CHAPTER IV
RESULTS AND DISCUSSION

4.1 Characterization of Crude Oil Samples

The crude oil samples were characterized for their water content, viscosity, density, and amount of asphaltenes and sediments. The results of characterization of crude oil samples are shown in Table 4.1.

Table 4.1 Characterization of crude oil samples

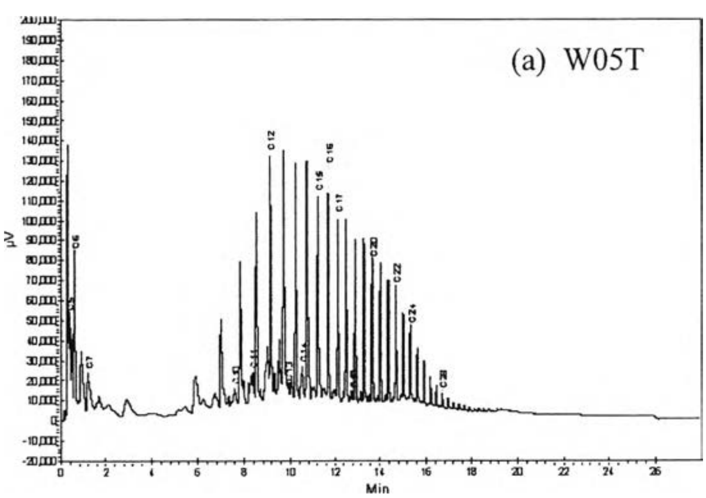
Wells	% water content	Viscosity (cP)	Density at 40°C	% Asphaltenes*	% Sediments*
W05T	0.50 ± 0.03	132 at 33.8°C	0.810	8.80	1.10
F09T	4.32 ± 0.07	262 at 33.5°C	0.980	12.49	3.99
A15T	4.90 ± 0.39	141 at 33.6°C	0.845	8.82	1.22
W09T	6.25 ± 0.06	150 at 34.1°C	0.850	2.30	1.31
C09T	8.32 ± 0.26	307 at 33.7°C	0.985	10.42	3.86
A02T	30.54 ± 0.27	228 at 34.3°C	0.940	1.59	0.33
D12T	43.55 ± 1.53	227 at 46.7°C	-	12.14	4.73
X09T	50.68 ± 0.26	325 at 34.7°C	-	4.64	1.64
B15T	52.94 ± 0.16	204 at 34.6°C	0.915	4.85	2.63
X12T	61.25 ± 0.35	301 at 34.9°C	0.990	8.54	1.60
B02T	71.31 ± 0.57	270 at 34.5°C	0.980	3.14	0.40
B24T	80.19 ± 0.32	320 at 34.1°C	-	1.19	0.78

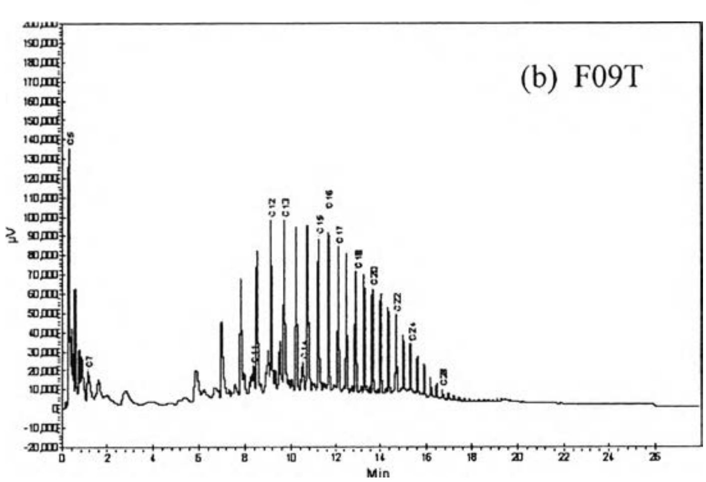
* Based on weight of crude oil

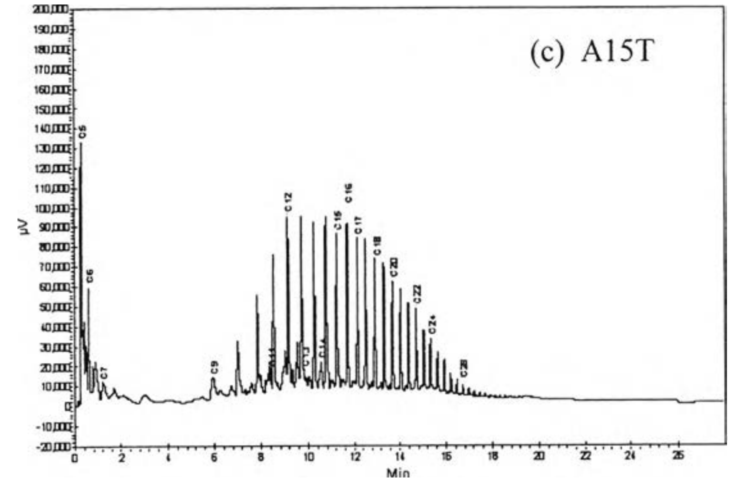
From characterization of the crude oil samples, A02T, D12T, X09T, B15T, X12T, B02T, and B24T well had high percent water content in the range of 30.54 to 80.19% and the remaining crudes had less than 10%.

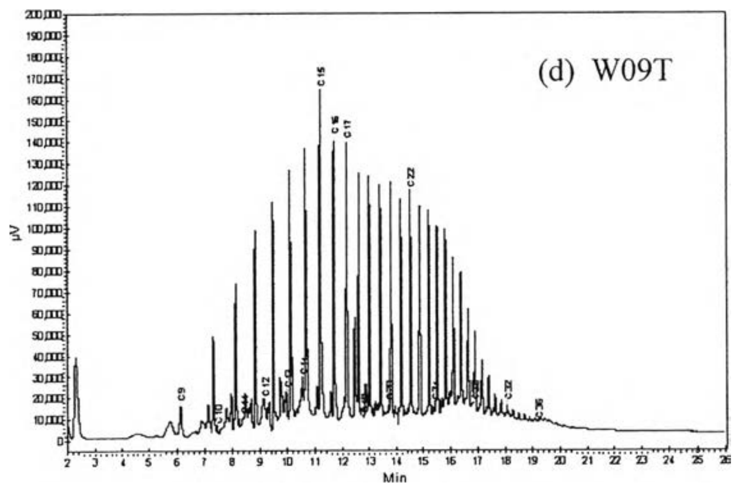
The amounts of asphaltenes found in all crudes were varied from 1-12%. As asphaltenes, resins, waxes and small solid particles strongly stabilize water-in-oil or oil-in-water emulsion by preventing droplets coalescence by forming a rigid film around the water droplets, the high amounts of asphaltenes of 8-12% (A15T, C09T, D12T, F09T, W05T, and X12T well) may have an effect on emulsion stability.

The crude oil samples were characterized by Sim-Dist GC and the chromatograms are shown in Figures 4.1. The crude oil samples from W05T, F09T, A15T, C09T, and D12T well show similar carbon number distribution in the range between 10 and 28, while crude oil samples from W09T, A02T, X09T, B15T, X12T, B02T, and B24T well show carbon number distribution in the wider range of 10-36.






(c) A15T
µV
Min


(d) W09T
µV
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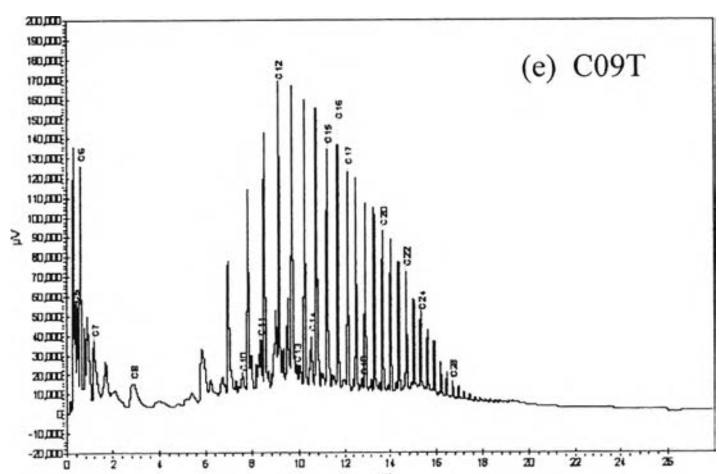
(e) C09T
µV
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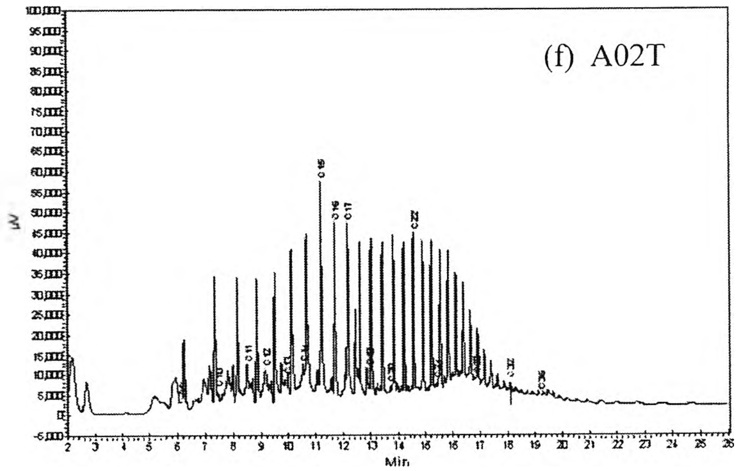
(f) A02T
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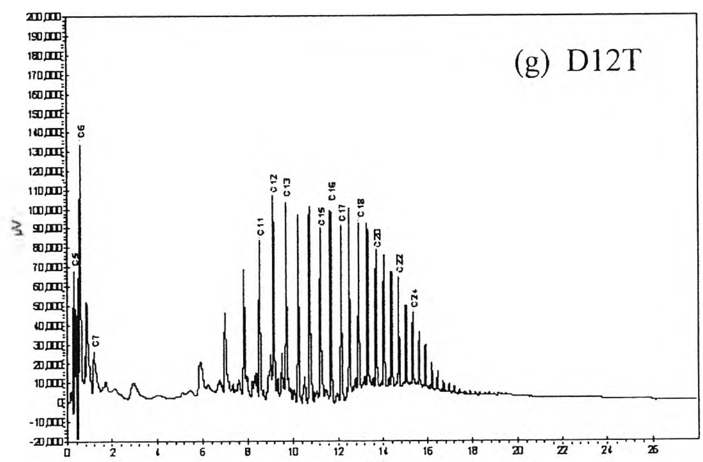
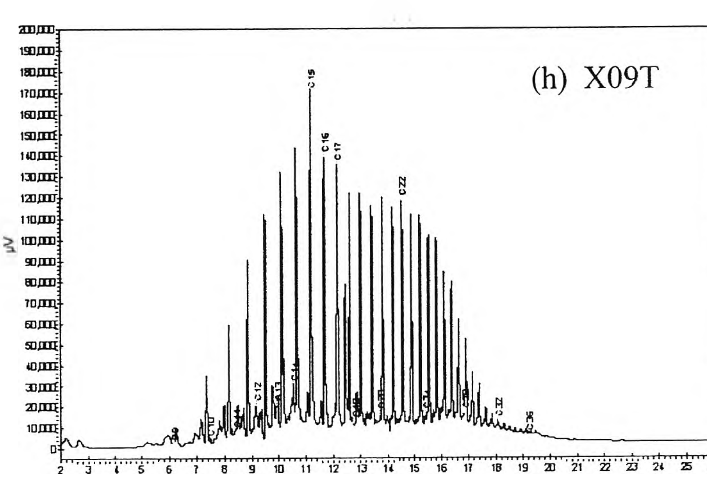

(g) D12T
µV
Min


(h) X09T
µV
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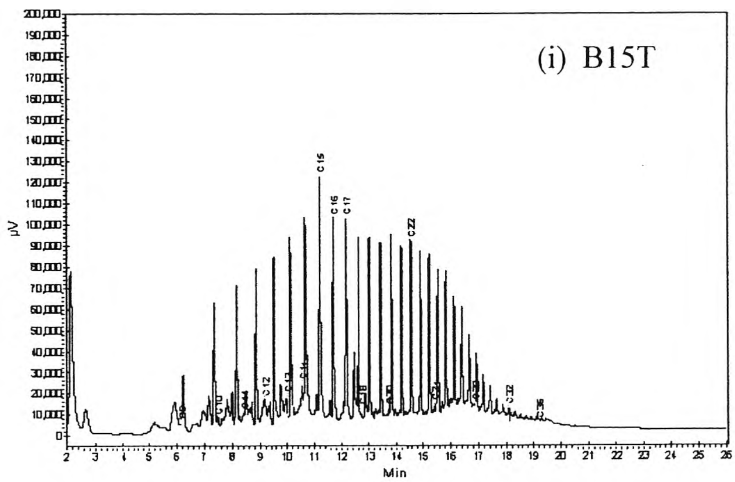
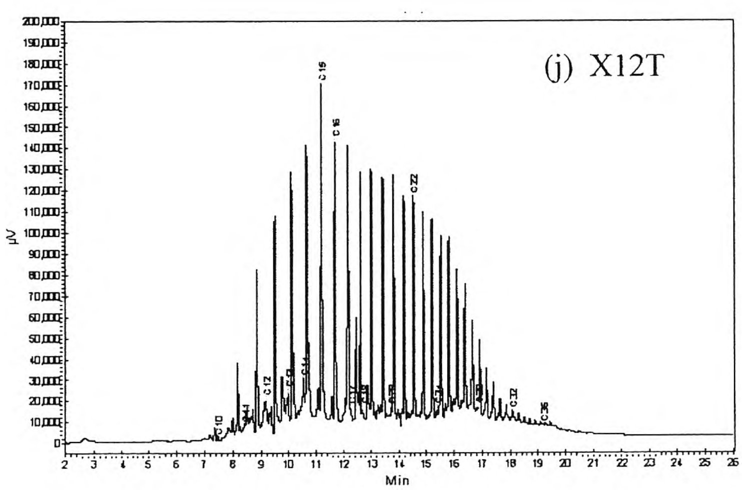

(i) B15T
μV
Min
C15
C16
C17
C22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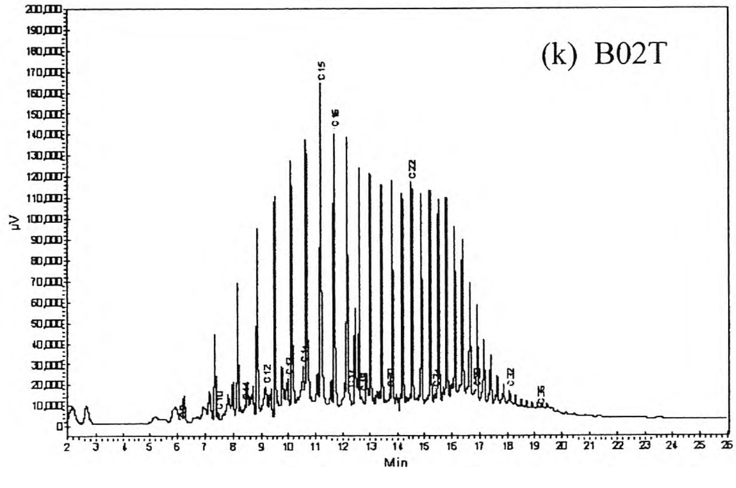
μV
Min
C15
C16
C22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μV
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C15
C16
C22

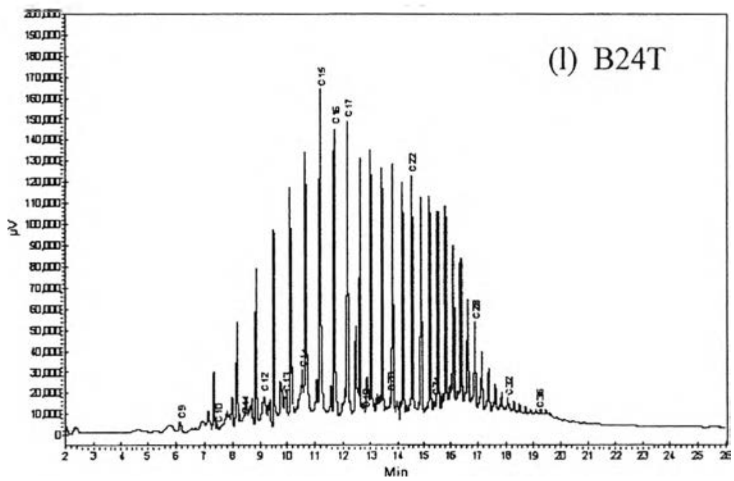


Figure 4.1 Carbon number distribution of 12 crude oil samples obtained by Sim-Dist GC.

The amount of water in crude oil was related to its viscosity and density. The higher the water content, the higher the viscosity of the crude oil in most crude oil except D12T, X09T, and B24T that their viscosities were very high and their densities could not be determined at 40°C while the water content of two crudes were 43.55%, 50.68%, and 80.19%respectively. Relationship between water content and viscosity was studied further by mixing two crude oils (W05T and B02T) at 6 different ratios (0.5, 14.7, 28.8, 43.0, 57.1, and 71.3%) without adding demulsifier as shown in Figure 4.2. The results showed that viscosity of crude oil was varied depending on the water content in crude. The viscosity of the crude oil can affect the emulsion stability as well as asphaltenes.

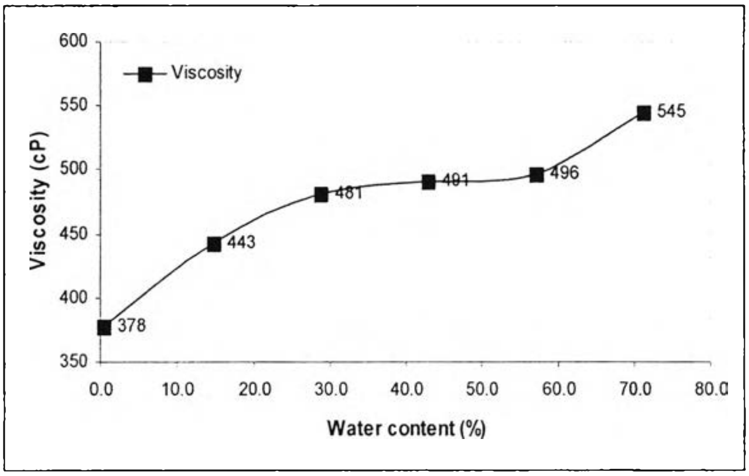
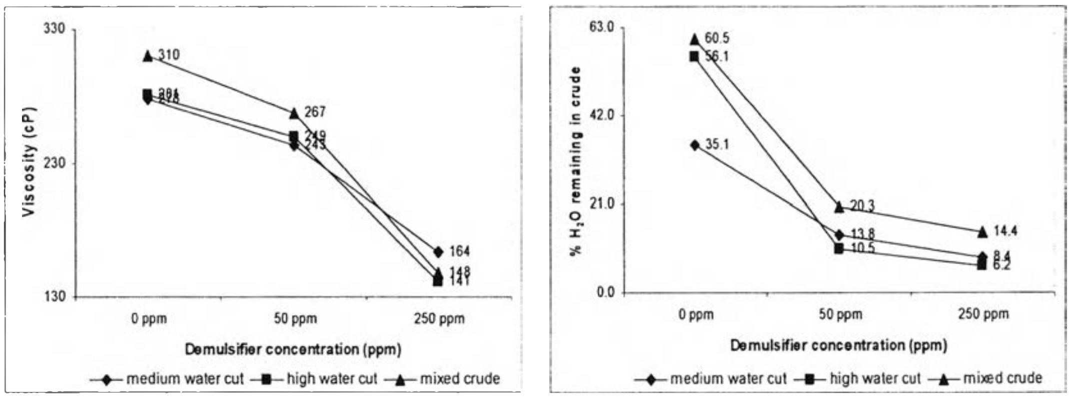


Figure 4.2 Relationship between viscosity and % water content in the absence of demulsifier at 30-31°C.

In some cases, demulsifiers were used in order to decrease the viscosity of the crude oil, for example, the application of a surfactant molecule for enhancing the flow properties of heavy or viscous crude oils during transporting the crude oils though pipelines (Al-Roomi *et al.*, 2004). The relationship between viscosity and demulsifier concentration was studied by mixing two crudes of two different levels of water cut of medium (43.0%) and high (71.3%) and the mixture of the four crudes (B15T : X12T : B02T : B24T = 1 : 1 : 2 : 2) with water content of 70.24% using Genapol ED 3060 as demulsifier at 55°C for 15 minutes. The results are shown in Figures 4.3 (a-b). It is seen that when the demulsifier concentration in crude oil increased, the viscosity of crude oil dramatically decreased, comparin g with the crude in the absence of the demulsifier. In addition, at higher demulsifier concentration, water remaining in crude also decreased.



(a) (b)

Figure 4.3 Relationship between viscosity and demulsifier concentration at 55°C for 15 min separation time.

4.2 Experimental Design Study

The design of experiment was performed to identify the sensitive parameters to changes in the output response. In this study, the demulsification via bottle test method was investigated by using 53.40% water content mixed crude (X09T : B15T : X12T : B02T = 1 : 1 : 1: 1). After demulsification was done under several conditions, according to the 2^3 factorial design (Table 3.3 and 3.4), in order to determine the percentage of water separation as the output response. The response of 2^3 factorial design are shown in Table 4.2.

Table 4.2 The observed response of all experiments

Treatment combination	Conditions			Response
	Temperature (°C)	Demulsifier concentration (ppm)	Demulsifier type	% Water separation
(1)	55	25	Teric PE 61	2
a	60	25	Teric PE 61	35
b	55	50	Teric PE 61	3
ab	60	50	Teric PE 61	36
c	55	25	Genapol ED 3060	40
ac	60	25	Genapol ED 3060	49
bc	55	50	Genapol ED 3060	42
abc	60	50	Genapol ED 3060	52

A normal probability plot was used as a method of analysis which provided a simple way to determine the factor effects to the observed response, % water separation, and is shown in Figure 4.4. It can be concluded that temperature (effect A), demulsifier type (effect C), and interaction effect between temperature and demulsifier type (effect AC) are the factors that are significant to water separation.

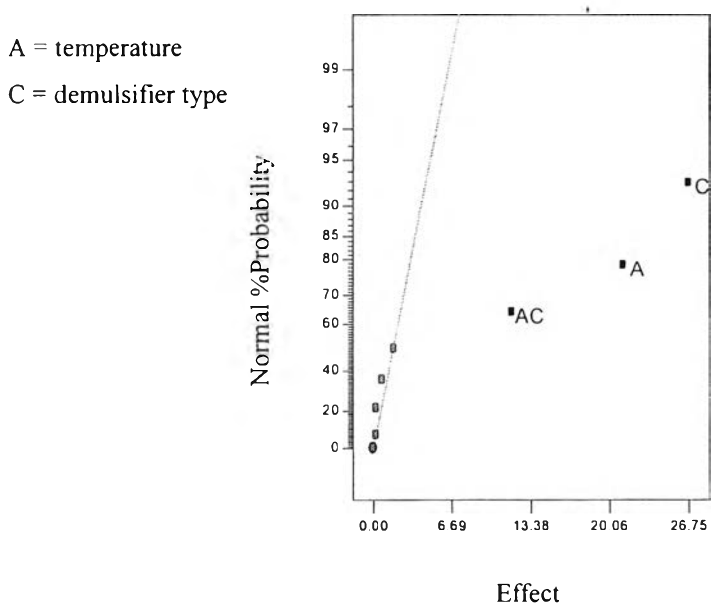


Figure 4.4 Normal % probability plot of the effects.

The analysis of variance was used to confirm the magnitude of these effects. The analysis of variance for %water separation, and is shown in Table 4.3. Base on the p-value of %water separation of each effect at less than 0.05, it confirms that these effects are significant. So, it can be said that the main effect of temperature (effect A), demulsifier type (effect C), and interaction between temperature and demulsifier type (effect AC) are the sensitive factors to percent water separation.

Table 4.3 Analysis of variance for percent water separation response (ANOVA)

Source	Sum of Squares	DF*	Mean Square	F-value**	P-value***
Model	2610.375	3	870.125	464.0667	< 0.0001
A	903.125	1	903.125	481.6667	< 0.0001
C	1431.125	1	1431.125	763.2667	< 0.0001
AC	276.125	1	276.125	147.2667	0.0003
Residual	7.5	4	1.875		
Cor Total	2617.875	7			

* DF = Degree of freedom.
** F-value = Mean square sample/mean square residue.
*** P- value = the smallest level of significance that would lead to rejection of the null hypothesis.

Plots of the main effect between factors and percent water separation in Figure 4.5 (a) shows the relationship between temperature (A) and % water separation, Figure 4.5 (b) shows the relationship between demulsifier type (C) and % water separation and Figure 4.6 shows the interaction of temperature and demulsifier type (AC) and % water separation.

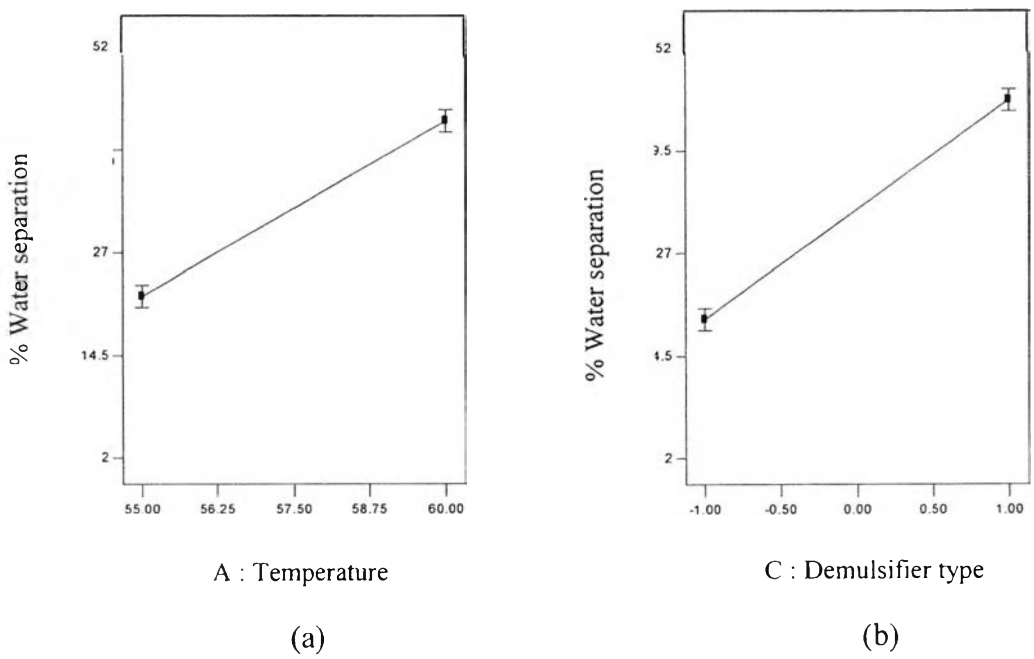


Figure 4.5 Main effect plots between factors and % water separation. (a) temperature and % water separation (b) demulsifier type and % water separation

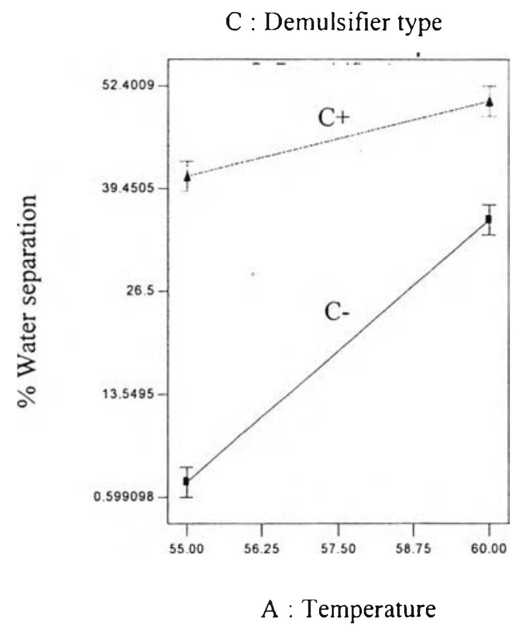


Figure 4.6 Interaction plot: AC interaction and % water separation.

The results showed that at high temperature and Genapol ED 3060 as demulsifier give high percent water separation. It can be concluded from experimental design that the effect of temperature (A), demulsifier type (C) and interaction between temperature and demulsifier type (AC) are important. Water separation rate perform better at 60°C and amine type shows better performance than Teric PE 61.

From the experimental design study, the factors that we must focus on are temperature and demulsifier type because these are the main factors that had a significant effect on the percent water separation.

4.3 Demulsification Study

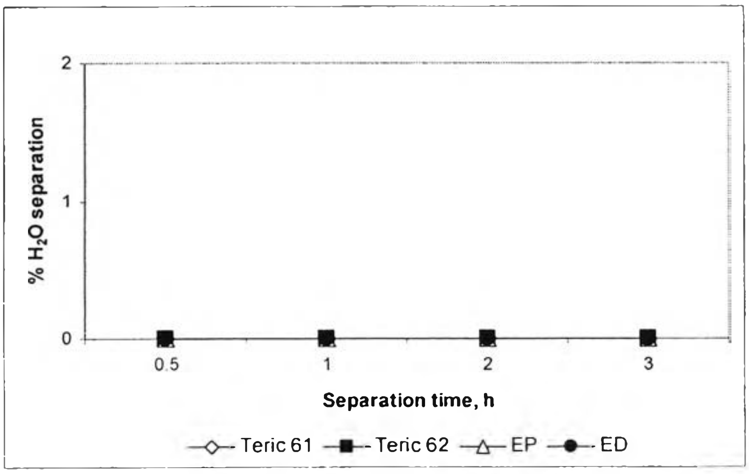
The bottle test was used to determine the capability of the investigated demulsifiers in breaking 12 crude samples and releasing free water. Free water separation from the crude sample and water remaining in the crude were measured, but the water remaining in the emulsion was determined by mass balance.

4.3.1 Screening of Demulsifiers

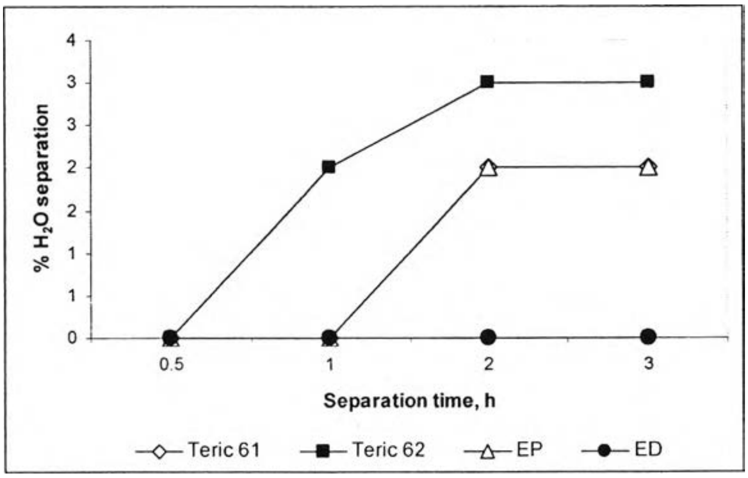
The bottle test was carried out for all crudes with original water present in crude using demulsifier concentration of 1000 ppm (w/w) at 60°C and separation time was varied up to 3 h. A blank was also measured for comparing the separated water in the absence of the demulsifier. The results of blank (crudes without demulsifier) are that the water couldn't separate out at every separation time except B02T and B24T that free water was separated at 2 h.

From the screening of demulsifiers in Figures 4.7 (a-l), Teric PE 61 and Genapol ED 3060 (ethylenediamine type) gave good water separation with crudes that had high water content (water content of at least 30%). When comparing the demulsification efficiency, the amine type had the quickest water separation rate while Teric PE 61 was the next in the rank. The water remaining in crude after demulsification are shown in Figures 4.8 (a-d). Teric PE 61 and amine type gave the water remaining in crude lower than 0.5% while Teric PE 62 and oxoalcohol type gave water remaining in crude higher than 0.5% for most crudes. The suitable demulsifiers for demulsification of all crude oil selected for further study were Teric PE 61 and Genapol ED 3060.

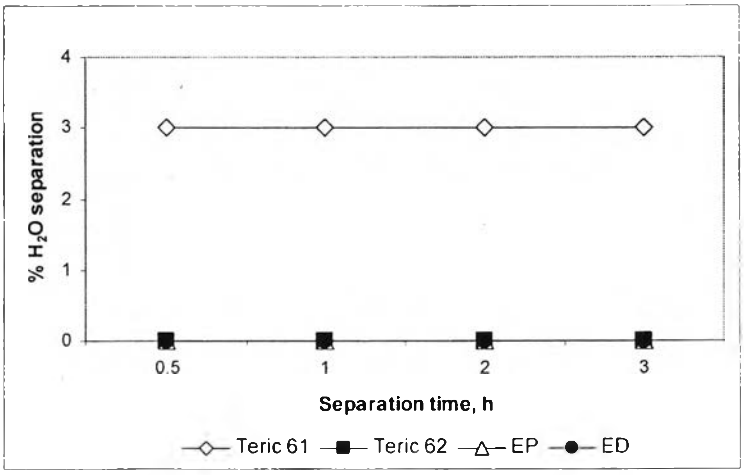
It can be explained that the amine type (ED 3060) performed the quickest rate of water separation because it has the branched molecule that gave good penetrability. So, it can quickly enter bulk solution and then spread into the oil and water interface (Zhang *et al.*, 2005).



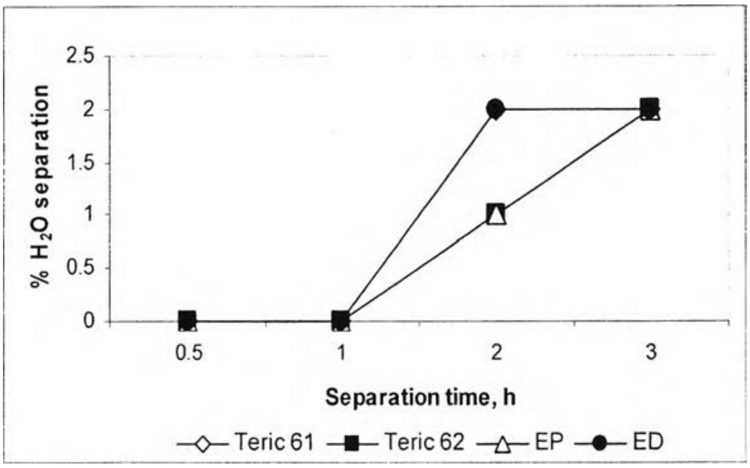
(a) W05T (water cut = 0.50%)



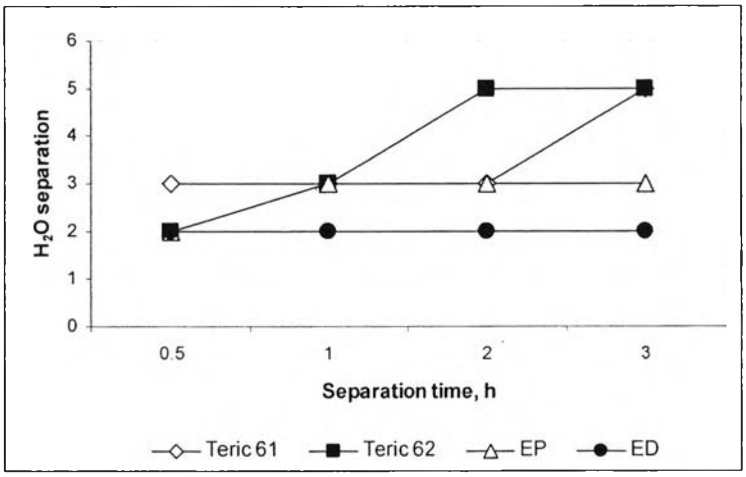
(b) F09T (water cut = 4.32%)



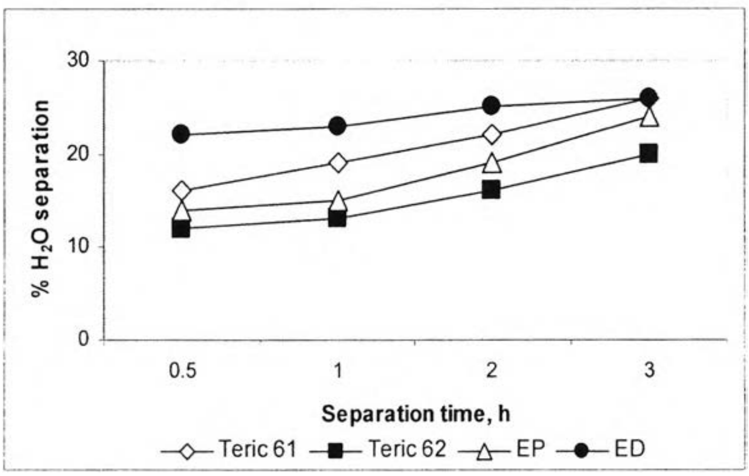
(c) A15T (water cut = 4.90%)



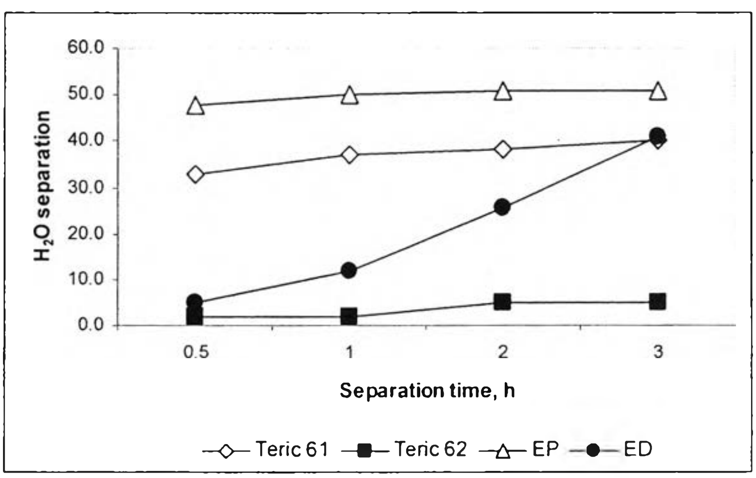
(d) W09T (water cut = 6.25%)



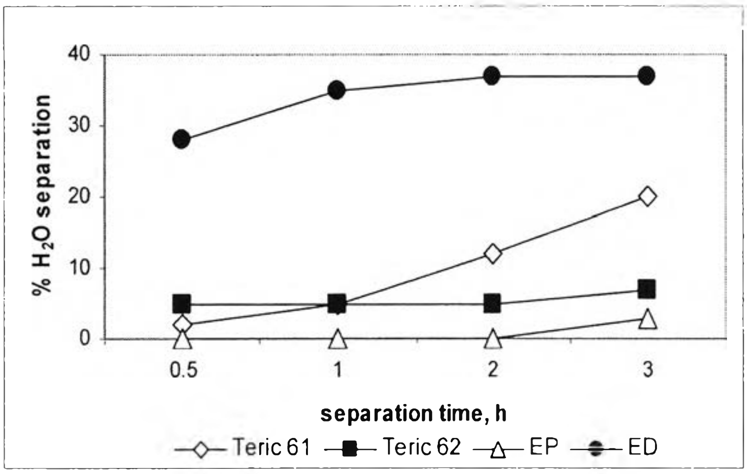
(e) C09T (water cut = 8.32%)



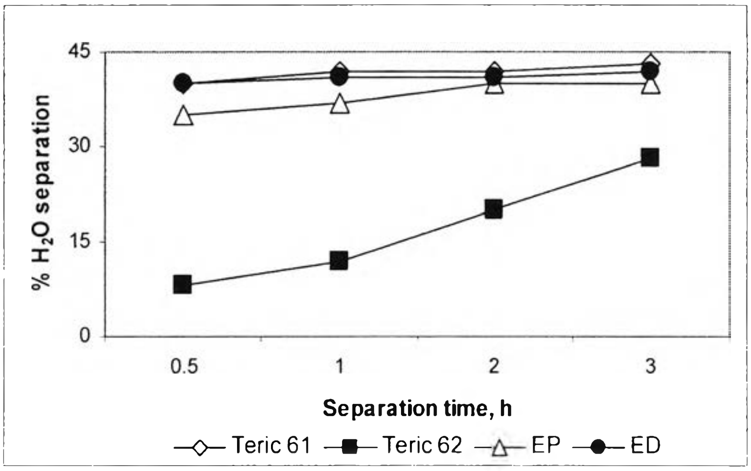
(f) A02T (water cut = 30.54%)



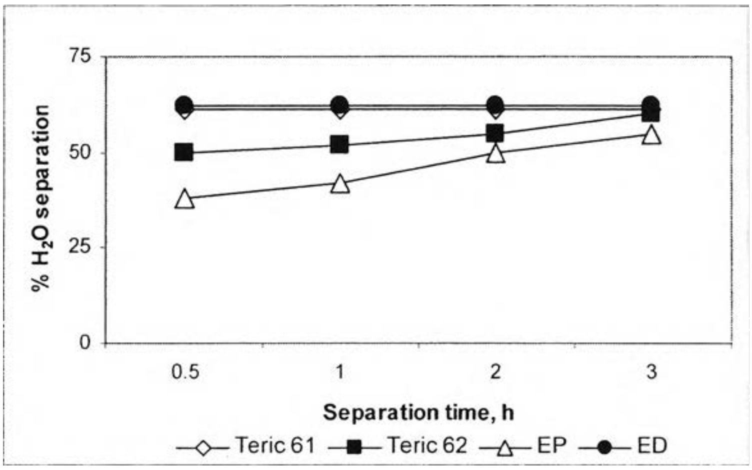
(g) D12T (water cut = 43.55%)



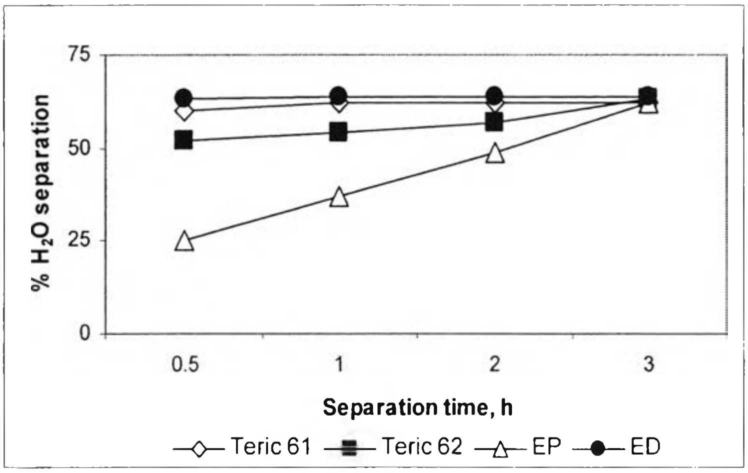
(h) X09T (water cut = 50.68%)



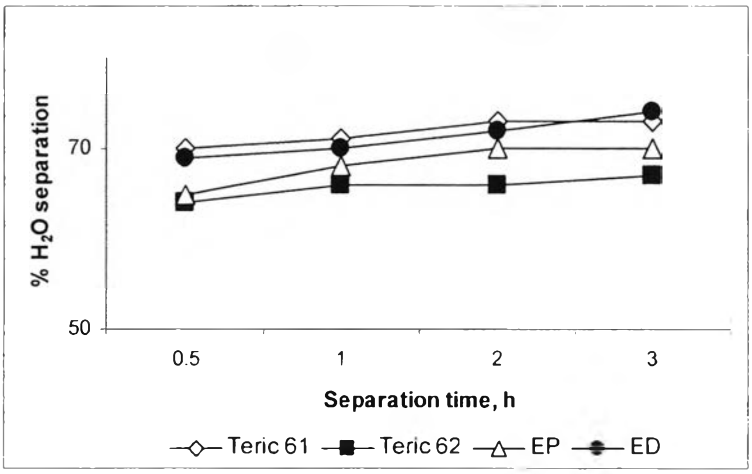
(i) B15T (water cut = 52.94%)



(j) X12T (water cut = 61.25%)

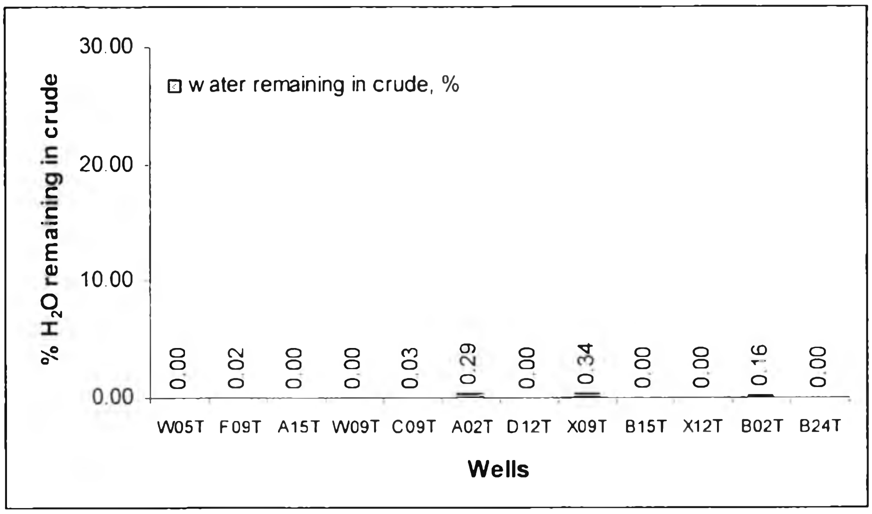


(k) B02T (water cut = 71.31%)

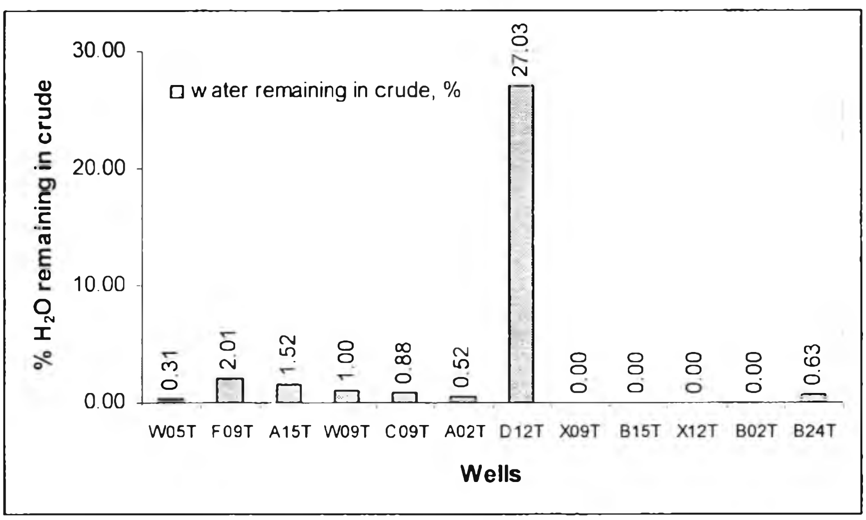


(l) B24T (w ater cut = 80.19%)

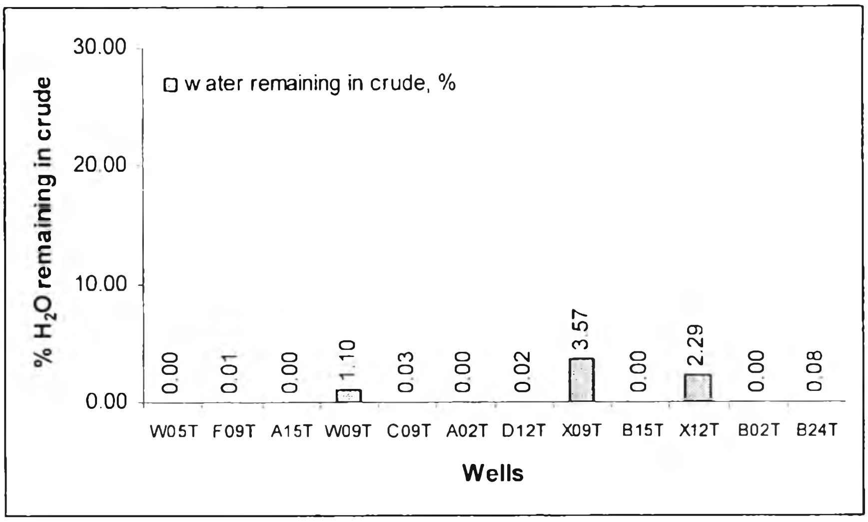
Figure 4.7 Screening of demulsifiers with original water in crudes at 60°C, demulsifier concentration of 1000 ppm with varying time.



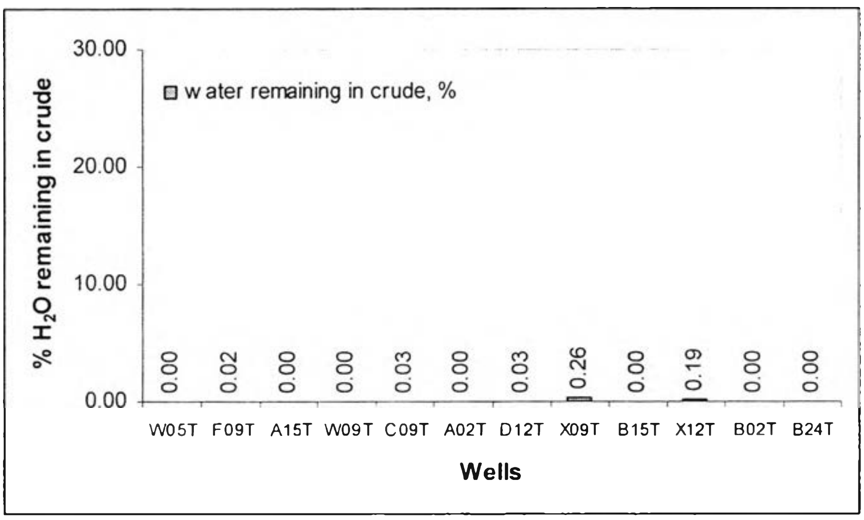
(a) Teric PE 61



(b) Teric PE 62



(c) Genapol EP 2584



(d) Genapol ED 3060

Figure 4.8 Water remaining in crude in screening of demulsifiers at 60°C, 1000 ppm, and 3 h.

4.4 Effect of Water-to-oil Ratio

The two crudes of W05T and B02T were mixed at different ratios. The water contents of mixed crudes are 0.50%, 14.7%, 28.8%, 43.0%, 57.1%, and 71.3%. The mixed crudes were demulsified at 60°C for 3 h and demulsifier concentration of 1000 ppm. The free water separated out is shown in Figures 4.9 and water remaining in crude is shown in Figures 4.10. The demulsification efficiency of Teric PE 61 and Genapol ED 3060 showed the same trend that the water separations of 86-100% can be obtained at the water content of at least 40%.

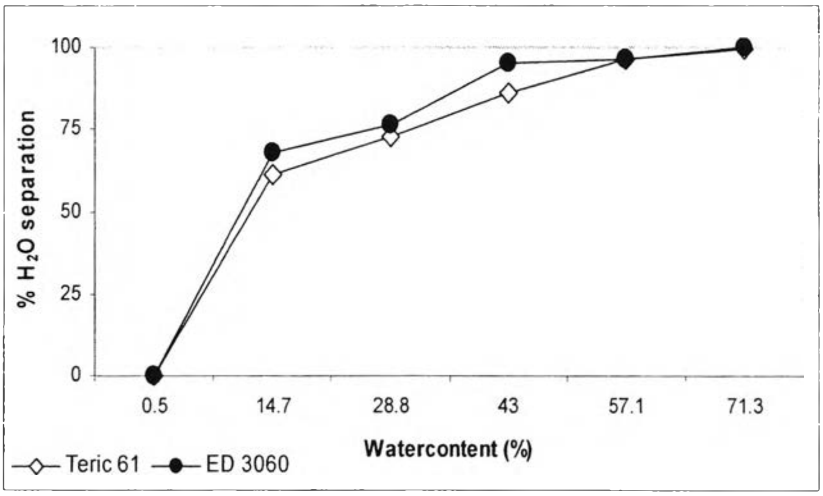


Figure 4.9 Effect of water-to-oil ratio on water separation using demulsifier concentration of 1000 ppm at 60°C for 3 h.

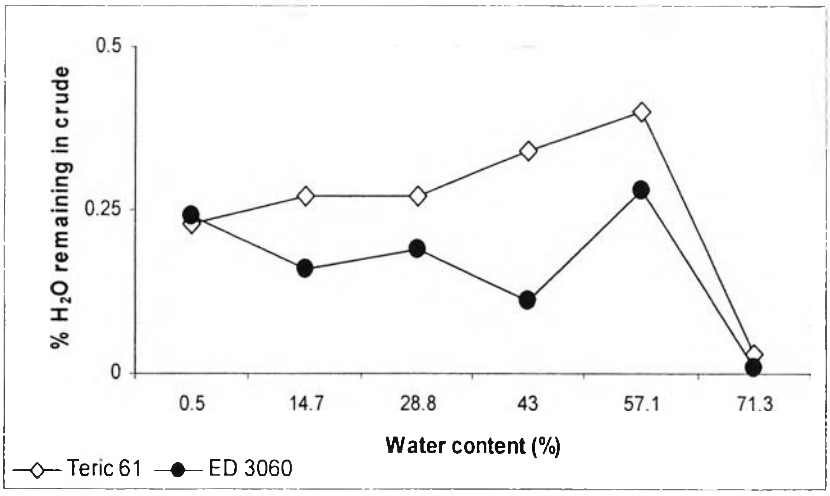
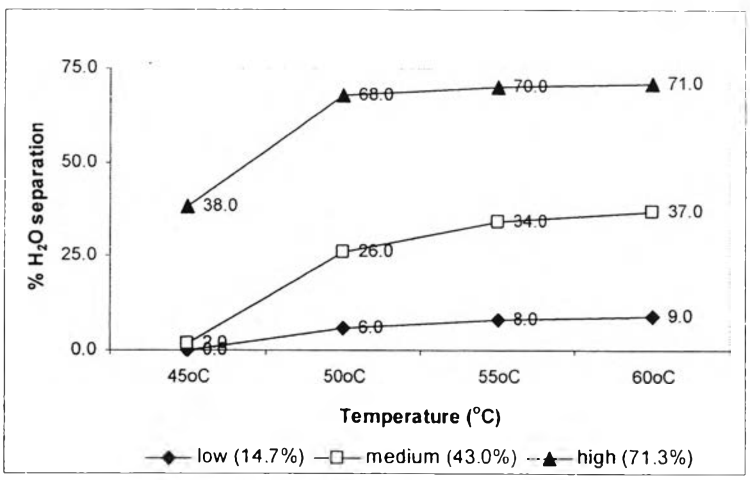


Figure 4.10 Effect of water-to-oil ratio on water remaining in crude using demulsifier concentration of 1000 ppm at 60°C for 3 h.

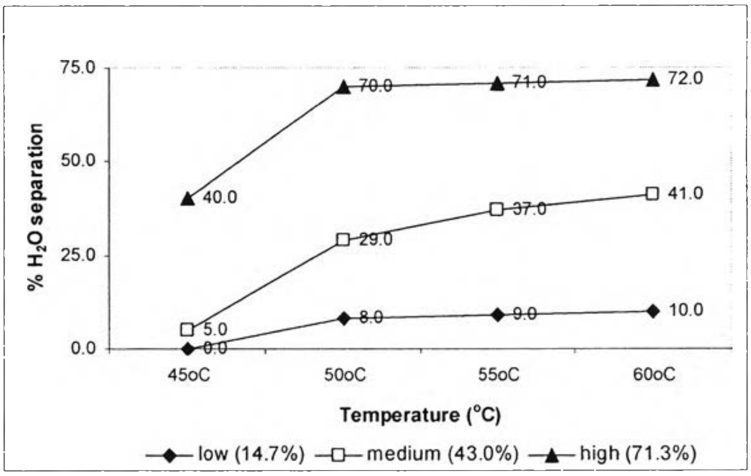
4.5 Effect of Temperature

According to the factorial design, the main factors that gave a significant effect on the output response were temperature and demulsifier type.

For demulsifier concentration of 500 ppm and 3 h separation time, temperature was varied at 45, 50, 55, and 60°C. The water separation by Teric PE 61 and Genapol ED 3060 are shown in Figures 4.11 (a-b). The results showed high water separation of at least 55°C. The higher the water content in crude (medium and high water cut), the better the water separation. Comparing the efficiency of two demulsifiers, Genapol ED 3060 and Teric PE 61 were found to be equally efficient. The water remaining is shown in Figures 4.12 (a-b). The water remaining in crude lower than 0.5 vol% can be obtained at temperature at least 55°C. These results can be concluded that the suitable temperature that gave the good water separation was 55°C.

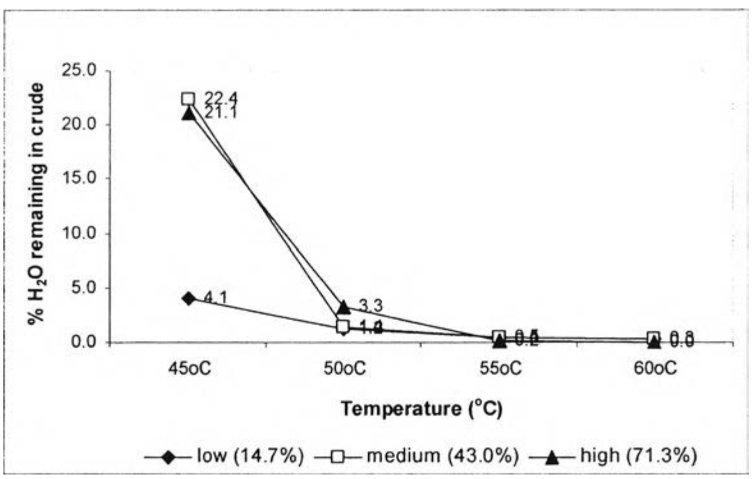


(a) Teric PE 61

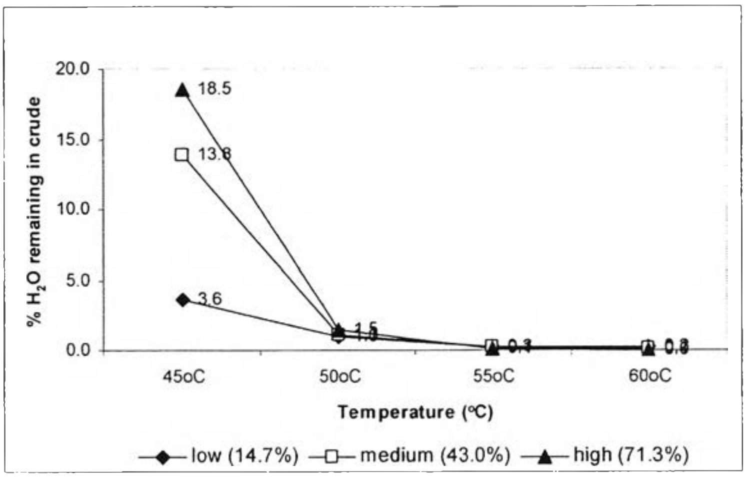


(b) Genapol ED 3060

Figure 4.11 Effect of temperature on water separation using demulsifier concentration of 500 ppm for 3 h.



(a) Teric PE 61



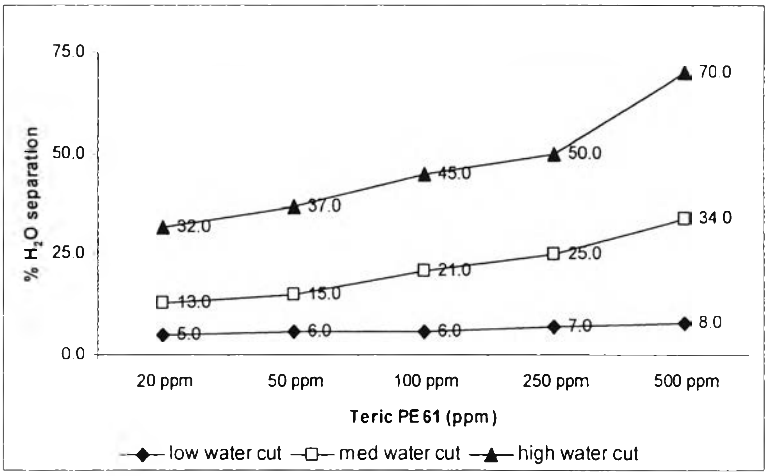
(b) Genapol ED 3060

Figure 4.12 Effect of temperature on water remaining using demulsifier concentration of 500 ppm for 3 h.

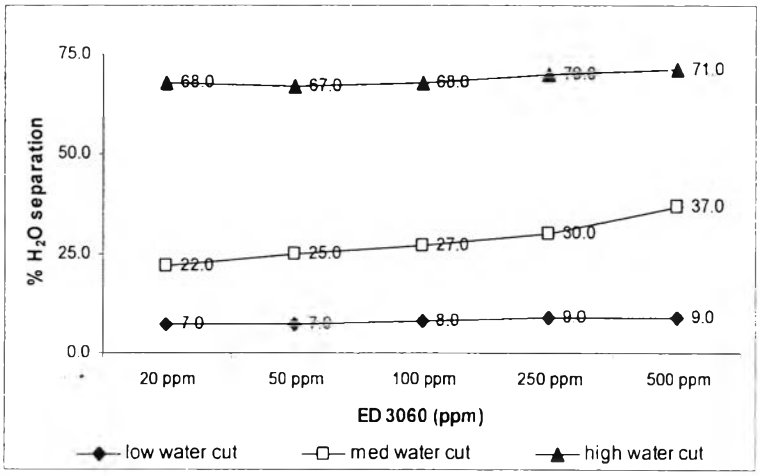
The results show that increasing the temperature results in reduction of the interfacial shear viscosity of the crude oil which leads to change the adsorption of the demulsifier at the interface and hence increase of the rate of the film drainage. In addition, the increasing in temperature also increases the number of effective collisions occurring between two dispersed water droplets prior to their coalescence (Abdel-Azim *et al.*, 2005).

4.6 Effect of Demulsifier Concentration

The mixed crude at three different water contents of low (14.7%), medium (43.0%), and high (71.3%) were demulsified at 55°C for 3 h and the demulsifier concentrations was varied in the range of 20-500 ppm. The free water separated out is shown in Figure 4.13 and water remaining in crude is shown in Figure 4.14. The results showed that free water can separate out better when using Genapol ED 3060. The water remaining in crude was lower than 0.5% when using demulsifier concentration of 50 ppm with medium and high water cut crude oil. While at demulsifier concentration of 20 ppm, only high water cut crude oil had water remaining lower than 0.5%. Therefore, it can be noted that the desired concentration was 50 ppm.

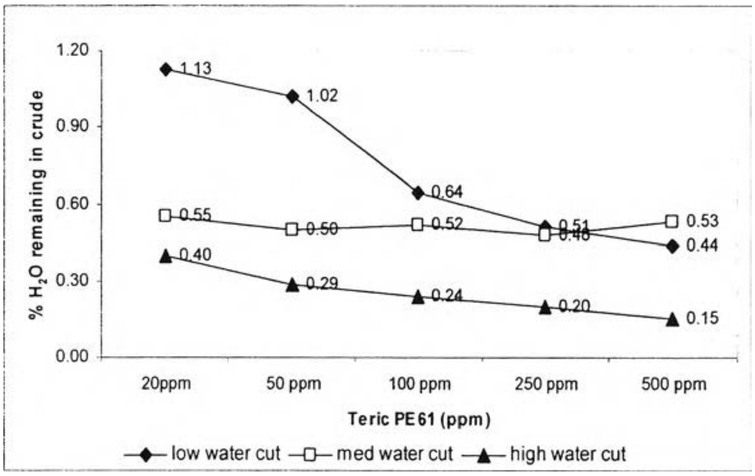


(a) Teric PE 61

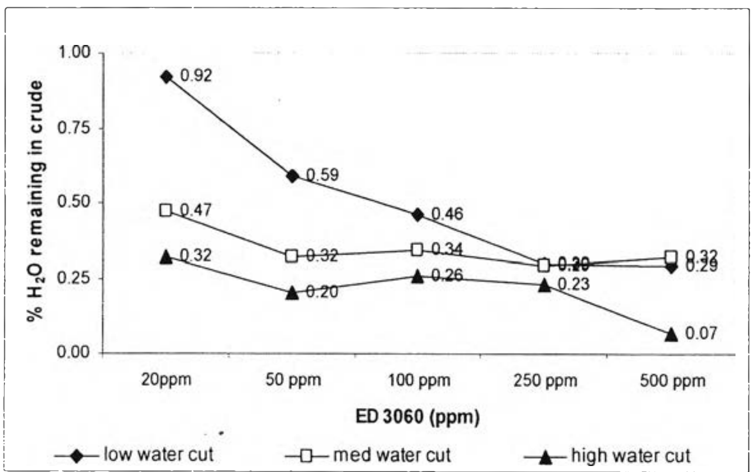


(b) Genapol ED 3060

Figure 4.13 Effect of demulsifier concentration on water separation at 55°C for 3 h.



(a) Teric PE 61



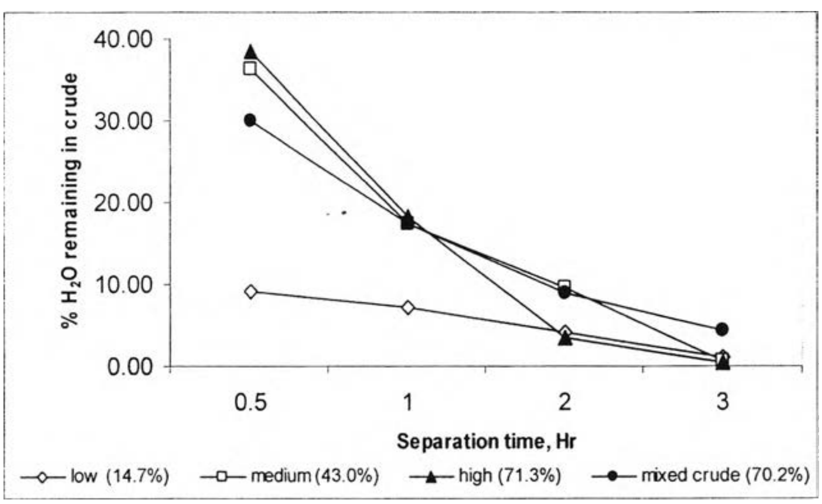
(b) Genapol ED 3060

Figure 4.14 Effect of demulsifier concentration on water remaining at 55°C for 3 h.

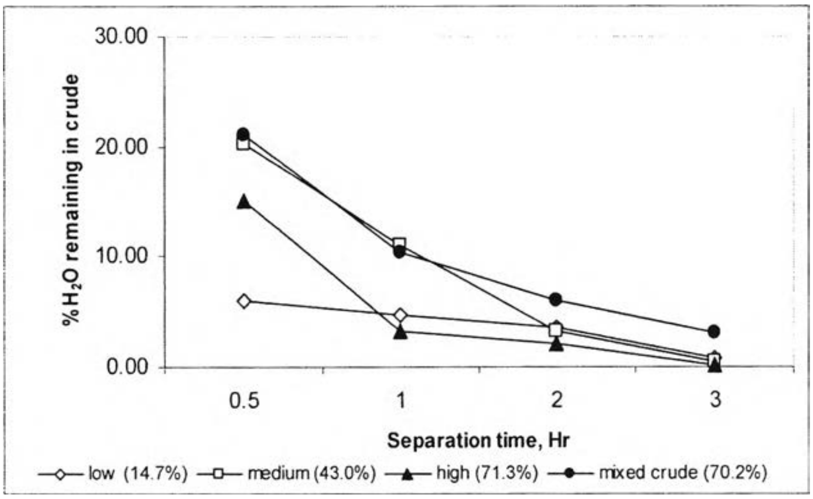
From the results, the higher the demulsifier concentration, the higher the demulsification efficiency. According to Krawczyk *et al.*, 1991, by increasing demulsifier concentration, the partition coefficient rate (partition coefficient (K_p) of demulsifiers (ratio of demulsifier concentration in the water droplet phase to concentration in the oil phase, at equilibrium) increased. Furthermore, according to Al-Sabagh *et al.*, 2002, by increasing demulsifier concentration, the adsorption of demulsifier molecules on the water droplet interface also increased, resulting in a decrease in interfacial tension, and an increase in water separation rate.

4.7 Effect of Separation Time

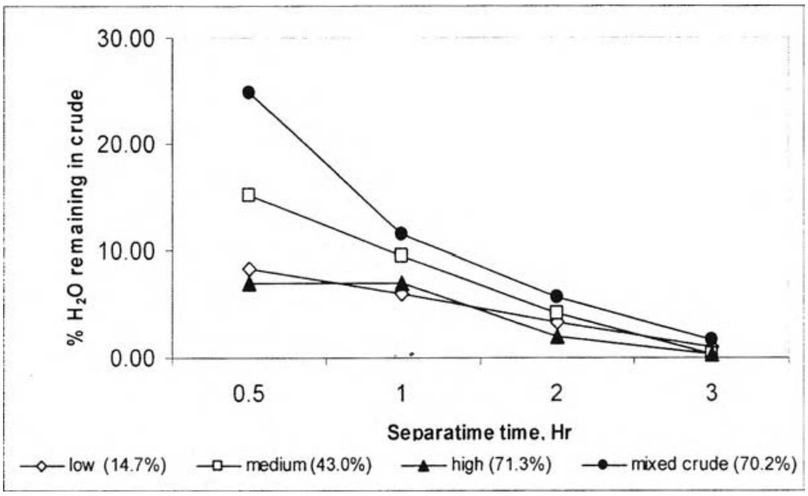
The mixed crude (W05T and B02T) at three different water contents of low (14.7%), medium (43.0%), and high (71.3% and 70.24%) water cut were demulsified at 55°C using the demulsifier concentrations of 20 and 50 ppm and separation time was varied from 0.5 to 3 h. The water remaining in crude is shown in Figures 4.15 (a-d). The results showed that all crudes had water remaining lower than 0.5 vol% at 3 h separation time when using demulsifier concentration of 50 ppm in both demulsifiers but 50 ppm of Genapol ED 3060 gave the water remaining in crude lower than 0.5% at 2 h with middle and high water cut crude oil. From these results, it can be noted that water remaining in crude was lower than 0.5% at 2 to 3 h separation time when 50 ppm of demulsifier concentration was added.



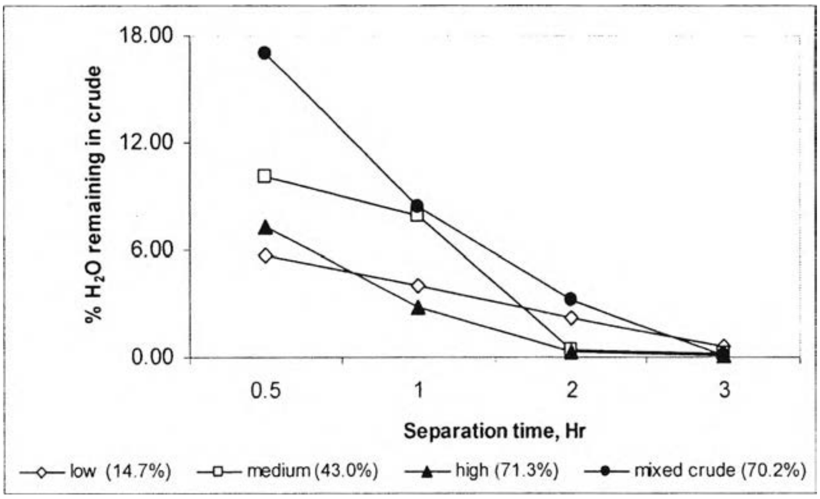
(a) Teric PE 61, 20 ppm



(b) Teric PE 61, 50 ppm



(c) Genapol ED 3060, 20 ppm

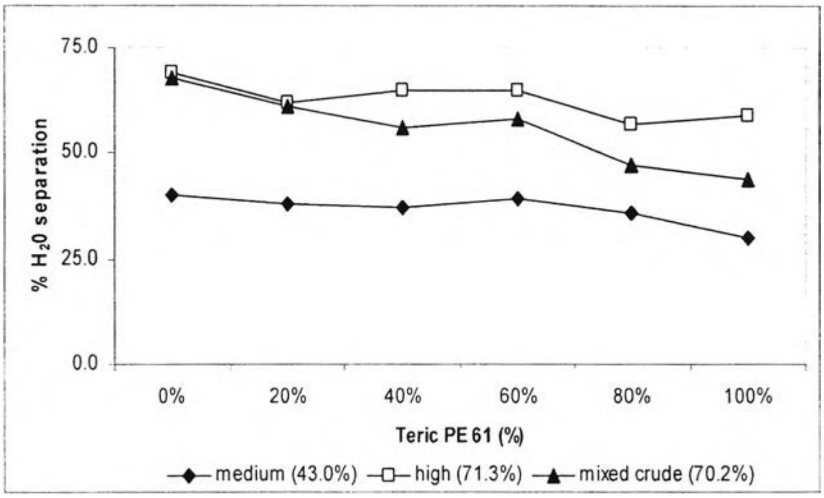


(d) Genapol ED 3060, 50 ppm

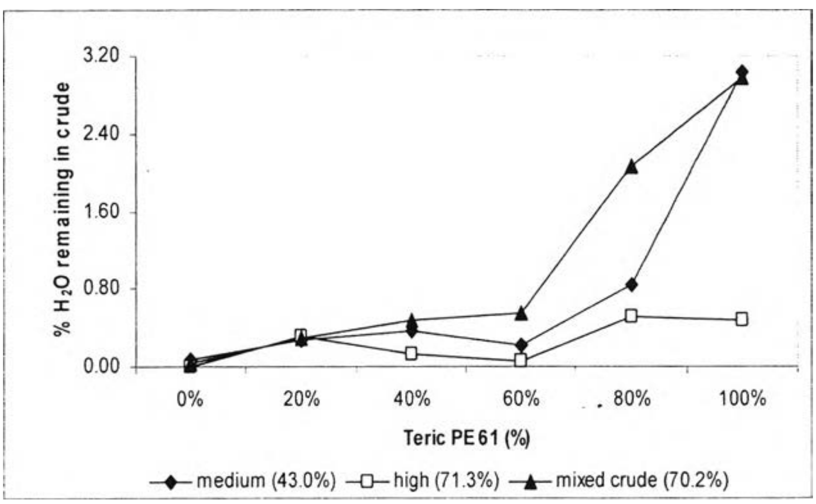
Figure 4.15 Effect of separation time on water remaining at 55°C using demulsifier concentrations of 20 and 50 ppm.

4.8 Optimum Conditions and Mixed Demulsifiers

The optimum conditions found were; demulsifier concentration of 50 ppm, 55°C, 3 h separation time. Furthermore, mixed demulsifiers were used in order to study the synergistic effect. The water separation and water remaining in crude are shown in Figures 4.16 (a-b). The highest water separation and water remaining in crude less than 0.5% were obtained from Genapol ED 3060 in every crude while at other ratios water separation was not higher than that obtained from Genapol ED 3060. Genapol ED 3060 gave the highest demulsification efficiency and the mixed demulsifiers of Teric PE 61 and Genapol ED 3060 showed no synergistic effect on demulsification. The observed ineffectiveness of mixed demulsifiers was theoretically due to the fact that both components were nonionic.



(a) Water separation



(b) Water remaining in crude

Figure 4.16 Demulsification using optimum conditions at 55°C and mixed demulsifiers of Teric PE 61 and Genapol ED 3060 at concentration of 50 ppm.

4.9 Large Scale Test

The large scale test was conducted using 250 ml mixed crude with water content of 70.24% (B15T : X12T : B02T : B24T = 1 : 1 : 2 : 2). Mixed crude was demulsified for 3 h using 50 ppm of 100%Genapol ED 3060 and temperature at 55°C. The results of water separation and water remaining in the crude are shown in

Figures 4.17. The results showed that at 2 h separation time and demulsifier concentration of 50 ppm of 100%Genapol ED 3060 separated water 60.0% and water remaining in crude was equal to 0.32%. It seemed that the large scale test gave the same efficiency in demulsificaton when compared with the lab scale test that was done in all experiments before.

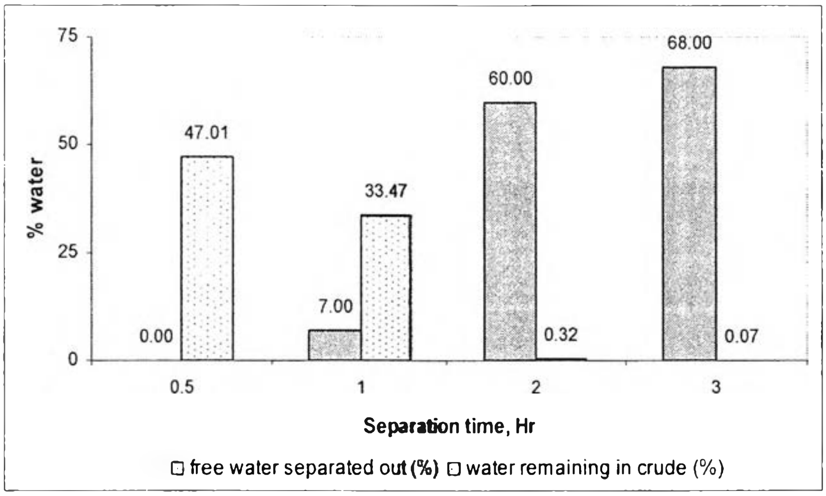


Figure 4.17 Large scale test (250 ml) at 55°C using demulsifier concentration of 50 ppm for 3 h by 100%Genapol ED 3060.

4.10 Economic Assessment

The data of demulsifier injection provided by the Company is demulsifier (solution form) injection 30 ppm per gross product while gross product equal to 60,000 bbl per day. Cost of commercial demulsifier (PT 5135) equal to 14,617 baht per 200 liters or 73.09 baht per liter. Therefore, the cost of demulsifier injection of the petroleum company is equal to 20,917 baht per day.

In this study, demulsification was performed at the optimum conditions. The mixed crude had a water content of 70.24%. The temperature and demulsifier concentration were studied at 55°C and 50 ppm. To decrease the viscosity of demulsifiers, solvent must be used, in this case, xylene was used. The diluted demulsifier was prepared by diluting in the solvent (the ratio of demulsifier : solvent = 1.5 : 1). Tables 4.5 and 4.6 show cost of demulsifiers and solvents, respectively.

Table 4.4 Cost of demulsifiers (Baht/L)

Demulsifier Type	Cost (Baht/L)
Teric PE 61	127.1
Teric PE 62	129.0
Genapol EP 2584	138.6
Genapol ED 3060	144.2

Table 4.5 Cost of solvents (Baht/L)

Solvent Type	Cost (Baht/L)
Xylene	27.2
Toluene	28.5

Cost of demulsifier injection (baht per day) of Teric PE 61 and Genapol ED 3060 by using demulsifier concentration in the range of 10-50 ppm is shown in Figure 4.18. As the commercial demulsifier consists of several unknown chemicals, the cost and amount of the demulsifier used by the Company could not be directly compared with those used and calculated in this study.

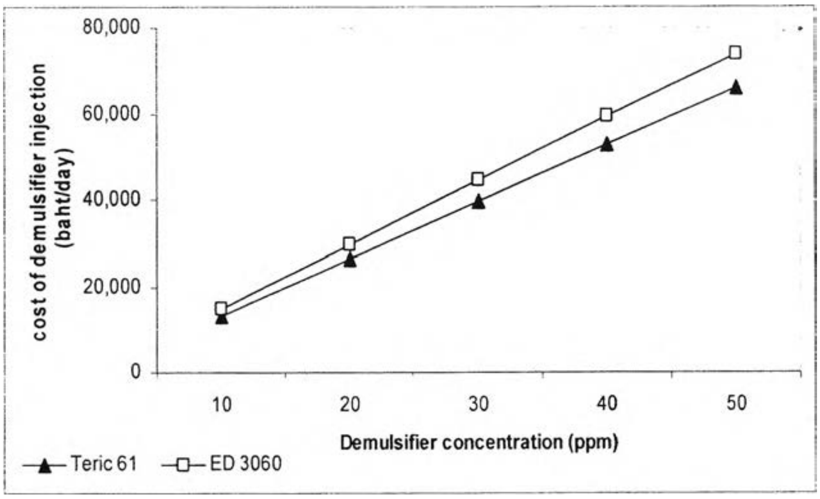


Figure 4.18 Cost of demulsifier injection at optimum condition with varying the demulsifier concentration.