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Applicability of Hydrogenated Palm Oil for Automotive Fuels

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ABSTRACT

From the viewpoint of primary energy diversification and CO_2 reduction, interests of using Biomass Fuel for transportation fuels are rising. Some kinds of FAME (Fatty Acid Methyl Ester), which are obtained from oil fats like vegetable oil using transesterification reaction with methanol, are getting popular for bio-diesel recently. As FAME has unsaturated carbon-carbon bonds which come from feed materials, its performance such as storage stability is concerned. And there are other points of concern, namely, poor cold flow properties and FAME's effect on car components.

In this current situation, technologies to produce high quality fuels from renewable sources, especially from vegetable oils, using petroleum refinery processes should be promising.

In this paper, we present our study of hydrogenating processes of palm oil, covering reactivity, distillate yields, evaluation of the obtained fuel, and its applicability as an automotive fuel.

1. INTRODUCTION

Sustainable automotive fuels are fuels that satisfy the conditions of "3E", namely, they are "economical", "environment-friendly", and promote "energy security". Over the last few decades, there has been ongoing development aimed at improving the environmental properties (i.e. exhaust gas reduction) of automotive fuels made from crude oil, which is excellent in terms of supply and economical efficiency. While the exhaust gas problem is largely a thing of the past thanks to ultra-deep desulfurization technology, the focus has shifted to issues of supply stability (diversification of resources) and environmental compatibility (CO_2 reduction) against a backdrop of spiraling crude oil prices and the global warming problem.

Many experts see the introduction of biomass fuels as a promising solution. We are beginning to see rapid adoption in Europe and America, and introduction of biomass fuel is planned in Japan as well. Experts anticipate growing use of biomass, and studies of technologies for producing automotive fuels from vegetable oil are also progressing rapidly. The prevailing technology today is to use FAME (fatty acid methyl ester), produced by reacting vegetable oil with methanol (ester exchange reaction). With this method, it is possible to turn vegetable oil into light oil with a consistency similar to diesel oil. FAME is mixed with diesel and used to fuel diesel vehicles, mainly in Europe. But due to its poor oxidative stability, FAME can only be mixed with diesel in limited quantities; biomass fuels with properties superior to FAME are needed.

2. PRELIMINARY STUDY (Mixed hydrocracking experiment with VGO)

(1)Feed oil

We used a Middle East VGO (Vacuum Gas Oil) + 20% palm oil mixture as feed.

(2)Process conditions

Using a circulation reactor and a common hydrocracking catalyst used in petroleum refining, hydrocracking activity (heavy fraction (360°C+) conversion rate) was evaluated at hydrogen pressure 10 MPa and reaction temperatures of 390°–410°C.

(3)Hydrocracking reactivity

Fig. 1 shows the Arrhenius plot of VGO by itself and the VGO/20% palm oil (PO) mixture. The VGO/PO mixture showed improved hydrocracking speed compared to VGO alone. This suggests that palm oil is more easily converted to into light fractions than is VGO.

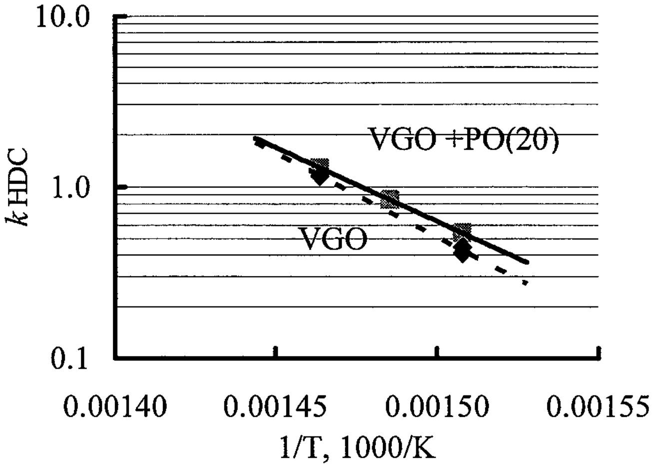

Fig.1 Arrehnius Plot of Hydrocracking Reaction

(4)Selectivity and quality of product oil

Fig. 2 shows the distribution of each fraction at a cracking rate of 60%. Compared to VGO only, naphtha and kerosene fractions decreased with the VGO/PO mixture. On the other hand, gas oil fraction increased.

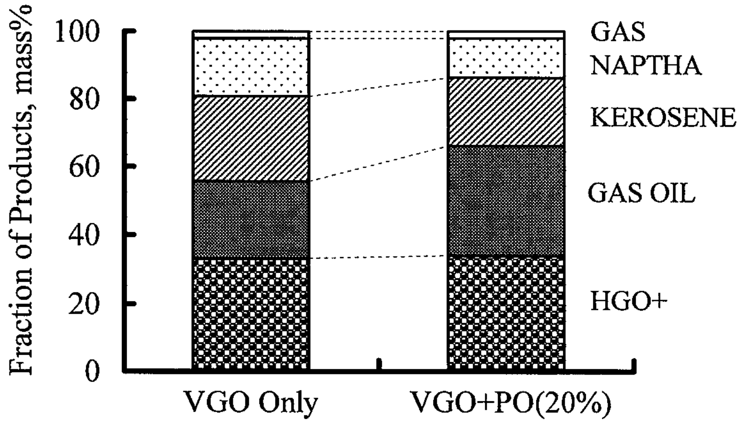

Fig.2 Fraction Yield of Hydrocracked VGO & VGO + Palm Oil

It is thought that this is because the hydrocarbon chains, generated by the hydrogenation of palm oil, are equivalent to the boiling point of the gas oil fraction.

The obtained gas oil fraction had qualities nearly equal to those of conventional diesel oil (Table1). It was thus shown that, by mixing palm VGO with palm oil and hydrocracking, high quality gas oil fraction can be obtained in high yield.

Table 1 Properties of Products Oil (Gas Oil Fraction)

		Product Oil (VGO+PO20)	Conventional Diesel
Density(@15℃)	g/cm^3	0.8174	0.8283
Sulfur	massppm	4	5
Oxygen	mass%	<0.1	<0.1
Aromatic	vol%	14	19
Distillate T90	℃	317	337.5

3. MAIN STUDY (Direct hydrogenation experiment)

3.1Feed oil

The feed oil was pretreated (decolorized, degummed, etc.), purified palm oil. Properties of the feed oil are shown in Table 2.

Table2 Properties of the Feed Oil for Direct Hydrogenation Experiment

		Purified Palm Oil
Density	g/cm3	0.9159
Higher Calorific Value	MJ/kg	39.5
Carbon	mass%	77.0
Hydrogen	mass%	11.5
Oxygen	mass%	11.4
Nitrogen	mass%	<0.1
Sulfur	mass ppm	<1.0
Pour Point	℃	25

3.2Hydrogenation conditions

Reaction temperature 240°–360°C; reaction pressure 6 MPa, 10 MPa; LHSV 0.5 h^{-1}. A hydrodesulfurization catalyst common in petroleum refining was used.

3.3 Experimental Results

(1)Properties of hydrogenated palm oil

The properties of the hydrogenated palm oil are shown in Table 3. The density is slightly less than conventional diesel and FAME. Distillation behavior, kinetic viscosity and other properties are within the range of gas oil. Moreover, the hydrogenated palm oil is sulfur free and aromatics free, so it can be called “clean fuel”. Another characteristic is that its cetane number (101) is much higher than that of common diesel oil or FAME. Furthermore, no impurities such as acid and alcohol were found in the oil. At reaction temperatures of 240°C and 250°C, a white substance was observed in the product oil, but further analysis confirmed this to be residual oxygen.

Table 3 Properties of Hydrogenated Palm Oil

	Hydrogenated Palm Oil (Reac.Press.10MPa)						Hydrogenated Palm Oil (Reac.Press.6MPa)			Palm FAME	Conventional Diesel Fuel
Reac.Temp ,℃	240	250	260	280	320	360	240	250	280		
Density(15℃) kg/m^3	794.5	783.9	782.5	782.5	782	781.5	800.7	782.7	782.2	876.1	821.6
Kinetic Viscosity(30℃) mm^2/s	5.47	4.36	4.23	4.13	4.10	4.03	—	4.23	4.17	5.65	3.32
Water mass ppm	274	852	35	31	49	30	333	62	38	500	90
Higher Calorific Value MJ/kg	46.2	46.9	46.9	47.1	47.2	47.2	46.0	46.9	46.9	39.9	45.9
Distillation Property T10 ℃	—	287.0	286.5	285.0	285.0	283.5	—	286.5	285.0	333.0	205.5
T50 ℃	—	292.5	292.0	290.5	291.0	290.0	—	292.0	291.0	354.0	280.0
T90 ℃	—	302.5	302.0	301.0	301.0	300.5	—	301.5	301.5	359.0	327.5
Carbon mass %	84.3	84.9	84.9	85.0	84.9	85.0	83.8	84.8	84.9	76.6	86.1
Hydrogen mass %	14.3	15.0	15.0	14.9	15.0	14.9	14.6	15.1	15.0	12.2	13.8
Sulfur mass ppm	2	<1	<1	<1	<1	<1	3	<1	<1	<1	4
Oxygen mass %	1.4	0.2	<0.1	<0.1	<0.1	<0.1	1.6	<0.1	<0.1	11.1	<0.1
Iodine Value	0.70	0.33	0.06	0.10	0.12	0.02	1.33	0.33	0.06	58.5	—
Formic Acid ppm	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	—
Acetic Acid ppm	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	—
Propionic Acid ppm	<1	<1	<1	<1	<1	<1	12	<1	<1	<1	—
Methanol ppm	<1	<1	<1	<1	<1	<1	<1	<1	<1	—	—
Ethanol ppm	<1	<1	<1	<1	<1	<1	<1	<1	<1	—	—
Propanol ppm	<1	<1	<1	<1	<1	<1	<1	<1	<1	—	—
Aldehyde ppm	<1	<1	<1	<1	<1	<1	<1	<1	<1	—	—

	Hydrogenated Palm Oil*	Palm FAME	Diesel Oil No.2
Cetane Number	101	62	61

*mixed sample :reac.temp. 280℃ (reac.press. 10,6MPa) ,reac.temp. 320℃ (reac.press. 10MPa)

Fig. 3 shows the fraction proportions in the hydrogenated oil at each reaction temperature. At reaction temperatures of 240° and 250°C, there were heavy fractions thought to be from uncracked vegetable oil.

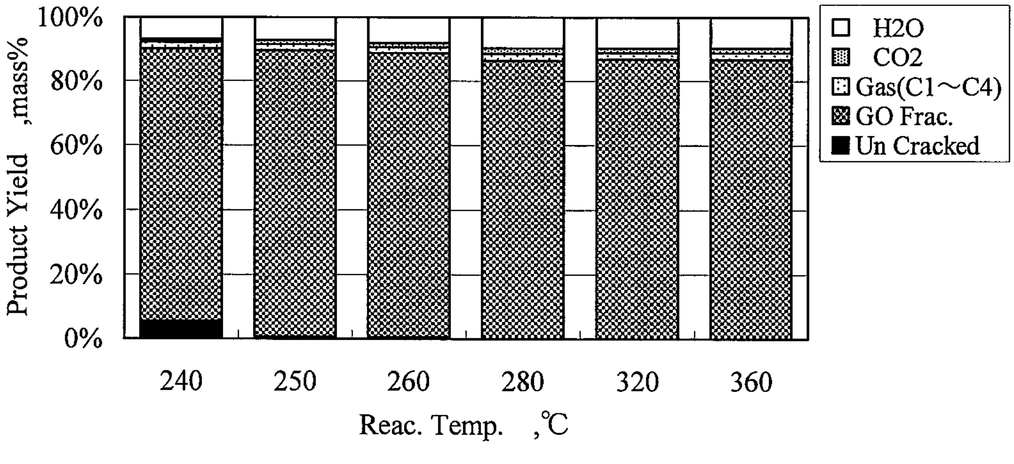

Fig.3 Fraction Yield of Hydrogenated Palm Oil

At temperatures of 260°C and higher, triglycerides have broken down completely, and it was confirmed that the products formed are approximately 85% gas oil fraction, 10% water, and 5% gases (CO_2, CH_4, C_3H_8).

Fig. 4 shows the ^{13}C NMR spectra of the hydrogenated oil at reaction temperatures of 240°C and 260°C. At 240°C, the temperature at which the white precipitate was observed, peaks from the unsaturated bonds and ester bonds were confirmed. The ester bond peak was confirmed to be from glycerides, which are traceable to the uncracked vegetable oil. At 260°C, no unsaturated bonds or ester bonds were detected. This confirmed that, in these conditions (reaction temperature of 260°C+), hydrogenation of the unsaturated bonds progressed 100% and the hydrodeoxygenation reaction also progressed completely.

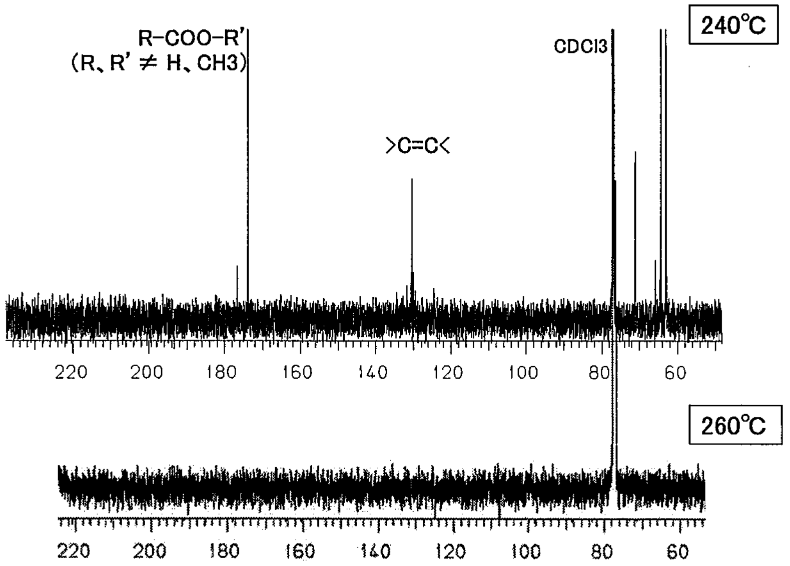

Fig.4 ^{13}CNMR Spectra of Hydrogenated Palm Oil

Analysis (gas chromatography, etc.) of the product oil showed that the gas oil fraction is largely straight chain hydrocarbons from C15 to C18, which are traceable to the palm oil alkyl chains. Although the palm oil-derived alkyl chains have carbon numbers of C16 and C18, in this hydrogenation process, hydrocarbons of C15 and C17 are formed, and their proportion increases as reaction temperature rises (Fig. 5). This is thought to be caused by progression of decarbonation in the hydrodeoxygenation reaction. That is, in the decarbonation reaction, oxygen is eliminated in the form of CO_2, and thus the carbon number of the hydrogenated oil decreases by one, and straight chain hydrocarbons of C15 and C17 are formed.

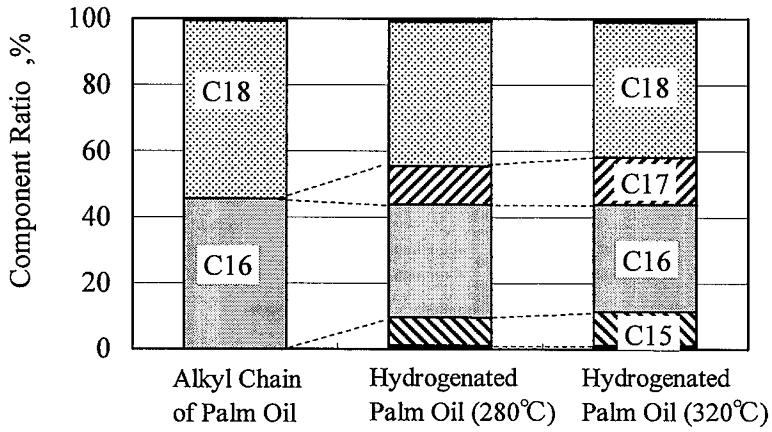

Fig.5 Carbon Number of Hydrogenated Palm Oil

(2) Oxidation stability of hydrogenated palm oil

Accelerated oxidation test results are shown in Table 4. Oxygen was bubbled through the oil, for 16 hours at 115°C. Acid values were measured before and after the test. Compared to FAME, the hydrogenated palm oil showed a much smaller acid value increase in the accelerated oxidization test, confirming its superior oxidation stability. This is because the oil's unsaturated bonds have been hydrogenated, and we can say that this allays concerns currently held about problems with FAME use.

Table 4 Oxidation Stability of Hydrogenated Palm Oil

		Hydrogenated Palm Oil	Palm FAME	Conventional Diesel Oil
Acid Value (before test)	mgKOH/g	0.00	0.26	0.00
Acid Value (after test)	mgKOH/g	0.03	10.4	0.07

(3) Cold flow properties of hydrogenated palm oil

The low-temperature performance of hydrogenated palm oil is shown in Table 5. The cloud point of the hydrogenated oil is about 20°C, slightly worse than FAME. Cloud point is the temperature at which wax (paraffin) begins to separate when oil chilled to a low temperature, and it serves as an important indicator of practical performance in automotive applications in low temperatures. The cloud point of hydrogenated palm oil (20°C) is much higher than the value prescribed in the JIS (Japan Industrial Standard) standard, and it cannot be used by itself in winter. This poor low-temperature performance is due to the fact that hydrogenated oil is a straight chain hydrocarbon (normal paraffin).

Table 5 Cold Flow Properties of Hydrogenated Palm Oil

		Hydrogenated Palm Oil	Palm FAME	Conventional Diesel Oil
Cloud point	℃	20	15	-6
Pour Point	℃	20.0	12.5	-30.0
CFPP	℃	22	11	-9

(4) Evaluation of hydrogenated oil in an actual vehicle (exhaust gas measurement test)

We evaluated the characteristics of the exhaust characteristic of the obtained hydrogenated oil. Two test fuels were used: one was base diesel fuel, the other was base fuel mixed with 20% hydrogenated palm oil. The test vehicle specifications and test drive mode, test fuel properties, are shown in Tables 6 and 7.

Table 6 Specifications of Test Vehicle

Displacement	2.0L
Fuel Supply System	Direct Injection
Fuel Injection System	Common Rail System
Transmission	5 Speed Manual
Test Mode	EC Mode

Table 7 Properties of Test Fuel (exhaust gas measurement test)

		Base Fuel	Base Fuel + Hydrogenated PO 20%	Hydrogenated PO
Density (15℃)	kg/m3	0.8283	0.8187	0.7852
Viscosity (30℃)	mm2/s	4.060	4.078	4.145
Higher Heating Value	J/g	45940	46130	47280
Distillation ℃	IBP	175.5	180.5	274.0
	T10	221.0	234.0	284.5
	T50	286.5	289.0	291.0
	T90	337.5	331.0	301.0
	EP	360.0	359.5	322.0
Cetane Number		60	67	101
Carbon	mass %	86.4	86.1	84.8
Hydrogen	mass %	13.5	13.8	15.1
Sulfur	mass ppm	4	3	<1

Test results are shown in Fig. 6. The Y-axis shows the rate of change from the base fuel. THC (total hydrocarbons) decreased 22%, CO decreased 15%, and PM decreased 11%. This is thought to be due to the higher cetane number or decreased amount of aromatic hydrocarbons that results when hydrogenated oil is added, but detailed analysis has not been carried out. We will perform additional tests and detailed analysis in the near future.

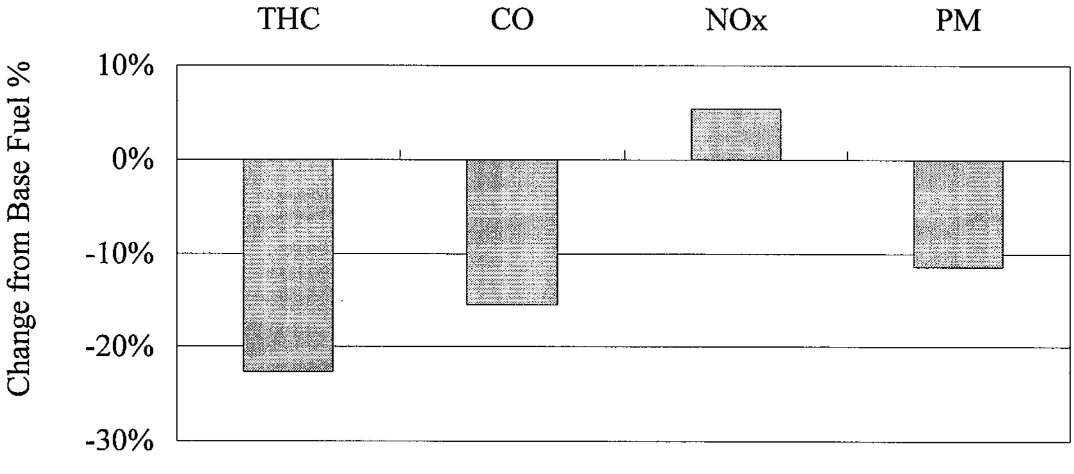

Fig.6 Vehicle Emission with Hydrogenated Palm Oil

4. CONSIDERATIONS

4.1 LCA evaluation of palm oil hydroprocessing

LCA (Life Cycle Assessment) evaluation of hydroprocessing of palm oil was performed. For comparison, we also evaluated diesel oil (petroleum) and palm FAME. For each oil, all processes from manufacture to consumption were considered, and CO_2 emissions and energy efficiency for each process were calculated.

The result is shown in Fig.7. WTT (well-to-tank) CO_2 per unit energy of hydrogenated palm oil and FAME would be higher than that of diesel oil. It is thought that this is largely caused by CO_2 generated in palm cultivation. However, as for TTW (tank-to-wheel) CO_2, because the "zero count" rule applies to both hydrogenated oil and FAME, WTW (well-to-wheel, or the total CO_2 generated from production to consumption) CO_2 for both hydrogenated oil and FAME ends up being lower than that of petroleum diesel.

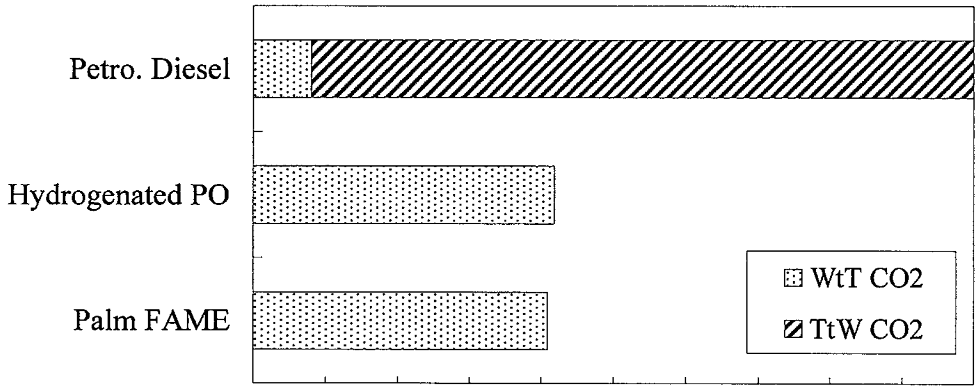

Fig.7 The Result of LCA-CO_2

The result of energy efficiencies is shown in Fig.8. Both hydrogenated PO and FAME were lower than that of petroleum diesel. This is due to the large amount of energy consumed in the palm oil extraction process. The energy efficiency of FAME is slightly lower than hydrogenated PO because of the energy needed to produce methanol, used in the manufacture of FAME.

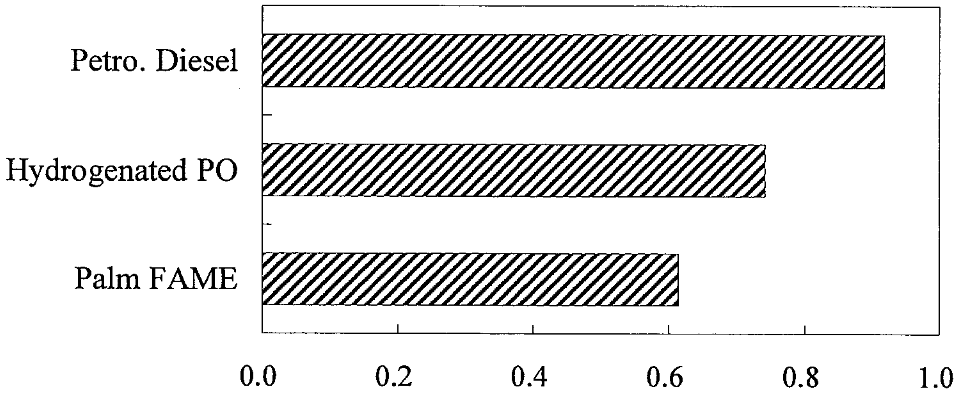

Fig.8 The Result of LCA-Energy Efficiencies

4.2 Hydrogenation reactivity

In the hydrogenation reaction of palm oil, it was shown that, in conditions in which complete hydrogenation of the unsaturated bonds was reached, the complete hydrodeoxygenation of the oil was also reached. Moreover, hydrodeoxygenation reactions include a dehydration reaction in which oxygen is eliminated as water (H_2O), and a decarbonation reaction in which oxygen is eliminated as carbon dioxide (CO_2) (Fig.9); both reactions were occurring in this processing. To eliminate a given quantity of oxygen, less hydrogen is consumed in decarbonation than in dehydration.

At such time when, through optimization of reaction conditions and catalysts, it becomes possible to control the hydrogenation reaction, we should select a reaction system based on which is best overall with respect to issues of hydrogen consumption, by-products, and LCA CO_2.

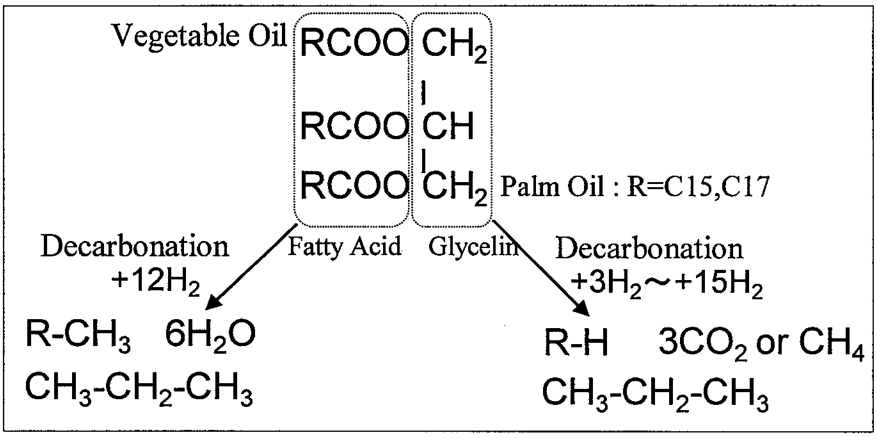

Fig.9 Scheme of Hydrodeoxygenation Reaction

4.3 Compatibility of hydrogenated palm oil for automotive fuels

As has been stated, the product oil obtained by hydrogenation is comprised mainly of straight chain hydrocarbons (normal paraffin) from C15 to C18. Distinctive properties of this oil are,

a) Better oxidation stability than FAME
b) Poor low-temperature properties
c) High cetane number.

If this hydrogenated oil is to be used as automotive fuel in the future, we think further study is required regarding the following points. With its high oxidation stability, it should be possible to mix hydrogenated PO with diesel in much higher proportion than the 5% upper limit now observed with FAME, owing to its lower stability and other problems. But it then becomes necessary to address the issue of low-temperature performance. We are planning the studies to improve cold flow property of Hydrogenated PO.

We evaluated the exhaust gas of real vehicles using short testing mode, and we are also planning to conduct prolonged endurance tests and to evaluate the oil's effects on car parts.

Furthermore, in any discussion of future automotive technologies to make use of the characteristics of hydrogenated oil, it is important that we take performance into account comprehensively, considering the goals of low sulfur, low aromatics, high cetane number, and good LCA results.

4.4 The problem of securing materials (environmental resources and food supply)

Palm oil and other vegetable oils (rapeseed, sunflower, soybean, corn, etc.) are used as cooking oils all over the world. If these oils are to be used for automotive fuels, it will probably not happen by getting people to use less for cooking. And if we simply increase cultivation, there is the risk of serious environmental destruction. We need to thoroughly consider how materials are to be secured, also looking at the use of non-edible vegetable oils such as Jatropha oil.

5. CONCLUSIONS

In our study of the hydrogenation of palm oil, the following things became clear.

a) By hydrogenating palm oil, it is possible to obtain from vegetable oil a hydrocarbon nearly equal to conventional diesel oil.
b) Hydrogenated PO was a straight chain hydrocarbon derived from the alkyl chains of the vegetable oil.
c) Hydrogenated PO has higher oxidation stability than FAME.
d) It is important that steps be taken to improve the low-temperature performance of hydrogenated PO, since it is poor compared to conventional diesel.
e) Evaluation of exhaust gases of vehicles running on conventional diesel mixed with 20% hydrogenated PO showed lower THC, CO, and PM than with base diesel alone.
f) LCA evaluation of hydrogenated PO, petroleum diesel oil, and FAME produced from palm showed that, although WTT-CO_2 of hydrogenated and FAME is higher that of diesel, WTW-CO_2 is lower due to the application of the biomass zero count rule.
g) LCA evaluation of hydrogenated PO, petroleum diesel oil, and FAME produced from palm showed that WTT energy efficiency was highest for petroleum diesel, followed by hydrogenated PO and then FAME.