 10 compounds were determined: fluoranthene, pyrene, chrysene, benzo(a)pyrene, benzo(k)fluoranthene, benzo(ghi)perylene, benzo(b)fluoranthene, anthanthrene,

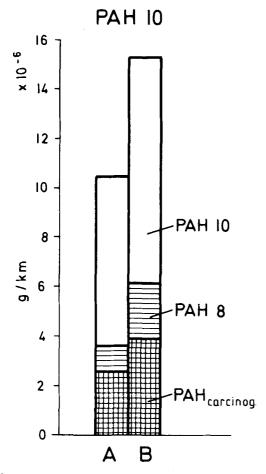


FIG. 3. Polycyclic aromatic hydrocarbon emissions. US-FTP 72 test (four-cylinder, four-stroke, DI/TC diesel engine with EGR, 2.3 l displacement, 1360 kg inertia weight). A, US-2D fuel; B, ester fuel.

perylene and indeno(1,2,3-cd)pyrene. Also, the respective quantities of these 10 compounds were summed up and denoted PAH (10). Because the 4-ring compounds fluoranthene and pyrene together yield ca. 70% of the PAH(10), faulty measurements (sampling) of these two PAH contribute most to errors in PAH(10). Therefore, a second sum of PAH consisting of eight compounds without fluoranthene and pyrene was made and denoted PAH(8). Furthermore, the sum of biologically active known compounds (chrysene, benzo(a)pyrene, benzo(b)fluoranthene and indeno(1,2,3-cd)pyrene) was denoted PAH carcinog. The PAH emissions of the ester fuel are in general slightly higher than those of the US-2D fuel, but the differences are within tolerance limits. In general, PAH emissions in absolute figures are very low (Fig. 3).

Engine road tests. The fuel was tested in a Volkswagen diesel Rabbit powered by a 1.6-l four-cylinder 4-stroke diesel engine with indirect injection. A mixture of ester fuel/diesel fuel, 1/1 was chosen and a total of 100 l of ester fuel was consumed. No changes in operation whatsoever could be observed. The smoke emissions were extremely low and only a faint smell of burnt fat was detected. Contrary to other observations (14), we could not observe any lower volumetric fuel consumption; in our test the fuel consumption was almost the same as when using diesel fuel. Long term engine tests, however, are still necessary to prove the quality of this fuel.

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