Production And Evaluation of Palm Oil Methyl Esters As Diesel Substitute

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ABSTRACT

The fast diminishing energy reserves, greater environmental awareness and increasing energy consumption have led to an intensified search for viable alternate sources of energy globally. In this respect PORIM/PETRONAS has patented an efficient process to produce methyl esters from palm oil with varying amounts of free fatty acid content. The process requires milder conditions i.e. low temperature (80 °C) and lower pressure (atmospheric) than the existing commercial processes. The production technology has been successfully demonstrated at a pilot plant (3,000 tonnes/year) scale and the technology is now ready for commercial exploitation.

Over the past few years, palm oil methyl esters has been extensively evaluated as diesel substitute in a wide range of diesel engines including stationary engines, passenger cars, buses and trucks. The last phase of an exhaustive field trial involving 36 buses is near completion. The buses are running on three fuels i.e. 100% palm oil methyl esters, 100% petroleum diesel (as control) and a 50:50 blend of the two fuels. So far very promising results have been obtained as follows:

1. *No modification of the diesel engine is required*
2. *Engine performance is very good*
3. *The exhaust emission is much cleaner with reduction in black smoke, NOx, CO and absence of SO_2*
4. *No abnormal wear and tear in engine components and no nozzle deposits*
5. *No engine oil dilution*
6. *Fuel consumption is comparable*

This paper describes the production technology and evaluation of the palm oil methyl esters as diesel substitute/diesel improver.

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INTRODUCTION

The fast diminishing energy reserves, greater environmental awareness and increasing energy consumption have led to an intensified search for viable alternative sources of energy globally.

In this respect, in recent years a great deal of attention has been directed to plant-based sources for fuels, in particular fuel for diesel engines. Among such sources are plants which produce oil directly. Vegetable oils which are renewable therefore have the greatest potential as an alternative source of fuel. Of all the vegetable oils available palm oil being the highest oil yielding crop would be the preferred choice *(Table 1)*.

The diesel engine application is widespread in agriculture and transport sector (buses, taxis and trucks). In Malaysia, the transport sector accounts for about 40% of the total diesel consumption.

The environmentalists in Malaysia have concern over the excessive black smokes, sulphur dioxide emission and other component gases like CO, CO_2 and NOx. PORIM has been interested in alternative fuel over the last decade. Palm oil methyl esters has been successfully used in many makes of engines including stationary engines, trucks, buses and taxis as diesel substitute.

This paper describes the production technology of palm oil methyl esters, the evaluation of palm oil methyl esters as diesel substitute as well as the economic viability of the project.

PRODUCTION TECHNOLOGY OF PALM OIL METHYL ESTERS

Commercially, methyl esters of fatty acids can be manufactured either by direct esterification of fatty acids or by transesterification of triglycerides. The esterification is carried out batchwise at 200°C - 250°C under pressure. In order to obtain a high yield, the water produced during the reaction has to be removed continuously. Esterification can also be done continuously in a counter - current reaction column using superheated methanol (Kreutzer, 1984).

TABLE 1. AVERAGE YIELD OF OIL PRODUCING CROPS

	Kg/Ha/year
Malaysian Palm Oil Malaysian	3636
Coconut Oil	1272
Peanut Oil	909
Soybean Oil	432
Rapeseed	999
Sunflowers	801

TABLE 2. PRODUCTION OF METHYL ESTERS FROM CRUDE PALM OIL, CRUDE PALM STEARIN AND CRUDE PALM KERNEL OIL

Starting material	*Feed rate*
Crude palm oil (3.2% FFA)	500 kg/hr
Methanol	113.3 kg/hr
Product	*Yield*
Methyl esters	475 kg/hr (95%)
Crude glycerol	65 kg/hr (91%)
(ca. 73% concentration)	
Starting material	*Feed rate*
Crude palm stearin (3.8% FFA)	500 kg/hr
Methanol	113.3 kg/hr
Product	*Yield*
Methyl esters	450 kg/hr (90%)
Crude glycerol	61.6 kg/hr (85%)
(ca. 73% concentration)	
Starting material	*Feed rate*
Crude palm kernel oil (1.25% FFA)	396 kg/hr
Methanol	85.9 kg/hr
Product	*Yield*
Methyl esters	364 kg/hr (92%)
Crude glycerol	49.3 kg/hr (83%)
(ca. 80% concentration)	

FFA = Free fatty acid

The predominant process for the manufacture of methyl esters is transesterification of triglycerides with methanol. The methanolysis of naturally - occurring oils and fats with methanol takes place quite readily at a temperature of about 50°C - 70°C at atmospheric pressure with excess methanol in the presence of an alkaline catalyst such as sodium hydroxide (Sonntage, 1982; Kreutzer, 1984; Freedman *et al.*, 1984; Farris, 1979). These mild reaction conditions, however, require an oil neutralised by means of alkaline refining, steam distillation or pre-esterification of free fatty acids.

A process has been developed by PORIM to convert crude palm oil, crude palm stearin and crude palm kernel oil with varying amounts of free fatty acids to methyl esters under mild conditions. The process which has been patented (Choo *et al.*, 1988) essentially consists of two steps:

(a) esterification of the free fatty acids present in the oil into methyl esters, followed by

(b) transesterification of the neutral glycerides mixture directly into methyl esters.

Such a process obviates the washing stage after esterification, which is economically advantageous. The schematic flow diagram of the process is shown in *Figure 1*.

Crude palm oil containing free fatty acids (3.2%) was mixed with methanol. The mixture was continuously fed into the esterification section consisting of a fixed bed reactor filled with solid catalysts. The temperature of the esterification reaction was maintained at 80 ± 5°C and the reaction pressure was maintained at 3 kg/cm^2. After the esterification reaction, the reactor effluent (unreacted glycerides and methyl esters, formed from FFA) was then pumped into the transesterification section consisting of two stirred tank reactors in series. The transesterification reaction was carried out at 70 ± 5°C under pressure (1 kg/cm^2) in two stages in the two stirred tank reactors. More than 80% of the glycerides were converted into methyl esters in the first stage of the reaction and the glycerol formed at this point was continuously removed in a separator. For the second stage reaction, an additional small amount of catalyst was added to push the reaction almost to completion, *i.e.* about 98%.

The glycerol formed during the second stage reaction was again separated in a second separator. The methanol in the glycerol phase of the first and second stage reactions was evaporated and purified for re-use. After removing the methanol, the glycerol phase with about 60-80% of glycerol can be purified on a factory scale according to the scheme in *Figure 2*. The ester phase containing excess methanol was pumped through n heat exchanger to evaporate off all the methanol. The methanol was again recovered and purified for re-use. The methyl ester was then pumped to the ester purification section. Traces of impurities (*e.g.* glycerol and soap) were removed by multi-stage water washing. A small quantity of hot water was used in each stage of washing and normally two to three washings were sufficient to clean up the esters. The methyl esters were then dried in a vacuum dryer before being pumped to the storage tank.

The methyl esters pilot plant which was constructed based on the forementioned PORIM/PETRONAS patented process has a capacity for producing 3,000 tonnes of methyl esters per year. The plant can process crude palm oil, crude palm stearin as well as crude palm kernel oil with FFA contents up to 30%. The novel aspect of the process is the esterification stage where solid acid catalysts are employed. Through pilot plant studies, it has been found that the esters and glycerol should be separated in the presence of methanol according to the process flow diagram as in *Figure 1*. Otherwise a reverse transesterification reaction would take place.

The conversion of crude palm oil into methyl esters can be run continuously with complete automation. The results of a typical trial run of crude palm oil are given in *Table 1*. It has also been demonstrated that the process is applicable to crude palm stearin and crude palm kernel oil (*Table 1*). The methyl esters of crude palm oil and crude palm stearin prepared by this process have been evaluated as diesel substitute and the results are very promising. In addition, the results of the trial run of palm kernel oil show that it is the easiest feedstock to deal with and the methyl esters which are of good quality have a ready application in the detergent industry. The fatty acid composition of these esters are shown in *Table 2*. The glycerol obtained from the pilot plant has been purified on a plant scale to a purity of 99.5% (B.P. grade) using the steps for the purification as in *Figure 2*.

EVALUATION OF PALM OIL METHYL ESTERS AS DIESEL SUBSTITUTE

Many researchers have investigated the possibility of using vegetable oils (straight or blended) as diesel substitute. A good account of their attempts was reported in the 1983 JAOCS on Symposium on Vegetable Oils as Diesel Fuels (Adams *et al.*, 1983; Klopfenstein and Wolker, 1983; Pryde 1983; Strayer *et al.*, 1983). The symposium

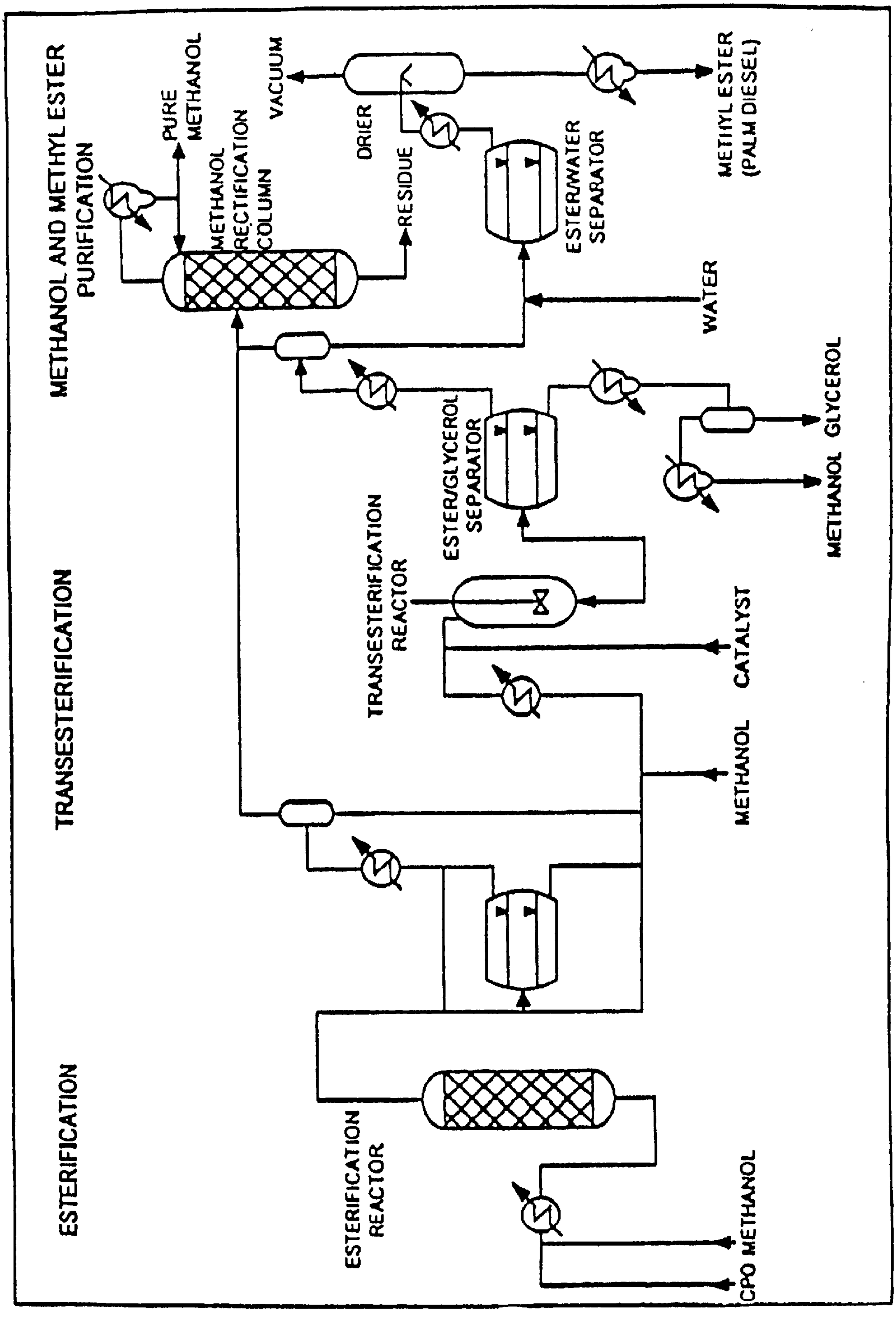

Figure 1. Schematic flow Diagram of palm oil methyl esters pilot plant

GLYCEROL

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WATER <---------- WATER DILUTION
WATER/GLYCEROL RATIO = 2/3

↓

SOAP KETTLE
SOAP <----------- SAPONIFICATION OF METHYL ESTERS
WITH NaOH FOLLOWED BY SALTING
OUT WITH NaCl

↓ GLYCERINE SOLUTION

ACID TREATMENT WITH CONCENTRATED H_2SO_4
AND ALUM TO pH 4.5

↓ FILTRATION

ALKALINE TREATMENT WITH 50% NaOH
SOLUTION TO pH 8

↓

EVAPORATION, TO 80% CONCENTRATION

↓

DISTILLATION, TO > 98.5% CONCENTRATION

↓

DEODORIZATION

↓

BLEACHING WITH ACTIVATED CARBON

↓

PURIFIED GLYCEROL, >99.5%

Figure 2. Glycerol purification process

revealed that vegetable oils have good potential as alternative fuels if the following problems could be overcome satisfactorily. These include high viscosity, low volatility, and the reactivity (polymerization) of the unsaturated hydrocarbon chains if the oils are highly unsaturated. These will give rise to coking on the injectors, carbon deposits, oil ring sticking and thickening and gelling of the lubricating oil as a result of contamination with vegetable oils.

It is possible to reduce the viscosity of the vegetable oils by incorporating a heating device to the diesel engine as has been successfully demonstrated in the Elsbett engine (Basiron and Ahmad Hitam, 1992). Other factors that may have long term effects on the engine are free fatty acids and gummy substances which are found in the crude vegetable oils. The incomplete combustion residues may contribute to the undesirable deposits on the engine components. The gummy substances may cause filter plugging problem. This will call for more regular and frequent services and maintenance of the engine. The long term effects of the oil on the engine are being monitored by various investigator.

Laboratory evaluation of palm oil methyl esters has been carried out including the determination of cetane number and the results, as shown in *Tables 3* and *4*, indicate that palm oil methyl esters could perform better than petroleum diesel. This is borne out by results obtained in stationary engine tests and field trials (both preliminary and exhaustive field trial (Phase I and Phase II)). The results of the field trials permit the following conclusions to be made:

- No modification of the engine is required.
- The performance of engines is generally good. The engines are easy to start with no knocking and with smooth running
- The exhaust gas emission of the engines is much cleaner with reduction of hydrocarbon, NOx, CO, and SO_2 contents, therefore it is more environmentally friendly
- The engine oil is still usable at the recommended mileage
- Palm oil methyl esters does not produce explosive air/fuel vapour. It also offers enhanced safety characteristic with higher flash point (174°C compared to 96°C of petroleum diesel)
- Carbon build-up on engine nozzles is normal except that the nature of carbon is different
- The fuel consumption of palm diesel is comparable to petroleum diesel (*e.g.* 3-4 km/L for the buses under trial)
- Palm oil methyl esters attacks low grade plastic and rubber products such as hoses, seal etc. and it also reacts with the binding material in cement floor

The second phase of the exhaustive field trial, which commenced in 1990 and involved 36 Mercedes Benz engines mounted on 36 buses, is in its final phase of testing. Some buses have already clocked in 300,000 km, the targeted mileage. Observations made to date in the trial confirm the positive findings on palm diesel obtained earlier. Meanwhile, crude palm stearin methyl esters have also been successfully tested in PORIM vehicles with no deleterious effects on the engines.

STORAGE AND TRANSPORTATION

The storage properties of the palm oil methyl esters are very good. It was found that there was little deterioration in the fuel quality parameters except the colour. After storing for more than six months in a storage tank, the colour has changed from orange to light yellow. This is due to the breakdown of carotenes in the methyl esters. The palm oil methyl esters has a high flash point and this makes its storage and transportation much safer.

ECONOMICS

The economics of palm oil methyl esters very much depend on world prices of palm oil, methanol, glycerol and crude petroleum oil (or diesel). A preliminary economic viability study shows that at the current diesel price of about RM650 per metric tonne (US$ 1- RM 2.6), the project will be viable if the crude palm oil price is below RM 800 and the glycerol price is about RM 3500. Nevertheless, the economics of the project would be very much enhanced if the valuable components like carotenes and Vitamin E in palm oil methyl esters are recovered and the resulting methyl esters are sold as oleochemical feedstock.

CONCLUSION

The technology for the production of methyl esters from crude palm oil, crude palm stearin and crude palm kernel oil with varying amounts of free fatty acids has been successfully demonstrated in a pilot plant scale operation. The methyl esters of crude palm oil is being evaluated exhaustively in 36 diesel engines mounted onto passenger buses. Some of the buses have travelled more than 300,000 km. No problem has been encountered so far. The exhaust emission contains less NOx, CO, CO_2 and no sulphur dioxide. The engines do not produce black smoke.

TABLE 3. FATTY ACID COMPOSITION OF METHYL ESTERS OF CRUDE PALM OIL (CPO), CRUDE PALM STEARIN (CPS) AND CRUDE PALM KERNEL OIL (CPKO)

	Fatty Acid Composition (%)											
	C6	C8	C10	C12	C14	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20
CPO	-	-	-	0.3	0.8	44.3	0.2	5.0	39.1	10.1	0.1	-
CPS	-	-	-	0.4	1.9	52.0	-	4.1	32.7	7.9	0.1	-
CPKO	0.5	3.0	2.8	44.9	16.0	10.1	-	2.4	17.1	2.8	0.2	0.2

TABLE 4. FUEL CHARACTERISTICS OF METHYL ESTERS OF CRUDE PALM OIL AND CRUDE PALM STEARIN

Product Test Conducted	Methyl Esters of CPO	Methyl Esters of CPS	Malaysian Diesel
Specific Gravity ASTM D1290°F	0.8700 @ 74.5	0.8713	0.8330 @ 60.0
Colour (visual)	Reddish	Orange	Yellow
Sulfur Content % WT. IP242	0.04	0.002	0.10% WT. IP 242
Visocity @ 40°C ASTM D445 (cST)	4.5	4.6	4.0
Pour Point/°C ASTM D97	16.0	17.0	15.0
Distillation D86			
I.B.P. °C	324.0	320.0	228.0
10% °C	330.0	331.0	258.0
20% °C	331.0	332.0	270.0
50% °C	334.0	335.0	298.0
90% °C	343.0	343.0	376.0
I.B.P. °C	363.0	349.0	400.0
Final Recovery ml	98.0	98.5	-
Gross heat of Combustion ASTM D2382 kJ/kg	40,135	39,826	45,800
Flash Point/°C PM cc ASTM D93	174	165	98
Conradson Carbon Residue ASTM D198 % wt.	0.02	0.05	0.14

TABLE 5. CETANE NUMBER OF CRUDE PALM OIL (CPO) METHYL ESTERS, PETROLEUM DIESEL (FROM EUROPE) AND THEIR BLENDS.

CPO Methyl Esters (%)	Petroleum Diesel (%)	Cetane Number (ASTM D613)
100	0	62.4
0	100	37.7
5	95	39.2
10	90	40.3
15	85	42.3
20	80	44.3
30	70	47.4
40	60	50.5
50	50	52.0
70	30	57.1

sulphur dioxide. The engines do not produce black smoke.

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