

Viscosities and Densities of Binary and Ternary Blends of Palm Oil + Palm Biodiesel + Diesel Fuel at Different Temperatures

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Vegetable oil-based fuels are promising alternative fuels for diesel engines because of their environmental and strategic advantages. In this work, binary and ternary blends of palm oil, biodiesel, and diesel fuel were prepared, and dynamic viscosities and densities of blends were measured as functions of temperature. The binary and ternary blends demonstrate a temperature-dependent behavior, and viscosities and densities decreased nonlinearly and linearly with temperature, respectively. The evaluation of the measured viscosities of binary and ternary blends was completed, and the best correlation was obtained by a polynomial regression.

Introduction

Vegetable oil-based fuels are sustainable sources of fuel because, as long as they are produced in an ecologically sustainable way, they will not run out. Depending upon the climate and soil conditions, different countries are looking for different types of vegetable oils as substitutes for diesel fuels. For example, soybean oil in the US, rapeseed and sunflower oils in Europe, and palm oil in Southeast Asia (mainly Malaysia and Indonesia) are being considered.¹ All vegetable oils contain significant proportions of at least four fatty acids. Of all of the world's vegetable oils and fats produced in 2007, palm oil had the largest tonnage.² Malaysia is one of the world's largest palm oil producers and exporters, and vegetable oil-based fuel can be produced from this raw material in this country. It is reported that the total crude palm oil production within Malaysia is approximately 15.8 million tons per year in 2007.³

Vegetable oils can be used as fuels in conventional diesel engines directly without any modification. Diesel engines with vegetable oils suffer from operational and durability problems for long-term operation. Vegetable oils are much more viscous, relatively more reactive to oxygen, and have higher cloud point and pour point temperatures than petroleum-based diesel fuel.

These problems can be solved if the vegetable oils are chemically modified to biodiesel, which is similar in characteristics to diesel.¹ Biodiesel has substantially different properties than vegetable oils and results in better engine performance. However, there are some drawbacks of biodiesel like higher cost and cold flow properties.

Blending is one of the methods to overcome drawbacks of vegetable oils and biodiesel in engine performance. It is important to know the basic properties of blends. The rheological properties of fuel must be studied to determine behavioral and predictive information for the design and optimization of heating and fuel injection systems.⁴ Viscosity is one of the important fuel properties; modern diesel engines have fuel-injection systems that are sensitive to viscosity changes. High viscosity leads to poor atomization of the fuel, incomplete combustion, choking of the fuel injectors, and ring carbonization.⁵

Density data are important in numerous chemical engineering unit operations. Fuel density data as a function of temperature

are needed to model the combustion processes and other applications.

Many studies have been done involving blending of vegetable oils or biodiesel with diesel fuel, recently.^{6–11} However, ternary blends of vegetable oils, biodiesel, and diesel fuel were rarely or possibly never studied and characterized.

The present work is motivated by the fact that there is no comprehensive study of ternary blending of vegetable oils and biodiesel with diesel fuel. The specific objective of this work is to prepare binary and ternary blends of palm oil, biodiesel, and diesel fuel and measure the dynamic viscosities and densities of these blends as a function of temperature.

Experimental Section

Materials. RBD (refined, bleached, and deodorized) palm oil was purchased from a local market; the acid value, iodine value, and water mass fraction of the oil were measured to be 0.5, 53.2, and $400 \cdot 10^{-6}$, respectively. Methanol (99.8 %) was obtained from Sigma-Aldrich, Malaysia. Pure potassium hydroxide (98.9 %) was used as a catalyst for transesterification and was obtained from the same company. Commercially available no. 2 grade automotive diesel fuel was used in this study.

Biodiesel Preparation. Production of biodiesel was carried out in a batch reactor through the transesterification of palm oil. The reactor included a 2.5 L jacketed glass, mechanical stirrer (Kika Werke) fitted with a stainless steel propeller, thermometer, and water-cooled reflux condenser. To prepare and control reaction temperature, a RCS and RC6 (LAUDA) hot water circulation bath was employed. The reactor was filled with RBD palm oil and potassium hydroxide (mass fraction 1 %) dissolved in methanol. The reaction was carried out with mole ratio of methanol to oil of 6:1 at 50 °C for 1 h. After the end of transesterification, the glycerol was separated by separatory funnel. The produced methyl esters were washed with hot 0.1 % aqueous tannic acid solution three times. The excess water and methanol were removed on a rotary evaporator at atmospheric pressure.

Fatty Acid Composition Analysis. The composition of the palm oil and biodiesel were analyzed by gas chromatography using an HP 6890 series gas chromatograph (GC) system equipped with a flame ionization detector (FID) and automated

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Table 1. Fatty Acid Compositions of Palm Oil and Palm Biodiesel

| | fatty acid mass percent | | | | |
|----------------|-------------------------|------|------|------|-------|
| | 16:0 | 16:1 | 18:0 | 18:1 | other |
| palm oil | 43.9 | 4.4 | 39.8 | 10.6 | 1.3 |
| palm biodiesel | 43.9 | 4.4 | 39.8 | 10.6 | 1.3 |

Table 2. Compositions of Diesel Fuel No. 2¹⁴

| carbon number | volume percent | | |
|---------------|----------------|----------------|-----------|
| | paraffins | cycloparaffins | aromatics |
| C10 | 0.9 | 0.6 | 0.4 |
| C11 | 2.3 | 1.7 | 1.0 |
| C12 | 3.8 | 2.8 | 1.6 |
| C13 | 6.4 | 4.8 | 2.8 |
| C14 | 8.8 | 6.6 | 3.8 |
| C15 | 7.4 | 5.5 | 3.2 |
| C16 | 5.8 | 4.4 | 2.5 |
| C17 | 5.5 | 4.1 | 2.4 |
| C18 | 4.3 | 3.2 | 1.8 |
| C19 | 0.7 | 0.6 | 0.3 |

split injector (Agilent 7683 automatic sampler). The column was a 60 m × 0.248 mm × 0.15 μm DB-23 capillary column (J & W Scientific, USA).

Blends Preparation. To prepare binary mixtures, palm oil (1), palm biodiesel (2), and no. 2 grade automotive diesel fuel (3) were blended at volume fraction of 95 %, 90 %, 85 %, 80 %, and 70 %. Ternary blends with various compositions were prepared by mixing palm oil and palm biodiesel with proper amounts of diesel fuel by volume.

Viscosity Measurements. Viscosities of binary and ternary mixtures were measured using a VT550 rotary viscometer (HAAKE, Germany) with a NV sensor. A RCS and RC6 (LAUDA) circulating water bath was employed to prepare and control the required measurement temperature by water circulation through the jacket of viscometer. The temperatures were checked with two digital thermometers in the water bath and the viscometer. The system was isolated from external factors. The viscometer was calibrated using published viscosity values for ethanol and water.¹² The measurement was started 5 min after the temperature reached its value over the range of (20 to 90) °C with 10 °C intervals. The uncertainties of the viscosity values are within the range of ± 0.01 mPa·s.

Density Measurements. Density measurements were carried out using a DMA 4500 density/specific gravity meter (Anton Paar, Austria). The adjustment of the density meter was checked using degassed bidistilled water; the measured value at 25 °C was compared with the corresponding value in the density tables,¹³ and the difference was ± 0.00005 g·cm⁻³. Blend densities were measured at temperatures from (15 to 90) °C, and the uncertainty in density measurements was ± 0.00005 g·cm⁻³.

Results and Discussion

Composition Analysis. The compositions of palm oil and palm oil biodiesel detected by GC-FID are presented in Table 1. The composition of diesel fuel no. 2 based on relative percentages of paraffins, cycloparaffins, and aromatics per carbon number is presented in Table 2.¹⁴

Viscosity Measurements. Dynamic viscosities of binary and ternary blends of palm oil, biodiesel, and diesel fuel were measured from (20 to 90) °C at 10 °C intervals. All viscosity data reported here are means of triplicate determinations.

Figures 1, 2, and 3 show the variations in viscosities of binary blends of palm oil + biodiesel, palm oil + diesel fuel, and biodiesel + diesel fuel with composition and temperature. The

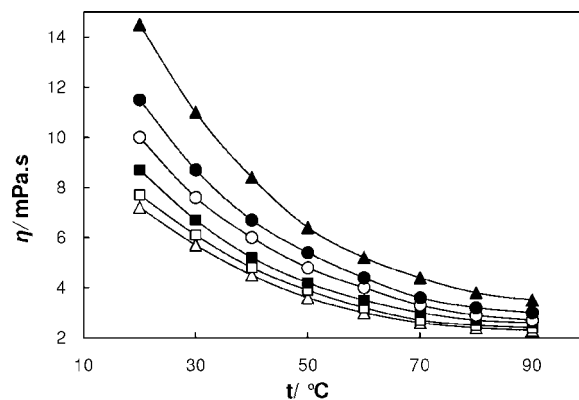


Figure 1. Viscosity η of palm oil–biodiesel blends at different volume fractions as a function of temperature. Δ , 100 % biodiesel; \square , 95 % biodiesel; \blacksquare , 90 % biodiesel; \circ , 85 % biodiesel; \bullet , 80 % biodiesel; \blacktriangle , 70 % biodiesel.

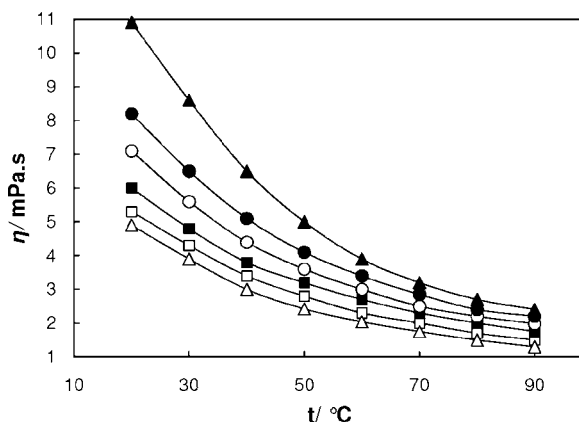


Figure 2. Viscosity η of palm oil–diesel blends at different volume fractions as a function of temperature. Δ , 100 % diesel; \square , 95 % diesel; \blacksquare , 90 % diesel; \circ , 85 % diesel; \bullet , 80 % diesel; \blacktriangle , 70 % diesel.

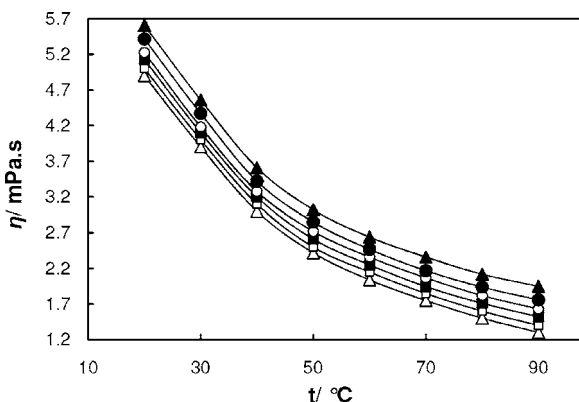


Figure 3. Viscosity η of palm biodiesel–diesel blends at different volume fractions as a function of temperature. Δ , 100 % diesel; \square , 95 % diesel; \blacksquare , 90 % diesel; \circ , 85 % diesel; \bullet , 80 % diesel; \blacktriangle , 70 % diesel.

results indicate that the binary blends demonstrate temperature-dependent behavior; their viscosities decrease nonlinearly with temperature. At a fixed temperature, the palm oil–diesel fuel and biodiesel–diesel fuel blend viscosities decrease with increasing volume fraction of diesel fuel in the mixture. The decrease in viscosity also can be seen with an increase in biodiesel volume fraction in the palm oil–biodiesel blend.

Figures 4, 5, and 6 show the effects of temperature and composition on dynamic viscosities of palm oil + biodiesel + diesel fuel blends. The ternary blends demonstrate nonlinearity temperature dependence behavior similarly to those of the binary

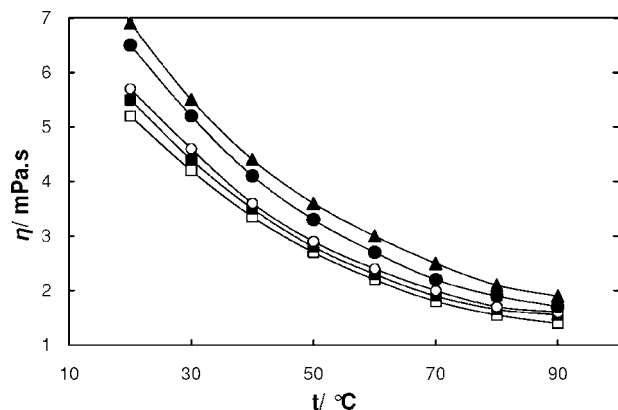


Figure 4. Viscosity η of palm oil–biodiesel–diesel fuel blends (high biodiesel content) at different volume fractions as a function of temperature. \square , 1.5 % oil, 3.5 % biodiesel, 95 % diesel; \blacksquare , 3 % oil, 7 % biodiesel, 90 % diesel; \circ , 4.5 % oil, 11.5 % biodiesel, 85 % diesel; \bullet , 6 % oil, 14 % biodiesel, 80 % diesel; \blacktriangle , 9 % oil, 21 % biodiesel, 70 % diesel.

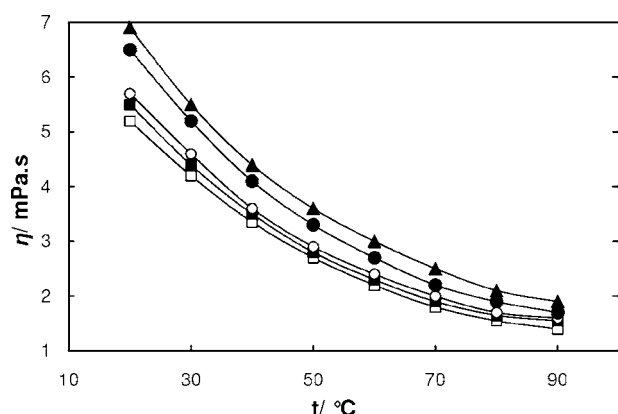


Figure 5. Viscosity η of palm oil–biodiesel–diesel fuel blends (equal oil and biodiesel contents) at different temperatures. \square , 2.5 % oil, 2.5 % biodiesel, 95 % diesel; \blacksquare , 5 % oil, 5 % biodiesel, 90 % diesel; \circ , 7.5 % oil, 7.5 % biodiesel, 85 % diesel; \bullet , 10 % oil, 10 % biodiesel, 80 % diesel; \blacktriangle , 15 % oil, 15 % biodiesel, 70 % diesel.

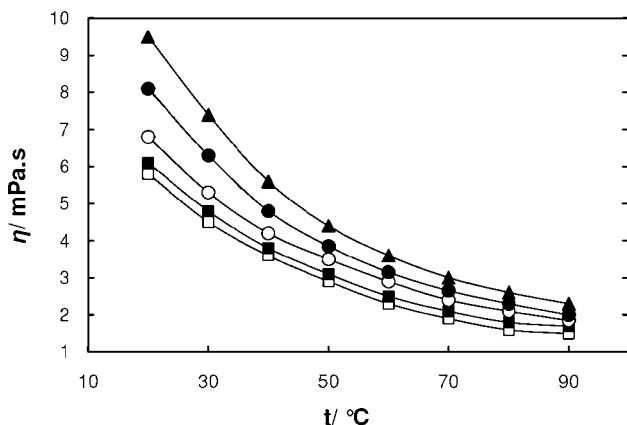


Figure 6. Viscosity η of palm oil–biodiesel–diesel fuel blends (high oil content) at different temperatures. \square , 3.5 % oil, 1.5 % biodiesel, 95 % diesel; \blacksquare , 7 % oil, 3 % biodiesel, 90 % diesel; \circ , 11.5 % oil, 4.5 % biodiesel, 85 % diesel; \bullet , 14 % oil, 6 % biodiesel, 80 % diesel; \blacktriangle , 21 % oil, 9 % biodiesel, 70 % diesel.

blends and, at a fixed temperature increase of diesel fuel content, reduce dynamic viscosity. The accuracy evaluation of the measured viscosities of binary and ternary blends was done by correlating them with temperature by means of linear, exponential, power, and polynomial equations. The best correlation was obtained using a polynomial equation ($R^2 = 0.99$).

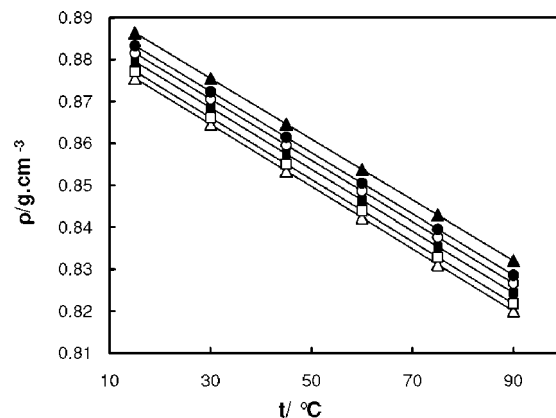


Figure 7. Density ρ of palm oil–biodiesel blends at different volume fractions as a function of temperature. \triangle , 100 % biodiesel; \square , 95 % biodiesel; \blacksquare , 90 % biodiesel; \circ , 85 % biodiesel; \bullet , 80 % biodiesel; \blacktriangle , 70 % biodiesel.

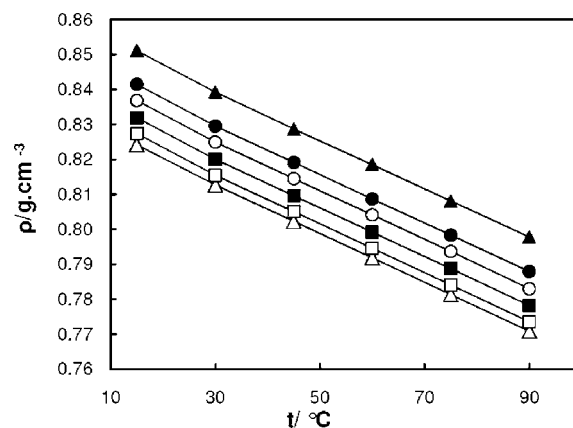


Figure 8. Density ρ of palm oil–diesel blends at different volume fractions as a function of temperature. \triangle , 100 % diesel; \square , 95 % diesel; \blacksquare , 90 % diesel; \circ , 85 % diesel; \bullet , 80 % diesel; \blacktriangle , 70 % diesel.

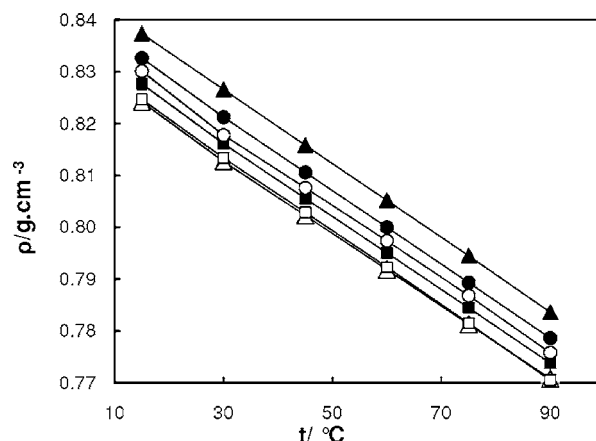


Figure 9. Density ρ of palm biodiesel–diesel blends at different volume fractions as a function of temperature. \triangle , 100 % diesel; \square , 95 % diesel; \blacksquare , 90 % diesel; \circ , 85 % diesel; \bullet , 80 % diesel; \blacktriangle , 70 % diesel.

Density Measurements. Figures 7, 8, and 9 present the densities of binary blends of palm oil + biodiesel, palm oil + diesel fuel, and biodiesel + diesel fuel. Figures 10, 11, and 12 show the effects of temperature and composition on dynamic viscosities of palm oil + biodiesel + diesel fuel blends. The results indicate that the binary and tertiary blends demonstrate temperature-dependent behavior and the liquid density of blends decreases linearly with the increase in temperatures. The accuracy of the density data was further evaluated by correlating

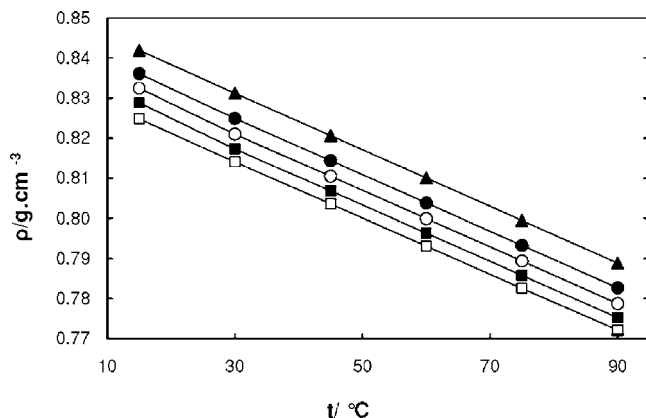


Figure 10. Density ρ of palm oil–biodiesel–diesel fuel blends (high biodiesel content) at different volume fractions as a function of temperature. \square , 1.5 % oil, 3.5 % biodiesel, 95 % diesel; \blacksquare , 3 % oil, 7 % biodiesel, 90 % diesel; \circ , 4.5 % oil, 11.5 % biodiesel, 85 % diesel; \bullet , 6 % oil, 14 % biodiesel, 80 % diesel; \blacktriangle , 9 % oil, 21 % biodiesel, 70 % diesel.

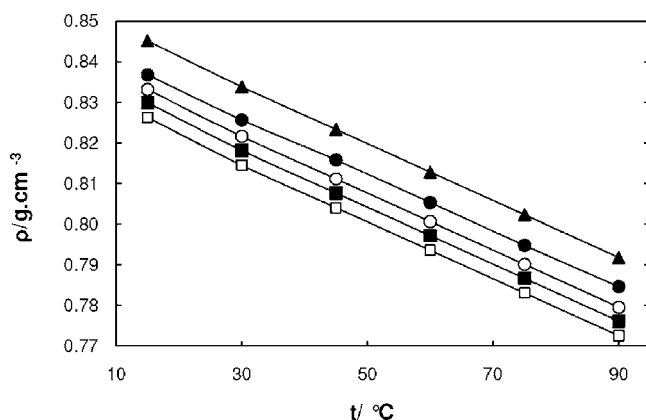


Figure 11. Density ρ of palm oil–biodiesel–diesel fuel blends (equal oil and biodiesel contents) at different temperatures. \square , 2.5 % oil, 2.5 % biodiesel, 95 % diesel; \blacksquare , 5 % oil, 5 % biodiesel, 90 % diesel; \circ , 7.5 % oil, 7.5 % biodiesel, 85 % diesel; \bullet , 10 % oil, 10 % biodiesel, 80 % diesel; \blacktriangle , 15 % oil, 15 % biodiesel, 70 % diesel.

them with temperature by means of a linear equation, and good correlations were obtained ($R^2 = 0.99$).

Conclusions

In this work the variations of viscosities and densities were measured when the no. 2 grade automotive diesel fuel is blended with biodiesel and palm oil. The binary and ternary blends demonstrate temperature-dependent behaviors. Viscosities and densities of blends decreased nonlinearly and linearly with temperature, respectively. The accuracy evaluation of the measured viscosities of binary and ternary blends was done by correlation, and the best correlation was obtained by using polynomial regression. For the density data the best correlation was obtained using a linear equation.

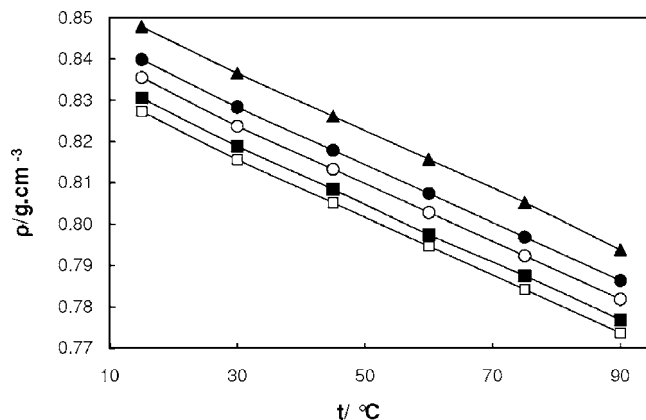


Figure 12. Density ρ of palm oil–biodiesel–diesel fuel blends (high oil content) at different temperatures. \square , 3.5 % oil, 1.5 % biodiesel, 95 % diesel; \blacksquare , 7 % oil, 3 % biodiesel, 90 % diesel; \circ , 11.5 % oil, 4.5 % biodiesel, 85 % diesel; \bullet , 14 % oil, 6 % biodiesel, 80 % diesel; \blacktriangle , 21 % oil, 9 % biodiesel, 70 % diesel.

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