

## CHAPTER IV

### RESULTS AND DISCUSSION

In this chapter, palm oil characterization, a comparative study of the phase behavior of diesel-palm oil alkyl ester-ethanol 99.5% and diesel-palm oil alkyl ester-butanol 99.9% (diesohol) three-component systems at different component concentrations, and the dependence of solubility on temperature will be presented. In addition, the fuel properties of the diesohol blends will be discussed and compared with those of diesel fuel.

#### 4.1 Palm Oil Characterization

A chromatogram of palm oil methyl ester is shown in Figure 4.1.

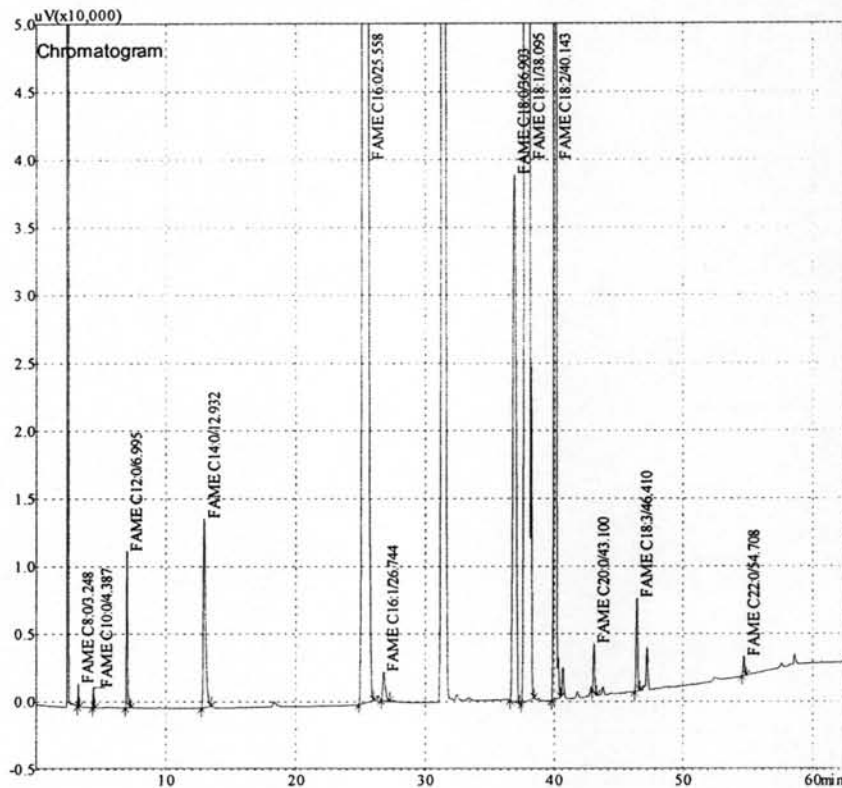


Figure 4.1 Chromatogram of palm oil methyl ester.

From the chromatogram, the observed peak was identified by comparison with the time of the standard. Since biodiesels –methyl, ethyl and butyl esters– produced in this thesis are derived from the same source, the palm oil, the chromatograms of those biodiesels were expected to have the same patterns. The chromatograms showed that the major composition in palm oil alkyl esters was Oleic (monounsaturated fatty acid) and Palmitic (medium-chain saturated fatty acid) which was the typical fatty acid composition of palm oil, as shown in Table 4.1. For quantitative analysis, the peak area was then converted to the concentration of each component based on the calibration curves. The analysis from the chromatogram showed that the molecular weight of palm oil used in this research is approximately 851 g/mol (calculation is shown in the Appendix).

**Table 4.1** Fatty acid composition (wt%) of the biodiesel (palm oil alkyl esters)

<b>Fatty acid</b>	<b>PME</b>	<b>PEE</b>	<b>PBE</b>
Caprylic (C8:0)	0.02	0.04	0.03
Capric (C10:0)	0.03	0.04	0.04
Lauric (C12:0)	0.30	0.41	0.37
Myristic (C14:0)	0.81	1.03	0.99
Palmitic (C16:0)	38.12	39.09	39.13
Palmitoleic (C16:1)	0.14	0.85	0.91
Stearic (C18:0)	3.44	2.36	2.34
Oleic (C18:1)	45.96	45.64	44.61
Linoleic (C18:2)	10.69	10.20	11.17
Linolenic (C18:3)	0.29	0.15	0.17
Arachidic (C20:0)	0.15	0.18	0.19
Behenic (C22:0)	0.05	0.02	0.03

## 4.2 Phase Behavior Definitions

Ternary phase diagrams are widely used to depict the phase behavior of three-component systems. First of all, the phase behavior definitions used in this research have to be announced. The physical appearance can be categorized in five conditions, as shown in Figure 4.2.

- *Clear Liquid 1 Phase*

Clear liquid 1 phase or liquid 1 phase, in short, is a single-phase liquid system. It looks homogeneous and clear. No crystallinity or particles are observed.

- *Clear Liquid 2 Phase*

Liquid 2 phase is a double-phase liquid system. Both layers are clear. No crystallinity or particles are observed.

- *Crystalline Liquid 1 Phase*

Crystalline liquid 1 phase is a single-phase liquid system. The whole system looks cloudy or turbid and flows like a liquid, but has the molecules in the liquid arranged and/or oriented in a crystal-like way.

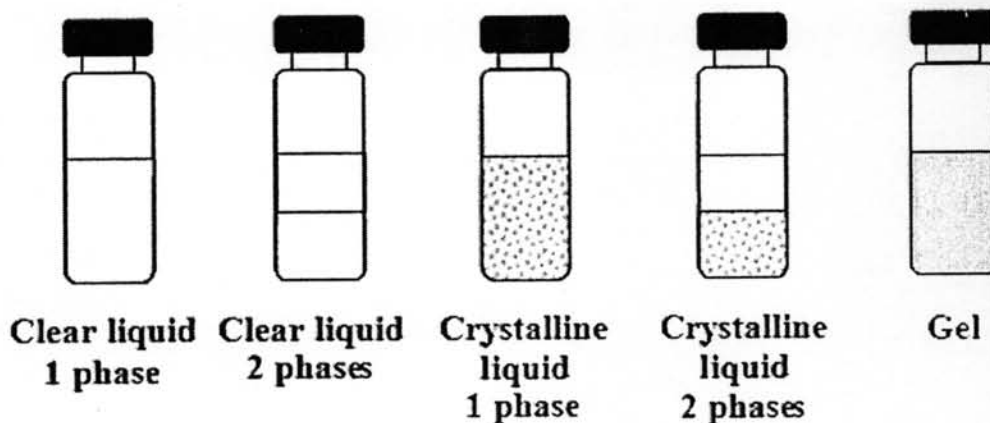
- *Crystalline Liquid 2 Phase*

Crystalline liquid 2 phases is a double-phase liquid system. This system must have at least one phase looking cloudy or turbid. However, the top layer is normally clear, while the bottom one is turbid.

Crystallization usually occurs at low temperatures. These crystals are semitransparent and disappear relatively quickly when the system temperature is increased.

- *Gel*

A gel is a non-moveable system which occurs at low temperatures. It is white and yellow-colored and is slow to dissolve when the system temperature is increased.



**Figure 4.2** Physical appearance of three-component systems (Adapted from Fernando and Hanna, 2004).

### 4.3 Effect of Temperature on Phase Stability

One of the main characteristics of diesel fuel is the stability at low temperatures. The fuel must be fluid and have good filterability. The production of three-component systems needs to evaluate the dependence of solubility on temperature for the determination of the ratio of components in order to obtain stable mixtures.

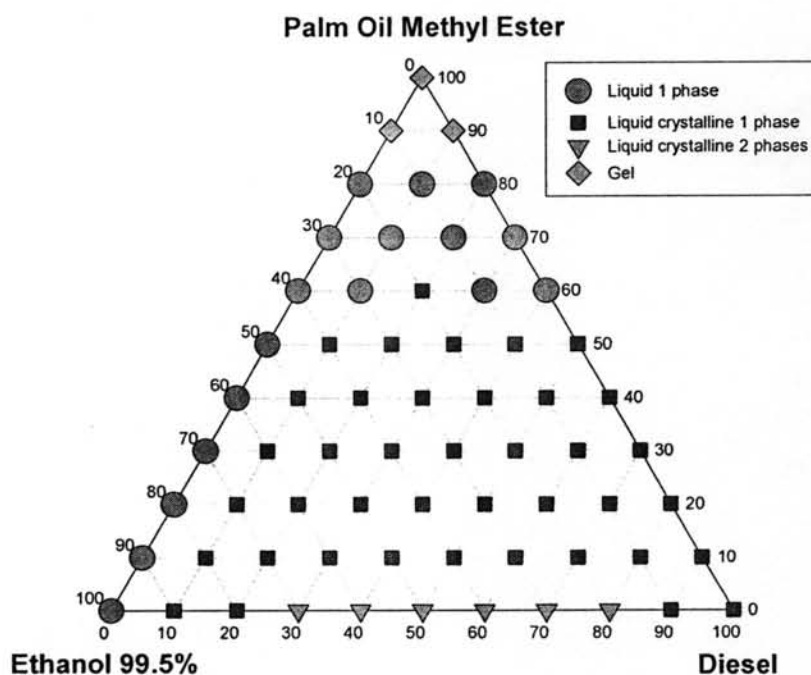
From previous work (Kwanchareon *et al.*, 2006), it was found that at room temperature, both ethanol 99.5% and ethanol 99.9% produced homogeneous solution of diesohol blends. However, since ethanol 99.5% is much cheaper than ethanol 99.9% and can be produced in our country, ethanol 99.5% was chosen to blend with diesel and biodiesel in order to study the phase behavior and fuel properties.

#### 4.3.1 Phase Behavior of Diesohol at 10°C

- *Diesel-Palm Oil Methyl Ester-Ethanol 99.5% (D-PME-E99.5%) System*

Figure 4.3 shows the solubility of the D-PME-E99.5% system at 10°C. From the figure, the circle points represent liquid 1 phase, the square points represent crystalline liquid 1 phase, the triangle points down represent crystalline liquid 2

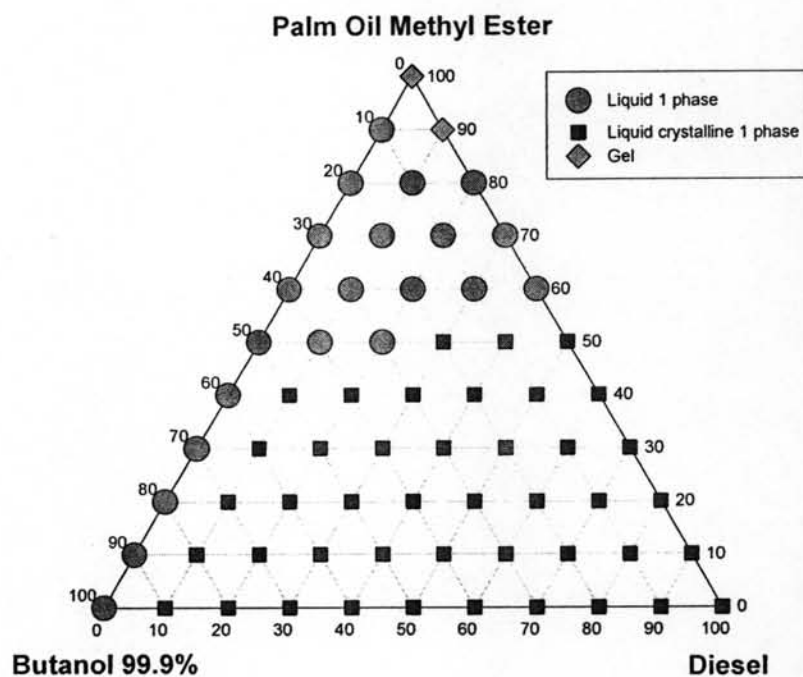
phases, and the diamond points represent gel condition. In the system, PME and ethanol were miscible, except in the mixture containing 10% by volume of ethanol in PME. For the solubility of ethanol in diesel fuel, since ethanol cannot be completely mixed with diesel fuel over a wide range of temperature (Xing-cai *et al.*, 2004, and Hansen *et al.*, 2005), the phase separation occurred at a ratio of 20 to 70% of ethanol in diesel fuel, in which the lower phase became cloudy. In addition, we can observe the tendency that the mixtures containing up to 50% by volume of PME were liquid crystalline 1 phases. At 10°C, it was a temperature below the pour point of PME which lead to gel the mixtures containing PME from 90 up to 100% by volume. The gel was white-colored and was slow to dissolve when the system temperature was increased. It seems reasonable to assume that it was the effect of the fatty acid in the biodiesel component (Knothe, 2005). And the other ratios were liquid 1 phase.



**Figure 4.3** Phase behavior of diesel-palm oil methyl ester-ethanol 99.5% (D-PME-E99.5%) system at 10°C.

- *Diesel-Palm Oil Methyl Ester-Butanol 99.9% (D-PME-B99.9%) System*

From Figure 4.4, we can see that the solubility in the case of the D-PME-B99.9% system was slightly increased when compared to the solubility in the case of D-PME-E99.5% at 10°C. It seems that at low temperatures, the effect of the larger alcohol as a blending component on the intersolubility of three-component system was minimal. The reason might be explained in that the other components, diesel and PME, which normally have higher pour point than alcohol, have stronger effects than alcohol.

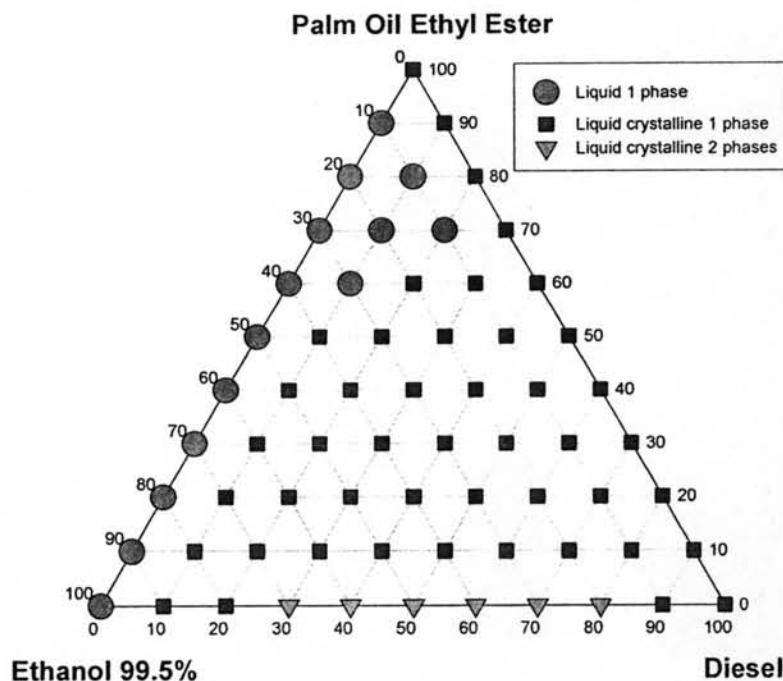


**Figure 4.4** Phase behavior of diesel-palm oil methyl ester-butanol 99.9% (D-PME-B99.9%) system at 10°C.



- *Diesel-Palm Oil Ethyl Ester-Ethanol 99.5% (D-PEE-E99.5%) System*

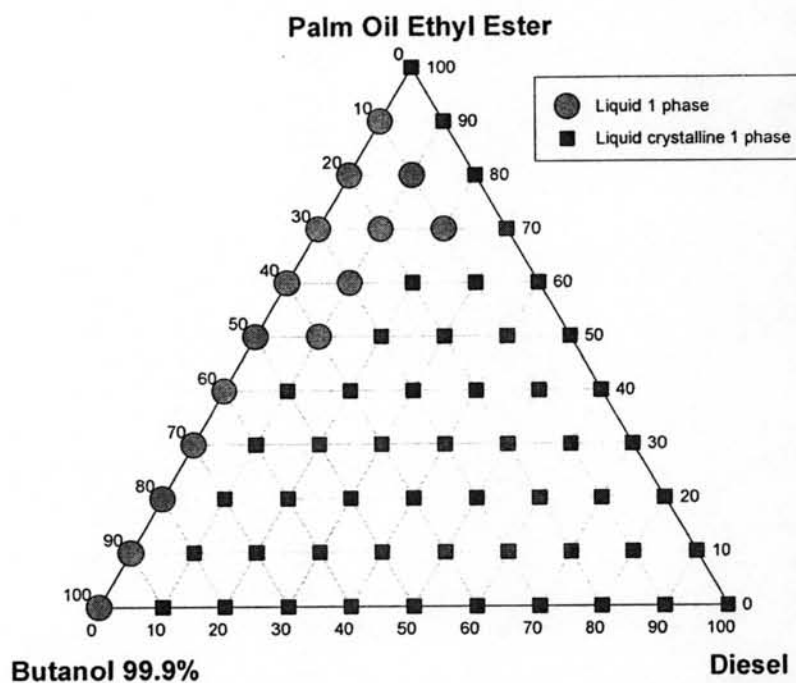
For the purpose of expanding the usage of bioethanol, PME in the three-component system was changed to PEE produced from the transesterification of palm oil with ethanol. Figure 4.5 shows the solubility of the D-PEE-E99.5% system at 10°C. It was found that the intersolubility of the PEE-E99.5% was not limited. Almost all the blends containing PEE were liquid crystalline which was affected by the solubility of PEE in diesel fuel. It seems that the solubility of PEE in diesel fuel was slightly decreased when compared to the solubility of PME. It could be explained that the PEE production via transesterification is slower than that of PME, resulting in an incomplete reaction, and it may have side reactions. Therefore, the mixtures containing PEE seem rather liquid-crystalline at low temperature, more than the mixtures containing PME. These crystalline materials might be mono- and di-glycerides (Lang *et al.*, 2001) which crystallized easily from the biodiesel (Gerpen, 2005).



**Figure 4.5** Phase behavior of diesel-palm oil ethyl ester-ethanol 99.5% (D-PEE-E99.5%) system at 10°C.

- *Diesel-Palm Oil Ethyl Ester-Butanol 99.9% (D-PEE-B99.9%) System*

Figure 4.6 shows that the solubility in the case of the D-PEE-B99.9% system was slightly increased when compared to the solubility in the case of D-PEE-E99.5% at 10°C. The liquid 2 phases was not observed, which means that butanol was miscible in diesel fuel and decreased the problem of phase separation occurring in the ethanol systems.

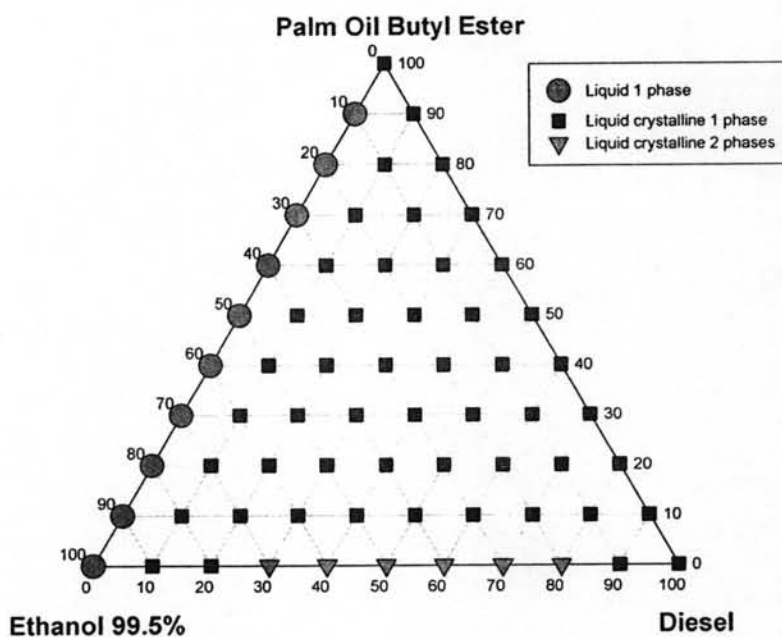


**Figure 4.6** Phase behavior of diesel-palm oil ethyl ester-butanol 99.9% (D-PEE-B99.9%) system at 10°C.



- *Diesel-Palm Oil Butyl Ester-Ethanol 99.5% (D-PBE-E99.5%) System*

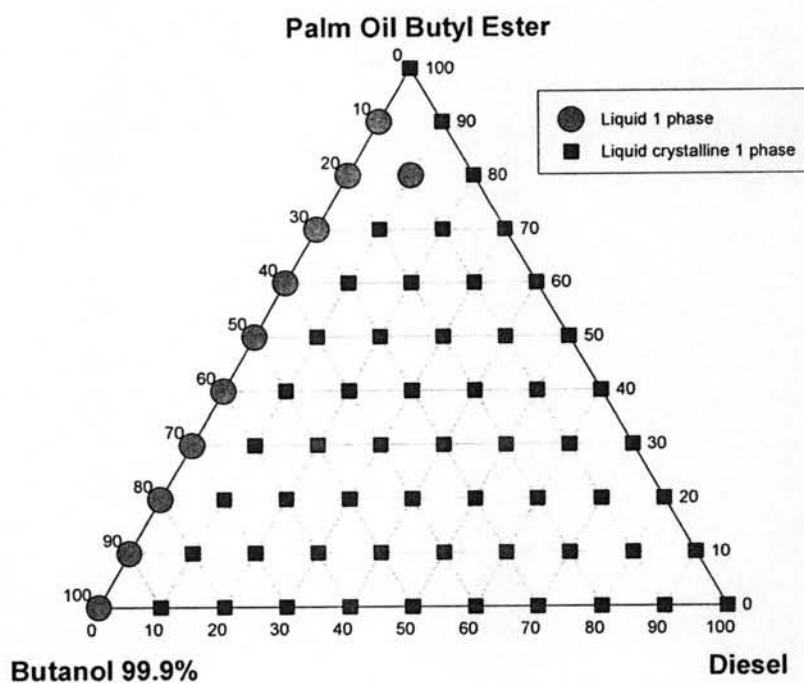
For studying the effect of various types of biodiesel on the phase behavior, butyl ester was chosen due to its advantage of its raw materials being derived from bioresources. The solubility of the D-PBE-E99.5% system at 10°C is shown in Figure 4.7. It can be observed that almost all the blends were liquid crystalline 1 phase except for the blends containing PBE and ethanol, since PBE and ethanol were miscible. However, the solubility of PBE in diesel fuel was slightly lower when compared to the solubility of PME and PEE. This might be explained as described in the D-PEE-E99.5% system.



**Figure 4.7** Phase behavior of diesel-palm oil butyl ester-ethanol 99.5% (D-PBE-E99.5%) system at 10°C.

- Diesel-Palm Oil Butyl Ester-Butanol 99.9% (D-PBE-B99.9%)  
System

Figure 4.8 shows the solubility of the D-PME-B99.9% system at 10°C. Although the use of butanol instead of ethanol decreased the problem of phase separation, the liquid crystalline 1 phase was observed at almost all ratios. This is because of the low solubility of PBE in diesel fuel.

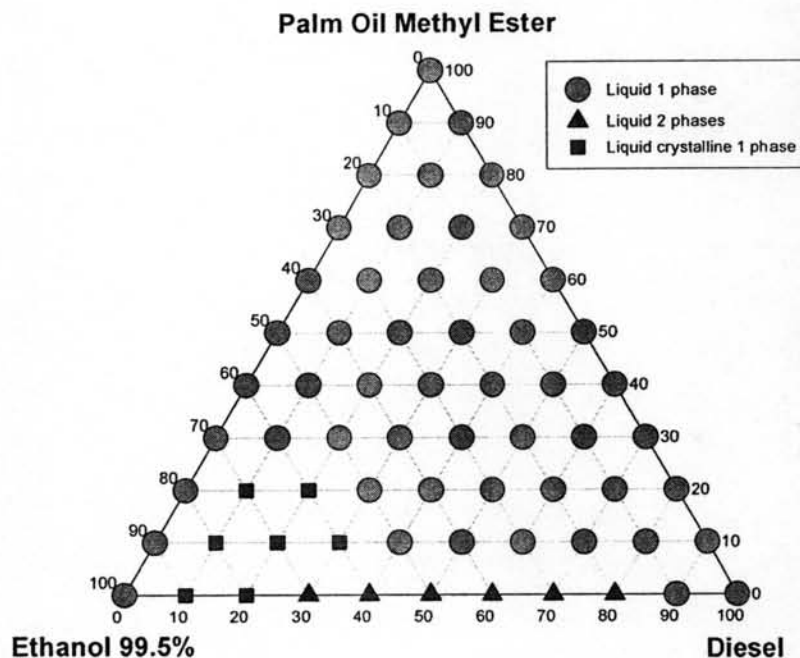


**Figure 4.8** Phase behavior of diesel-palm oil butyl ester-butanol 99.9% (D-PBE-B99.9%) system at 10°C.

#### 4.3.2 Phase Behavior of Diesohol at 20°C

- *Diesel-Palm Oil Methyl Ester-Ethanol 99.5% (D-PME-E99.5%) System*

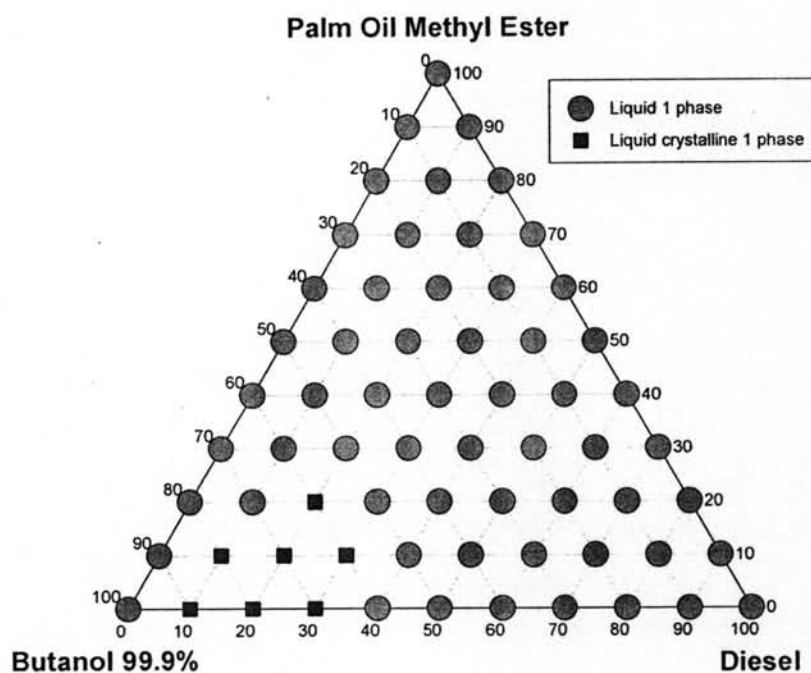
As shown in Figure 4.9, at 20°C, almost all the blends were liquid 1 phase except for the ratios of ethanol 20 to 70% with diesel. These ratios were liquid 2 phases. However, when the diesel concentration was lower than 40% and ethanol concentration was 60 to 90%, semitransparent crystals appeared in the solution. These results have the same trend as those earlier reported by Fernando and Hanna (2004). These crystals disappeared relatively quickly when the system temperature was increased. Since these crystals appeared when the ethanol concentration was higher than PME, it could be assumed that the majority of the crystals were alcohol (Fernando and Hanna, 2004).



**Figure 4.9** Phase behavior of diesel-palm oil methyl ester-ethanol 99.5% (D-PME-E99.5%) system at 20°C.

- Diesel-Palm Oil Methyl Ester-Butanol 99.9% (D-PME-B99.9%)  
System

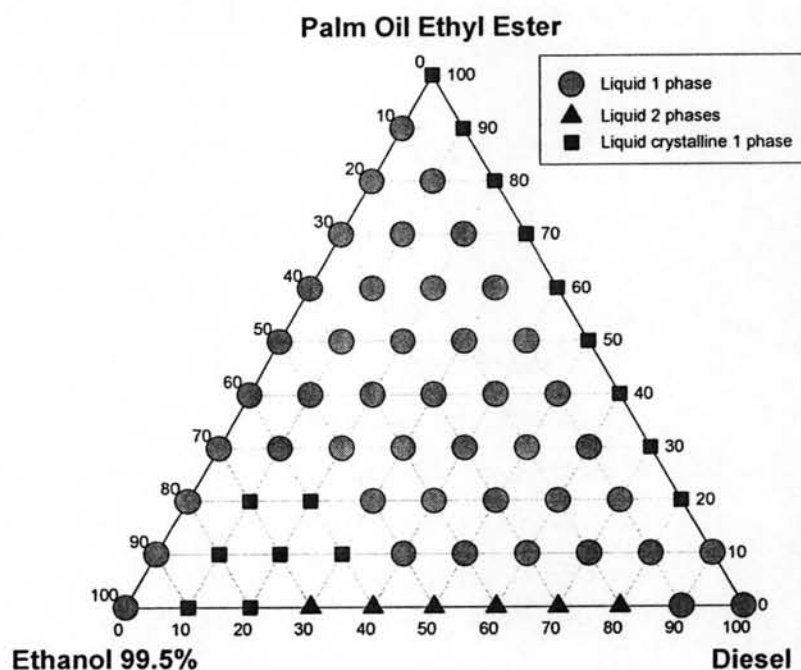
Figure 4.10 shows the solubility of the D-PME-B99.9% system at 20°C. In this system, almost all the blends were liquid 1 phase except for the ratios of butanol 60 to 90% by volume. These ratios were liquid crystalline 1 phase. From the figure, it can be seen that at 20°C, the intersolubility of diesel-butanol was higher than the intersolubility of diesel-ethanol since the liquid 2 phases was not observed. The reason is that butanol has higher carbon numbers than ethanol, which means it is more soluble in diesel fuel. This implies that the use of butanol decreased the problem of phase separation, which was a crucial problem of the diesel-ethanol blend.



**Figure 4.10** Phase behavior of diesel-palm oil methyl ester-butanol 99.9% (D-PME-B99.9%) system at 20°C.

- *Diesel-Palm Oil Ethyl Ester-Ethanol 99.5% (D-PEE-E99.5%) System*

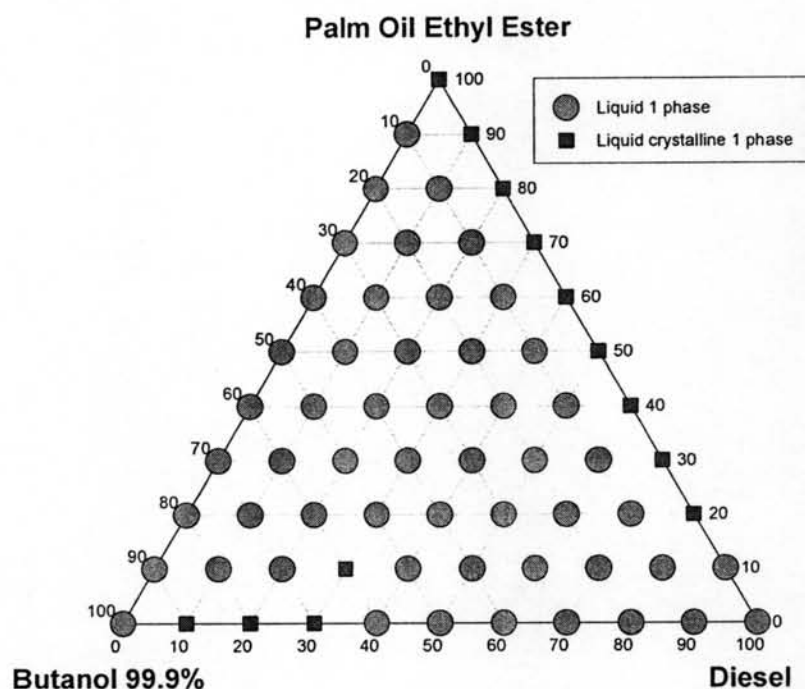
In this system, there was a liquid crystalline 1 phase at the ratio of ethanol 60 to 90% by volume, as shown in Figure 4.11. In addition, some crystals occurred in the blends of more than 10% by volume of PEE and diesel without ethanol. These crystals might be mono- and di-glyceride (Lang *et al.*, 2001) which crystallized easily from the biodiesel (Gerpen, 2005). For the blends of ethanol and diesel fuel without PEE, at 20°C, the solubility remained limited at the ratio of 20 to 70% ethanol in diesel fuel which had liquid 2 phases.



**Figure 4.11** Phase behavior of diesel-palm oil ethyl ester-ethanol 99.5% (D-PEE-E99.5%) system at 20°C.

- *Diesel-Palm Oil Ethyl Ester-Butanol 99.9% (D-PEE-B99.9%) System*

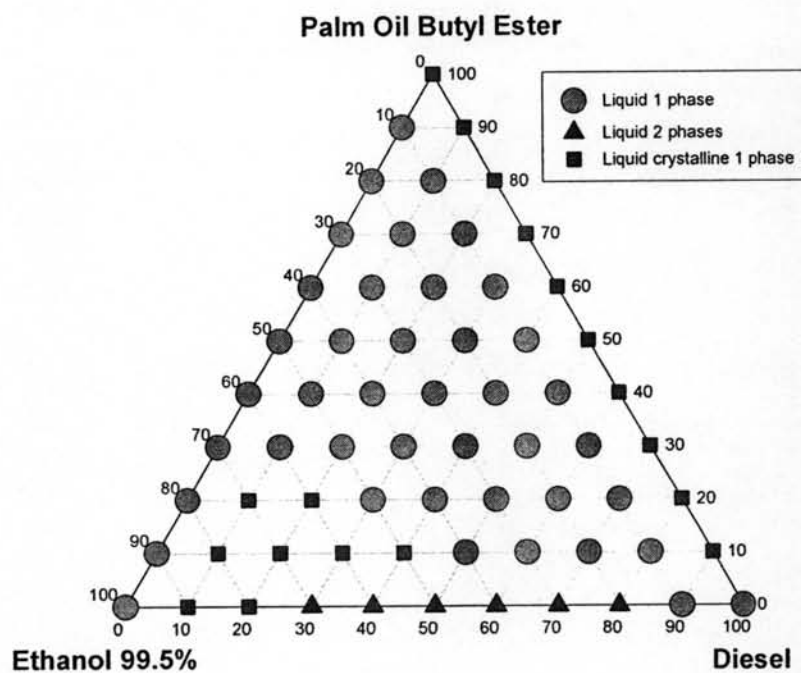
The solubility in the case of the D-PEE-B99.9% system was slightly increased when compared to the solubility in the case of the D-PME-E99.5% at 20°C. For consideration of the intersolubility of three-component system, only one ratio appeared in the liquid crystalline 1 phase which was a blend of 30% diesel, 10% PEE, and 60% butanol. The liquid 2 phases was not observed.



**Figure 4.12** Phase behavior of diesel-palm oil ethyl ester-butanol 99.9% (D-PEE-B99.9%) system at 20°C.

- *Diesel-Palm Oil Butyl Ester-Ethanol 99.5% (D-PBE-E99.5%) System*

From Figure 4.13, the phase behavior of the D-PBE-E99.5% system at 20°C was found to be the same as that of the D-PEE-E99.5% system at the same temperature.

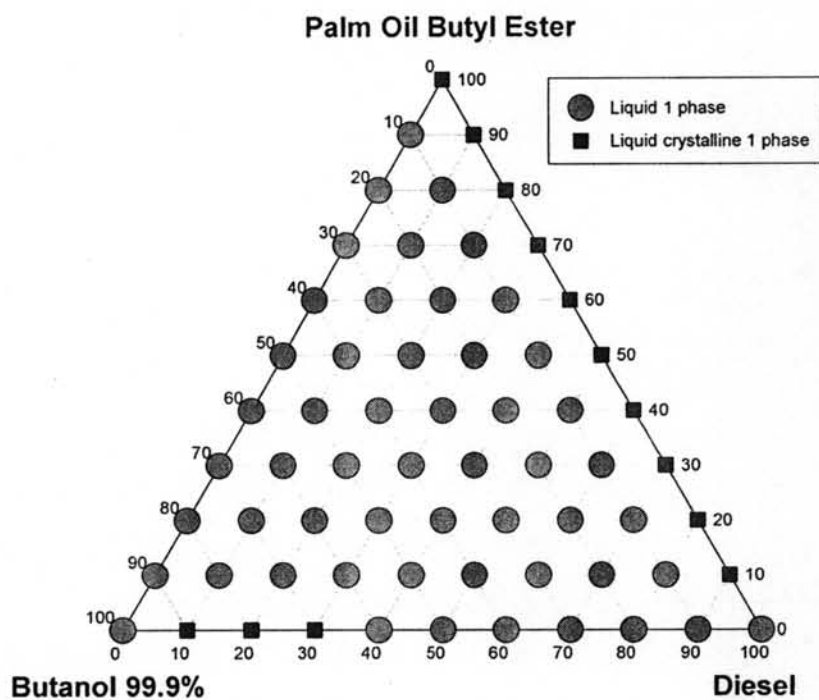


**Figure 4.13** Phase behavior of diesel-palm oil butyl ester-ethanol 99.5% (D-PBE-E99.5%) system at 20°C.



- *Diesel-Palm Oil Butyl Ester-Butanol 99.9% (D-PBE-B99.9%) System*

Figure 4.14 shows the solubility of the D-PBE-B99.9% system at 20°C. It can be seen that the blends of D-PBE-B99.9% at all ratios were liquid 1 phase while some blends of D-B99.9% and D-PBE were liquid crystalline 1 phase. It is assumed that the D-PBE-B99.9% three-component system had higher solubility than D-B99.9% and D-PBE.

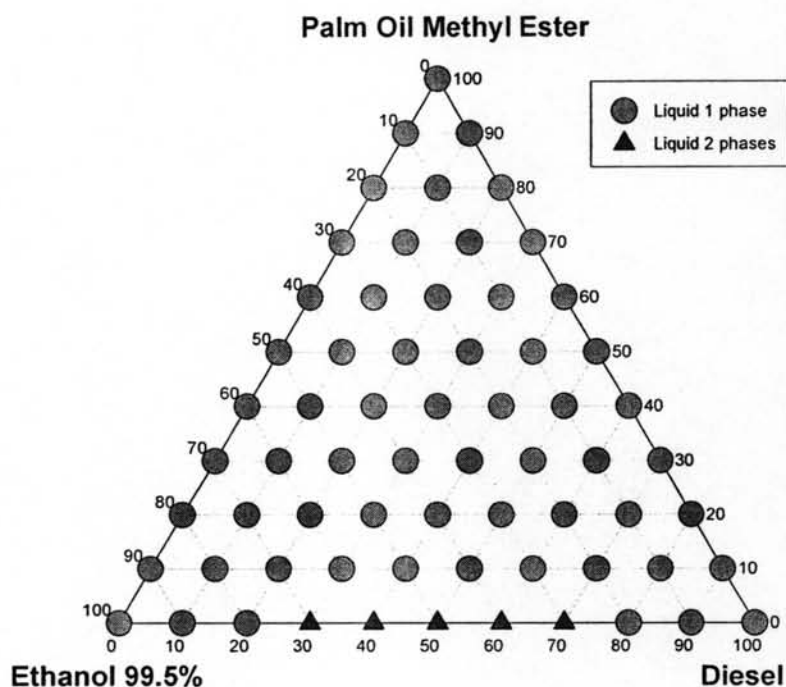


**Figure 4.13** Phase behavior of diesel-palm oil butyl ester-butanol 99.5% (D-PBE-B99.9%) system at 20°C.

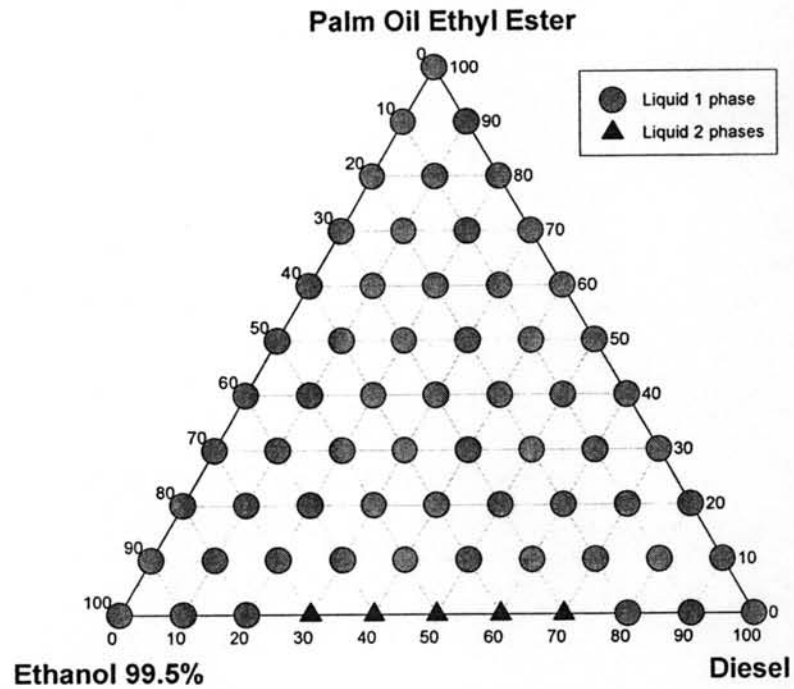
### 4.3.3 Phase Behavior of Diesohol at 30°C

- *Diesel-Palm Oil Alkyl Ester-Ethanol 99.5% Systems*

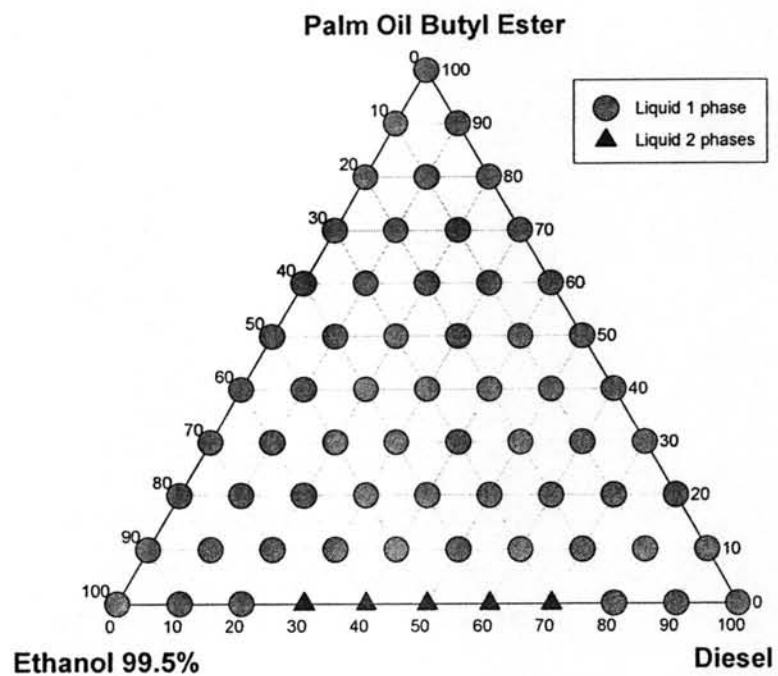
Figures 4.15-4.17 shows the solubility of the D-PME-E99.5%, D-PEE-E99.5%, and D-PBE-E99.5% systems at 30°C. As shown in these figures, there was still observed the problem of phase separation at the ratios of ethanol 30 to 70% with diesel. However, the other blends, which have palm oil alkyl ester as an additive, were liquid 1 phase. This might indicate that the use of biodiesel could solve the problem of fuel instability. This result agrees well with the results found by Letcher, in 1983. They proposed that biodiesel is like a co-solvent which acts as a bridging agent through molecular compatibility and allows stable blends to be achieved.



**Figure 4.15** Phase behavior of diesel-palm oil methyl ester-ethanol 99.5% (D-PME-E99.5%) system at 30°C.



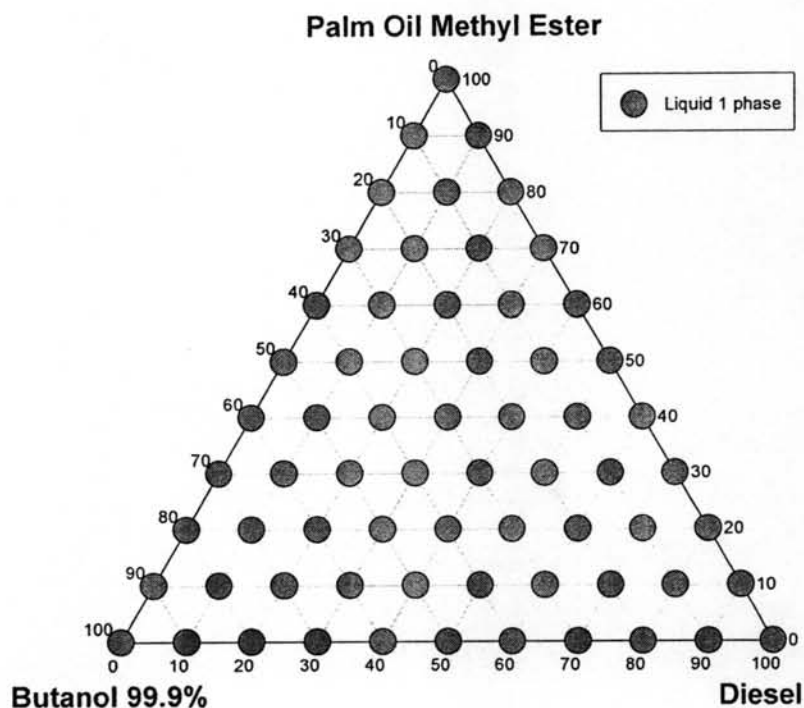
**Figure 4.16** Phase behavior of diesel-palm oil ethyl ester-ethanol 99.5% (D-PEE-E99.5%) system at 30°C.



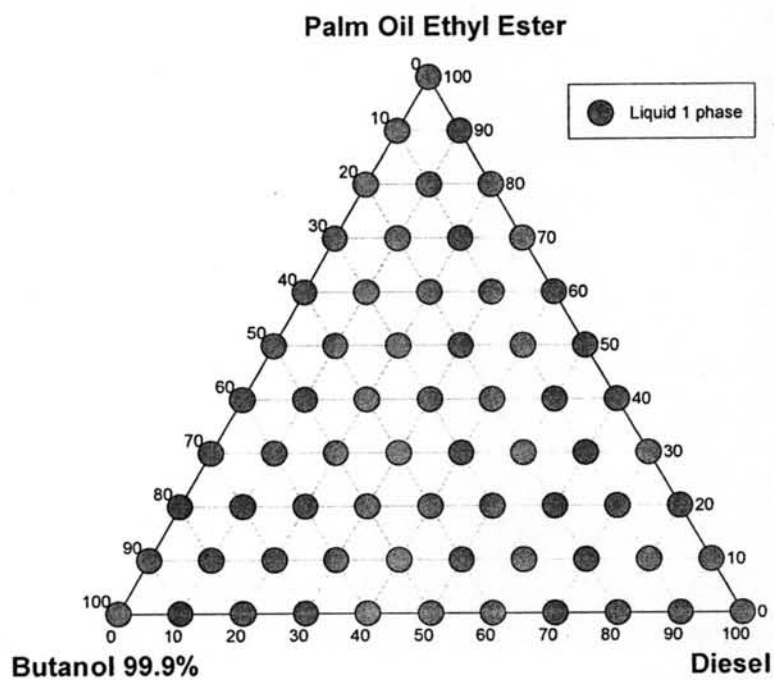
**Figure 4.17** Phase behavior of diesel-palm oil butyl ester-ethanol 99.5% (D-PBE-E99.5%) system at 30°C.

- *Diesel-Palm Oil Alkyl Ester-Butanol 99.9% System*

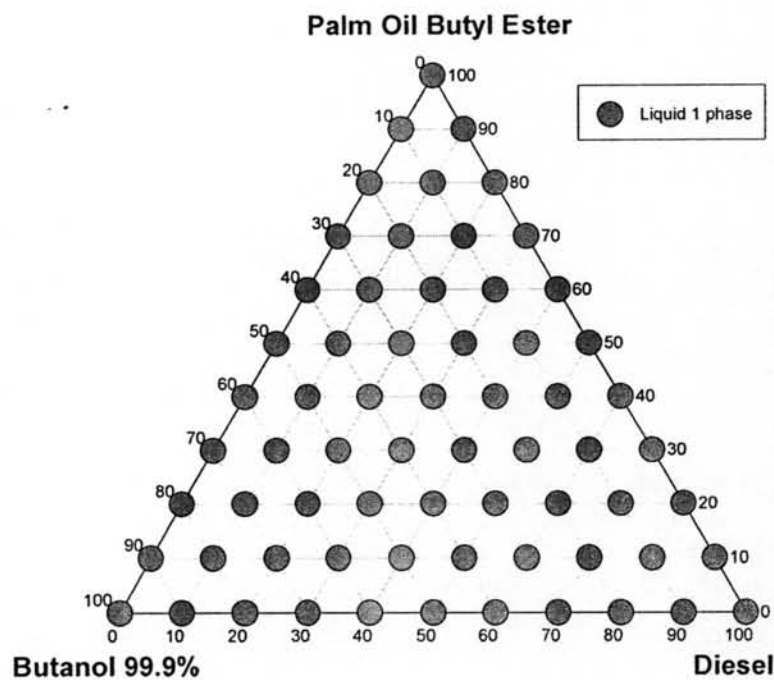
For the purpose of using butanol instead of ethanol to solve the problem of fuel instability, the solubility of similar three-component systems was investigated. As shown in Figures 4.18-4.20, in the D-PME-B99.9%, D-PEE-B99.9%, and D-PBE-B99.9% systems at a temperature of 30°C, no problems of phase separation were observed. It was found that the use of butanol in diesohol could solve the problem of fuel instability because of more solubility in the diesel fuel.



**Figure 4.18** Phase behavior of diesel-palm oil methyl ester-butanol 99.9% (D-PME-B99.9%) system at 30°C.



**Figure 4.19** Phase behavior of diesel-palm oil ethyl ester-butanol 99.9% (D-PEE-B99.9%) system at 30°C.

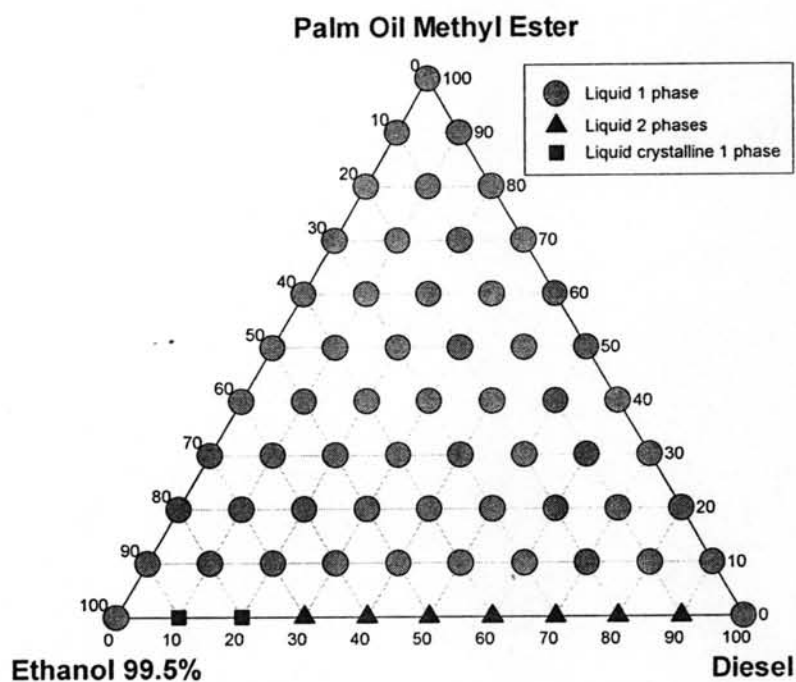


**Figure 4.20** Phase behavior of diesel-palm oil butyl ester-butanol 99.9% (D-PBE-B99.9%) system at 30°C.

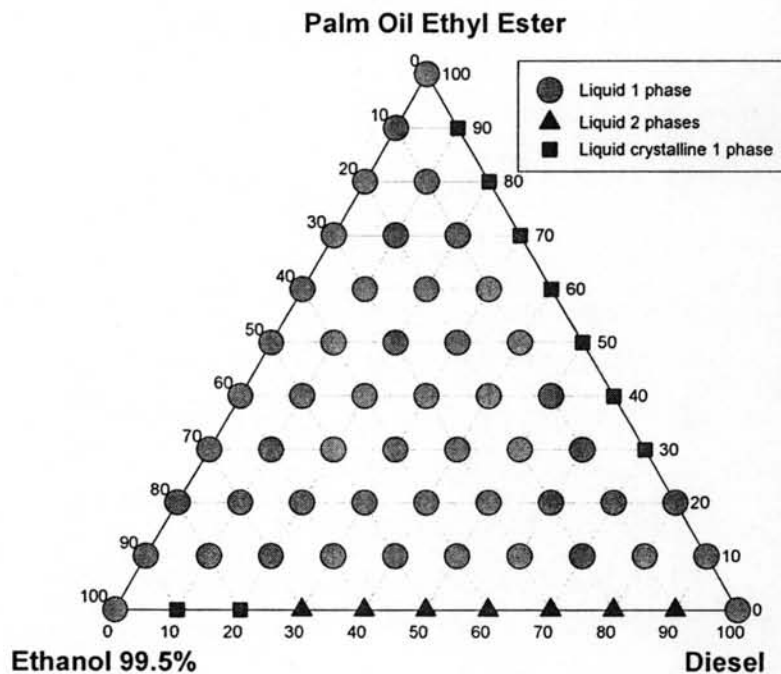
#### 4.3.4 Long Term Stability at Room Temperature

- *Diesel-Palm Oil Alkyl Ester-Ethanol 99.5% Systems*

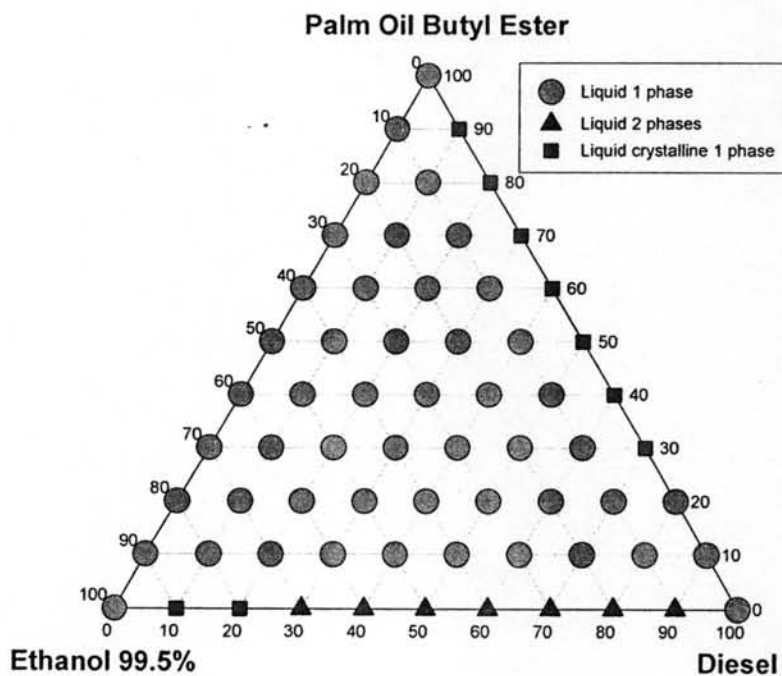
After observing the stability of the blends at different temperatures for 7 days, the long term stability of the blends was observed by keeping them at room temperature for 3 months. As shown in Figures 4.21-4.23, the results showed that the mixture of diesel and PEE in the range of 30-90% by volume changed to liquid crystalline 1 phase. This result was also observed in the mixture of diesel and PBE. However, the mixtures of the three-component system remained liquid 1 phase. This indicated that the use of biodiesel as additive in stabilizing the blends increased the intersolubility of diesel and ethanol 99.5%.



**Figure 4.21** Long term stability of diesel-palm oil methyl ester-ethanol 99.5% (D-PME-E99.5%) system at room temperature.



**Figure 4.22** Long term stability of diesel-palm oil ethyl ester-ethanol 99.5% (D-PEE-E99.5%) system at room temperature.

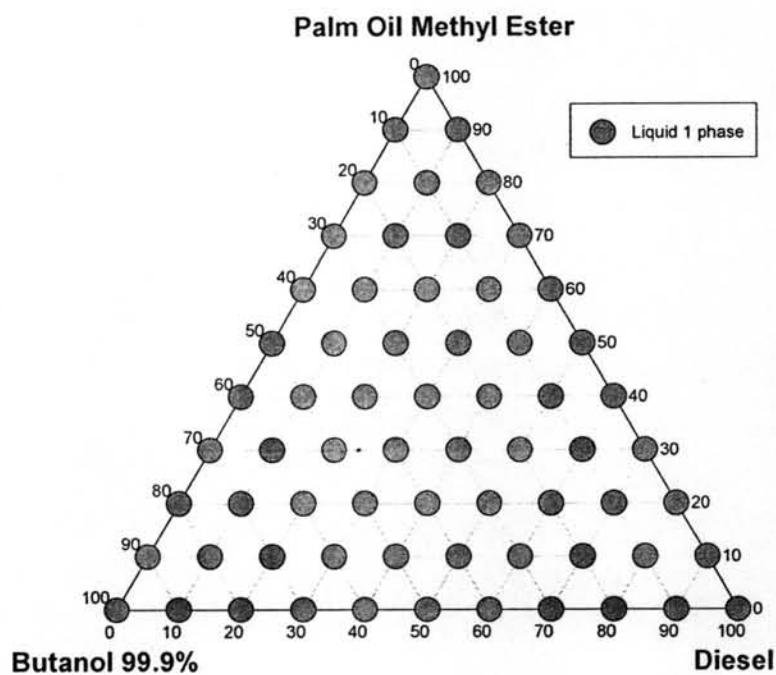


**Figure 4.23** Long term stability of diesel-palm oil butyl ester-ethanol 99.5% (D-PBE-E99.5%) system at room temperature.

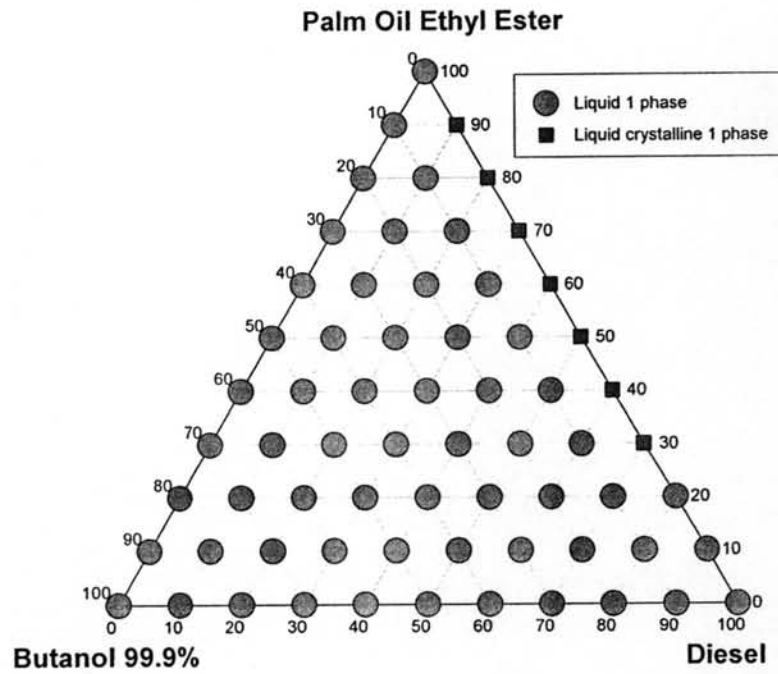


- *Diesel-Palm Oil Alkyl Ester-Butanol 99.9% Systems*

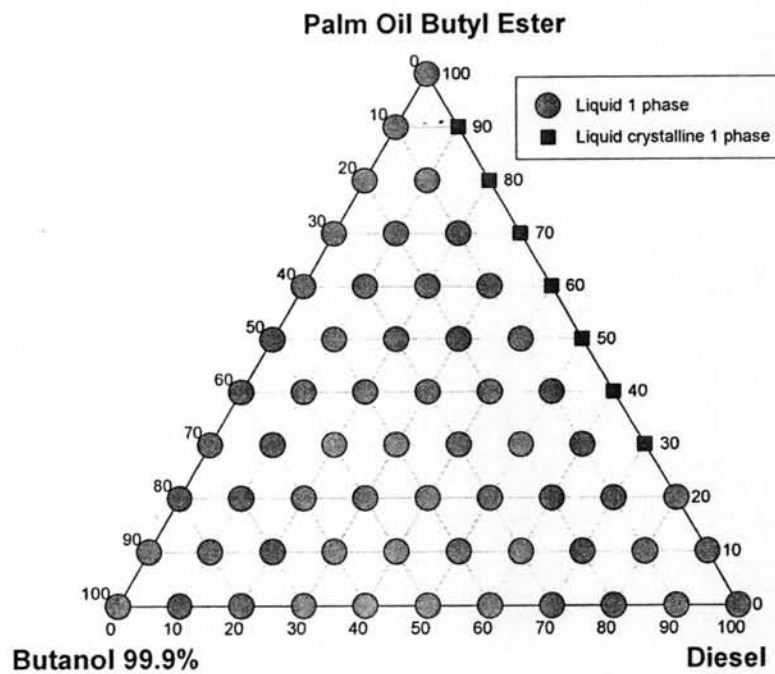
For the long term stability of the butanol blends system, as shown in Figure 4.24-4.26, the results showed that butanol was still miscible in diesel fuel. This indicated that the use of butanol in diesohol could eliminate the problem of phase separation observed in the diesel-ethanol system. The mixture of diesel and PEE, and the mixture of diesel and PBE in the range of 30-90% by volume was changed to the liquid crystalline 1 phase. However, the mixtures that have PME, PEE, or PBE as an additive remained liquid 1 phase.



**Figure 4.24** Long term stability of diesel-palm oil methyl ester-butanol 99.9% (D-PME-B99.9%) system at room temperature.



**Figure 4.25** Long term stability of diesel-palm oil ethyl ester-butanol 99.9% (D-PEE-B99.9%) system at room temperature.



**Figure 4.26** Long term stability of diesel-palm oil butyl ester-butanol 99.9% (D-PBE-B99.9%) system at room temperature.

#### 4.4 Fuel Properties Testing

The requirements for diesel fuel are like ordinary automotive fuel; it is required to be a clear, single-phase liquid. In addition, the fuel properties according to the standard limit for diesel fuel have to be acceptable. The previous work from Kwanchareon *et al.* (2006) found that diesohol blends containing 5% ethanol had very close fuel properties compared to diesel fuel. And the blend of 80% diesel, 15% biodiesel, and 5% ethanol was the most suitable ratio for diesohol production. Therefore, to study the effect of the diesohol blends on the fuel properties, two blends of diesel with each alcohol and each biodiesel were selected, as shown in Table 4.2.

**Table 4.2** Component ratio of the sample for fuel property testing

Sample No.	Component ratio (%)					
	Diesel	Biodiesel			Alcohol	
		PME	PEE	PBE	Ethanol	Butanol
1	80	15	-	-	5	-
2	80	15	-	-	-	5
3	80	-	15	-	5	-
4	80	-	15	-	-	5
5	80	-	-	15	5	-
6	80	-	-	15	-	5
7	85	10	-	-	5	-
8	85	10	-	-	-	5
9	85	-	10	-	5	-
10	85	-	10	-	-	5
11	85	-	-	10	5	-
12	85	-	-	10	-	5

Laboratory tests were then carried out using ASTM to determine the following properties: density at 15°C, kinematic viscosity at 40°C, flash point, pour

point, heat of combustion, cetane index, and oxidation stability, as shown in Table 4.3.

**Table 4.3** Test methods of diesel fuel according to ASTM

Property	Test Method
Density at 15°C	ASTM D 4052
Kinematic viscosity at 40°C	ASTM D 445
Flash point	ASTM D 93
Pour point	ASTM D 97
Heat of combustion	ASTM D 240
Cetane index	ASTM D 976
Oxidation stability for biodiesel	EN 14112

#### 4.4.1 Density at 15°C

Determination of the density (mass per unit volume at a specified temperature) or relative density (the ratio of the density of a material at a stated temperature to the density of water at a stated temperature) of petroleum and its products is necessary for the conversion of measured volumes to volumes at the standard temperature of 15°C. From Table 4.4, it can be seen that the density of diesohol blends varied from 0.8354 to 0.8386 g/cm<sup>3</sup>. Increasing the portion of biodiesel in the blends leads to increase the density of those blends because biodiesels have a higher density than diesel fuel. In addition, it can be noticed that diesohol containing PME has higher density than the blends containing PEE and PBE. This is because the pure PME has a higher density than the other two components. These results have the same tendency as reported earlier by Lang *et al.* (2001) and Shi *et al.* (2005). For the effect of ethanol and butanol on density, the D-biodiesel-B99.9% systems are likely to have a higher density than the D-biodiesel-E99.5% systems. This is due to the fact that the density of butanol is higher than that of ethanol. However, all the blends have acceptable density values because they are very close to the density of diesel fuel.

**Table 4.4** Density at 15°C of the diesel, biodiesels, alcohols, and their blends

No.	Ratio						Density at 15°C (g/cm <sup>3</sup> )
	%D	%PME	%PEE	%PBE	%E99.5%	%B99.9%	
1	80	15	-	-	5	-	0.8383
2	80	15	-	-	-	5	0.8392
3	80	-	15	-	5	-	0.8378
4	80	-	15	-	-	5	0.8386
5	80	-	-	15	5	-	0.8370
6	80	-	-	15	-	5	0.8381
7	85	10	-	-	5	-	0.8361
8	85	10	-	-	-	5	0.8372
9	85	-	10	-	5	-	0.8359
10	85	-	10	-	-	5	0.8368
11	85	-	-	10	5	-	0.8354
12	85	-	-	10	-	5	0.8364
13	Diesel						0.8348
14	Palm Oil Methyl Ester						0.8760
15	Palm Oil Ethyl Ester						0.8716
16	Palm Oil Butyl Ester						0.8685
17	Ethanol 99.5%						0.7890
18	Butanol 99.9%						0.8100

#### 4.4.2 Kinematic Viscosity at 40°C

Viscosity affects the atomization of a fuel upon injection into the combustion chamber and eventually the formation of engine deposits. The higher the viscosity, the greater the tendency of the fuel to cause such problems. Lower viscosity leads to greater pump and injector leakage, reducing maximum fuel delivery, and thus decreasing power output. The viscosity of diesel, the three biodiesels, the two alcohols, and their blends are shown in Table 4.5. The addition of alcohol (ethanol or butanol) to diesel lowers fuel viscosity, but it can be compensated for by adding biodiesel, which is likely to yield an overall viscosity close to diesel fuel. The viscosity of the blends was varied from 2.57 to 2.84 mm<sup>2</sup>/s. It can be seen that the viscosity increases with chain length (number of carbon atoms). Accordingly, diesohol containing PBE and/or butanol has higher viscosity as compared to others, since the viscosity decreased in the order of PBE > PEE > PME and butanol > ethanol.

**Table 4.5** Kinematic viscosity at 40°C of the diesel, biodiesels, alcohols, and their blends

No.	Ratio						Kinematic viscosity at 40°C (mm <sup>2</sup> /s)
	%D	%PME	%PEE	%PBE	%E99.5%	%B99.9%	
1	80	15	-	-	5	-	2.63
2	80	15	-	-	-	5	2.73
3	80	-	15	-	5	-	2.72
4	80	-	15	-	-	5	2.80
5	80	-	-	15	5	-	2.73
6	80	-	-	15	-	5	2.84
7	85	10	-	-	5	-	2.57
8	85	10	-	-	-	5	2.66
9	85	-	10	-	5	-	2.63
10	85	-	10	-	-	5	2.71
11	85	-	-	10	5	-	2.65
12	85	-	-	10	-	5	2.71
13	Diesel						2.72
14	Palm Oil Methyl Ester						4.48
15	Palm Oil Ethyl Ester						4.80
16	Palm Oil Butyl Ester						5.60
17	Ethanol 99.5%						1.08
18	Butanol 99.9%						3.64 <sup>(a)</sup>

<sup>(a)</sup> Measured at 20°C



#### 4.4.3 Flash Point

Flash point is the lowest temperature at which a fuel will ignite when exposed to an ignition source. In this study, the flash point for D-biodiesel-E99.5% systems was found to be extremely low, in the range of 15-17°C, as presented in Table 4.6. Ethanol blends with diesel fuel had similar flash points of ethanol (Ajav and Akingbehin, 2002, Fernando and Hanna, 2004). Since the effect of alcohol on the flash point of diesohol blends is predominant, the use of various types of biodiesel did not significantly affect the flash point of those blends. The storage and handling of flammable liquids was also established by the National Fire Protection Association (NFPA) in the US. Liquids such as gasoline and ethanol are Class I liquids, as they have flash points below 37.8°C, whereas diesel fuel is Class II with a flash point above 37.8°C. So D-biodiesel-E99.5% blends would also be classified as Class I liquids, and require safer handling when filling up a vehicle's fuel tank and could use the same infrastructure as gasoline.

However, the use of butanol instead of ethanol to blend with diesel fuel and biodiesel possibly raises the flash point of the blends to about 38 to 42°C, which comes from the fact that butanol has a higher flash point than ethanol. D-biodiesel-B99.9% blends would also be classified as Class II liquid, the same class as diesel fuel. Therefore, D-biodiesel-B99.5% blends can be used and handled more safely than D-biodiesel-E99.9% blends.

**Table 4.6** Flash point of the diesel, biodiesels, alcohols, and their blends

No.	Ratio						Flash Point (°C)
	%D	%PME	%PEE	%PBE	%E99.5%	%B99.9%	
1	80	15	-	-	5	-	17
2	80	15	-	-	-	5	39
3	80	-	15	-	5	-	15.7
4	80	-	15	-	-	5	41
5	80	-	-	15	5	-	15
6	80	-	-	15	-	5	41
7	85	10	-	-	5	-	15
8	85	10	-	-	-	5	38
9	85	-	10	-	5	-	15
10	85	-	10	-	-	5	42
11	85	-	-	10	5	-	16
12	85	-	-	10	-	5	41
13	Diesel						62.5
14	Palm Oil Methyl Ester						178
15	Palm Oil Ethyl Ester						182
16	Palm Oil Butyl Ester						192
17	Ethanol 99.5%						13.5
18	Butanol 99.9%						35

#### 4.4.4 Pour Point

Pour Point is the lowest temperature at which a liquid can flow. When the fuel approaches the pour point, it becomes cloudy due to the formation of crystals and the solidification of the fuel. Solids and crystals rapidly grow and agglomerate, clogging fuel lines and filters and causing major operability problems (Knothe, 2005). For this study, the pour points of all blends were lower than that of diesel fuel, as shown in Table 4.7. Although biodiesels have higher pour points (max. 12°C) than diesel fuel, they would not affect the pour points of the blends due to the extremely low pour points of alcohols (ethanol and butanol).

#### 4.4.5 Heat of Combustion

Heat of combustion measures the energy content in a fuel. It is an important property of the diesohol blends that determines the suitability of these materials as alternatives to diesel fuel. The values of the gross heat of combustion of the blends ranged from 39.30 to 44.50 MJ/kg, as listed in Table 4.8. For the gross heat of the three biodiesels, it was slightly increased with chain length but remained significantly lower than diesel fuel. In addition, it can be noticed that alcohols which normally have low gross heat (24.84 MJ/kg for ethanol and 36.05 MJ/kg for butanol) reduced the gross heat of combustion of the blends. However, the blends containing butanol have higher gross heat than the blends containing ethanol.

#### 4.4.6 Cetane Index

Cetane index has an effect on the engine start up, combustion control, and engine performance. A lower cetane index gives poorer ignition properties. As shown in Table 4.9, all the blends had a cetane index higher than diesel fuel. It is assumed that the high cetane values of biodiesel can compensate for the cetane value decrease caused by the presence of alcohol in the fuels. Taking this fact into account, it is assumed that blends of D-biodiesel-alcohol may improve the cetane index, which is a crucial problem of D-alcohol blends. There are also some arguments that, because of the significant effect of alcohol content on the distillation characteristic of diesohol, the diesel standard parameter of "cetane index" is not applicable to

diesohol (Apace Research Limited on Issues Raised in Discussion Paper on Diesohol).

**Table 4.7** Pour point of the diesel, biodiesels, alcohols, and their blends

No.	Ratio						Pour Point (°C)
	%D	%PME	%PEE	%PBE	%E99.5%	%B99.9%	
1	80	15	-	-	5	-	3
2	80	15	-	-	-	5	3
3	80	-	15	-	5	-	3
4	80	-	15	-	-	5	3
5	80	-	-	15	5	-	3
6	80	-	-	15	-	5	3
7	85	10	-	-	5	-	3
8	85	10	-	-	-	5	3
9	85	-	10	-	5	-	3
10	85	-	10	-	-	5	3
11	85	-	-	10	5	-	3
12	85	-	-	10	-	5	3
13	Diesel						6
14	Palm Oil Methyl Ester						12
15	Palm Oil Ethyl Ester						6
16	Palm Oil Butyl Ester						3
17	Ethanol 99.5%						-117.3
18	Butanol 99.9%						-89.5

**Table 4.8** Heat of combustion of the diesel, biodiesels, alcohols, and their blends

No.	Ratio						Heat of Combustion (°C)
	%D	%PME	%PEE	%PBE	%E99.5%	%B99.9%	
1	80	15	-	-	5	-	43.80
2	80	15	-	-	-	5	44.05
3	80	-	15	-	5	-	39.30
4	80	-	15	-	-	5	43.93
5	80	-	-	15	5	-	43.70
6	80	-	-	15	-	5	44.35
7	85	10	-	-	5	-	43.70
8	85	10	-	-	-	5	44.45
9	85	-	10	-	5	-	43.90
10	85	-	10	-	-	5	44.33
11	85	-	-	10	5	-	44.00
12	85	-	-	10	-	5	44.50
13	Diesel						45.65
14	Palm Oil Methyl Ester						39.83
15	Palm Oil Ethyl Ester						40.00
16	Palm Oil Butyl Ester						40.30
17	Ethanol 99.5%						24.84
18	Butanol 99.9%						36.05

**Table 4.9** Cetane index of the diesel, biodiesels, alcohols, and their blends

No.	Ratio						Cetane Index
	%D	%PME	%PEE	%PBE	%E99.5%	%B99.9%	
1	80	15	-	-	5	-	53.2
2	80	15	-	-	-	5	52.1
3	80	-	15	-	5	-	*
4	80	-	15	-	-	5	*
5	80	-	-	15	5	-	*
6	80	-	-	15	-	5	*
7	85	10	-	-	5	-	52.0
8	85	10	-	-	-	5	51.8
9	85	-	10	-	5	-	*
10	85	-	10	-	-	5	*
11	85	-	-	10	5	-	*
12	85	-	-	10	-	5	*
13	Diesel						47.7
14	Palm Oil Methyl Ester						52.3
15	Palm Oil Ethyl Ester						*
16	Palm Oil Butyl Ester						*
17	Ethanol 99.5%						*
18	Butanol 99.9%						*

\* Not measured.

#### 4.4.7 Oxidation Stability of Biodiesel

Oxidation stability affects biodiesel primarily during extended storage. Generally, factors such as the presence of air, elevated temperatures, or the presence of metals facilitate oxidation. However, the influence of compound structure of the fatty esters, especially unsaturation, is even greater (Dunn *et al.*, 2003). The reason for autoxidation is the presence of double bonds in the chains of many fatty compounds. The autoxidation of unsaturated fatty compounds proceeds with different rates depending on the number and position of double bonds (Frankel, 1998).

Biodiesels produced in this study which were derived from the same vegetable oil (palm oil), had an oxidation stability ranging from 8.54 to 10.12 hours. This value is higher than the minimum value (6 hours) of the biodiesel methyl ester standard according to EN 14112.

**Table 4.10** Oxidation stability of the biodiesels

<b>Biodiesel</b>	<b>Oxidation Stability (hours)</b>
Palm Oil Methyl Ester	9.78
Palm Oil Ethyl Ester	10.12
Palm Oil Butyl Ester	8.54