CHAPTER IV
RESULT AND DISCUSSION

4.1 Microemulsion Formation

The objective of this study was to investigate the relationship between the efficiency of froth flotation and the ultra-low interfacial tension (IFT) of wastewater containing diesel. Alfoterra 145-5PO (Branch alcohol propoxylated sulfate, sodium salt) was used as a surfactant to form the ultra-low IFT with diesel because Alfoterra has a proper HLB for diesel-water system and expected to form middle phase microemulsion. The effect of surfactant concentration was studied.

From the previous work (Watcharasing, 2004), the microemulsion formation of diesel with Alfoterra showed only two obvious phases, which were the water and oil phases. The layer of the middle phase was very thin, and it could not be clearly observed visually. Consequently, the measurement of the phase transformation became difficult to identify whether the system had a middle phase or not. Hence, the phase diagram of diesel with Alfoterra is not shown here. The IFT of the system was measured by the spinning drop tensiometer to examine the existence of Winsor Type II microemulsions.

In Figure 4.1, the IFT of the system decreases rapidly when Alfoterra concentration increases from 0.05 to 0.10 wt%. And then, it increases gradually with the increase in the Alfoterra concentration from 0.10 to 0.5 wt%. This is because the repulsive force between the anionic head groups of Alfoterra increases with the increase in the Alfoterra concentration. Therefore, micelle is difficult to form leading to lower oil solubilization, but higher IFT as shown by Equation (4.1), Chun-Huh's equation.

$$\gamma \ \alpha \ SP^{-2} \qquad (4.1)$$

where; γ = interfacial tension

SP = solubilization parameter

The minimum IFT around 3.025×10^{-2} mN/m was found at 0.10 wt% of Alfoterra is considered to be in the range of the ultra-low IFT (10^{-2}-10^{-3} dyne/cm) which is typically observed in a system with the middle phase microemulsion formation. Consequently, it can be concluded that the phase behavior study of the diesel system using Alfoterra as a surfactant can form the middle phase or Winsor Type III microemulsion. So, the Alfoterra concentration of 0.10 wt% was selected for future study.

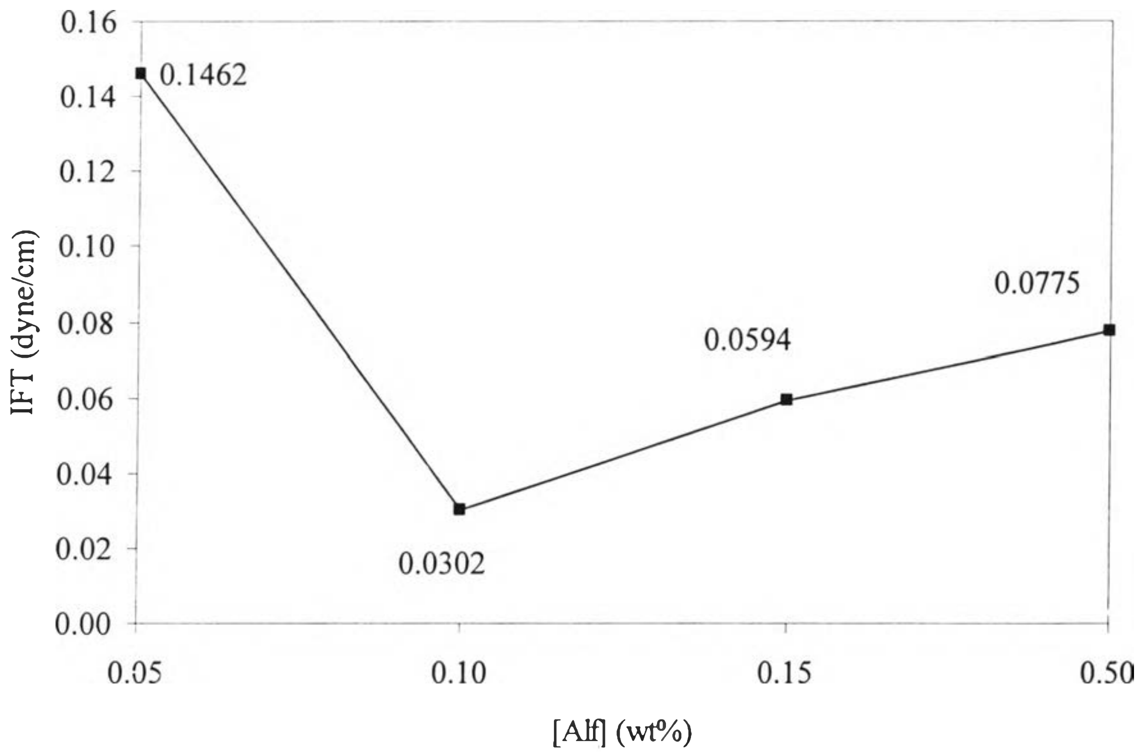

Figure 4.1 IFT as a function of Alfoterra concentration at 5 wt% of NaCl with oil to water ratio = 1:1 (v:v), and 30 °C.

4.2 Study of Colloidal Gas Aphrons

This study investigated the efficiency of colloidal gas aphrons (CGAs) in diesel removal at the ultra-low IFT of diesel system. Alfoterra 145-5PO (Branch alcohol propoxylated sulfate, sodium salt) was used as a surfactant to form the CGAs. The effect of stirring speed of homogenizer, stirring time of homogenizer, surfactant concentration, and NaCl concentration was study.

Oil removal and enrichment ratio were considered as significant parameters for the performance of CGAs in diesel removal. In addition, CGAs stability, gas hold up, and separation ratio were also determined.

4.2.1 Effect of Stirring Speed on Performance of CGAs in Diesel Removal

As a result of effect of stirring speed of homogenizer, the colloidal gas aphron stability and gas hold up increase with increasing stirring speed from 4000 to 8000 rpm as shown in Figures 4.2 and 4.3. This is because when the solution is agitated further, the stability increases due to an increase in surface area. However, that only slightly affects oil removal in the range of study. At the speed of 4000 rpm, the oil removal is lower than that at 5000 rpm because gas hold up is lower than 0.6, a critical value for CGAs to form. Figure 4.4 illustrates the effect of stirring speed on oil removal. As a result, the effect of stirring speed on oil removal is corresponding to the separation and enrichment ratios as shown in Figures 4.5 and 4.6. Therefore, the stirring speed of 5000 rpm is the optimum speed and minimum requirement.

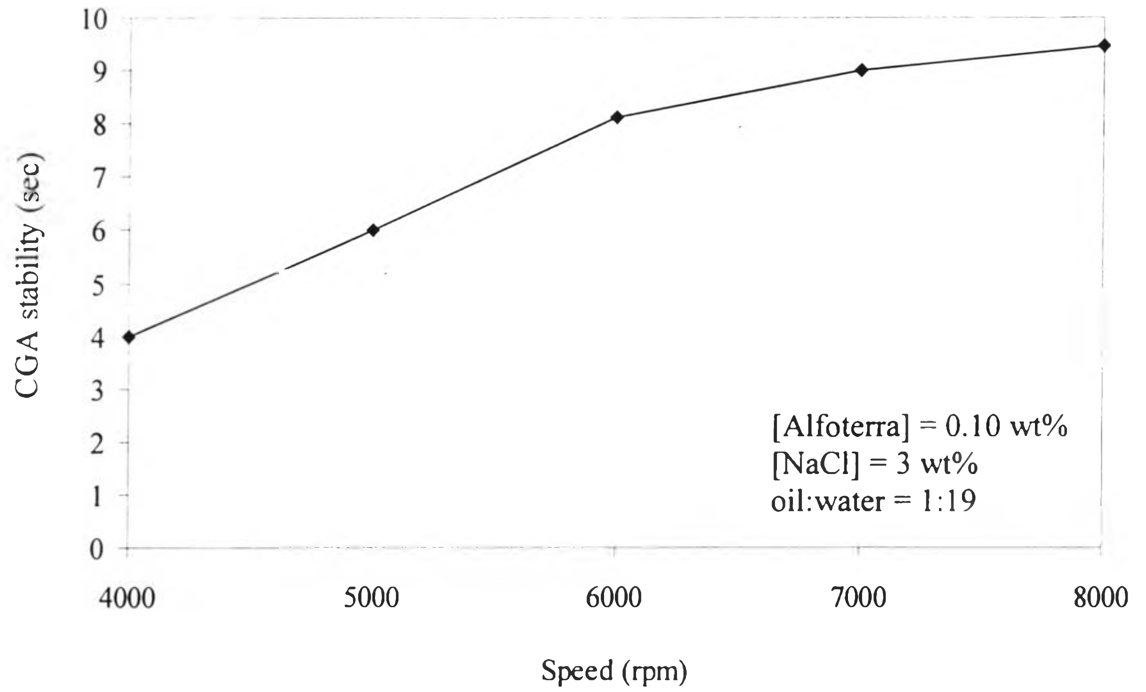

Figure 4.2 Colloidal gas aphron stability at different stirring speed: [Alfoterra] = 0.10 wt%, [NaCl] = 3 wt%, oil:water ratio = 1:19.

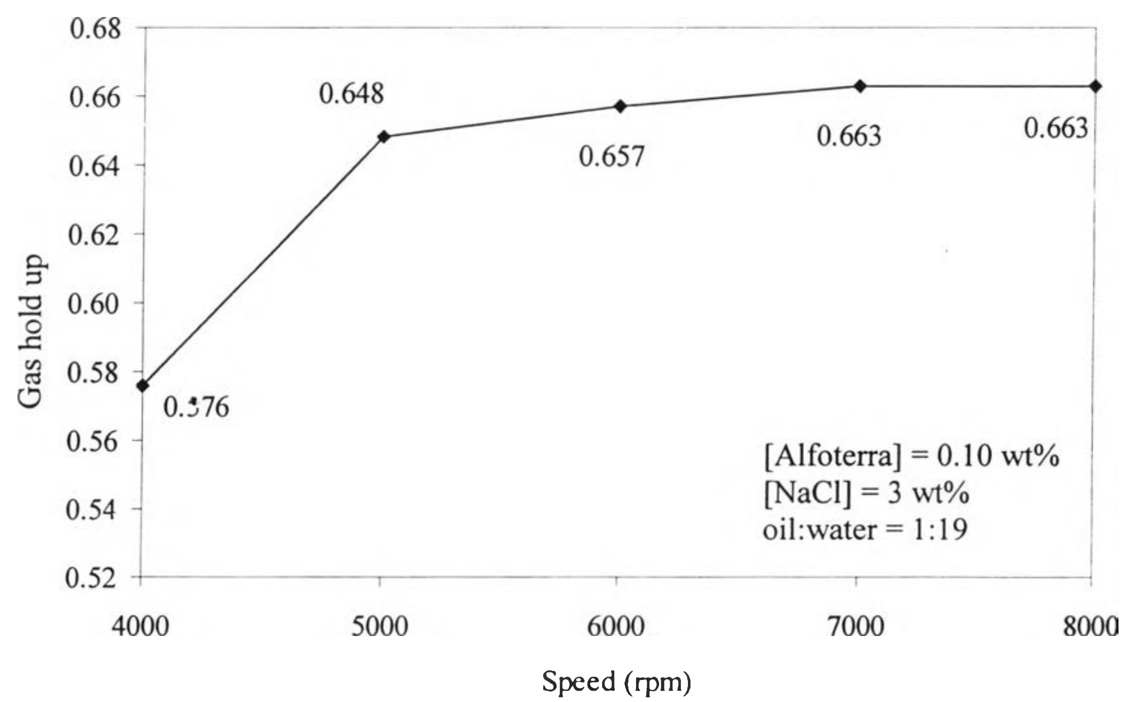

Figure 4.3 Gas hold up at different stirring speed: [Alfoterra] = 0.10 wt%, [NaCl] = 3 wt%, oil:water ratio = 1:19.

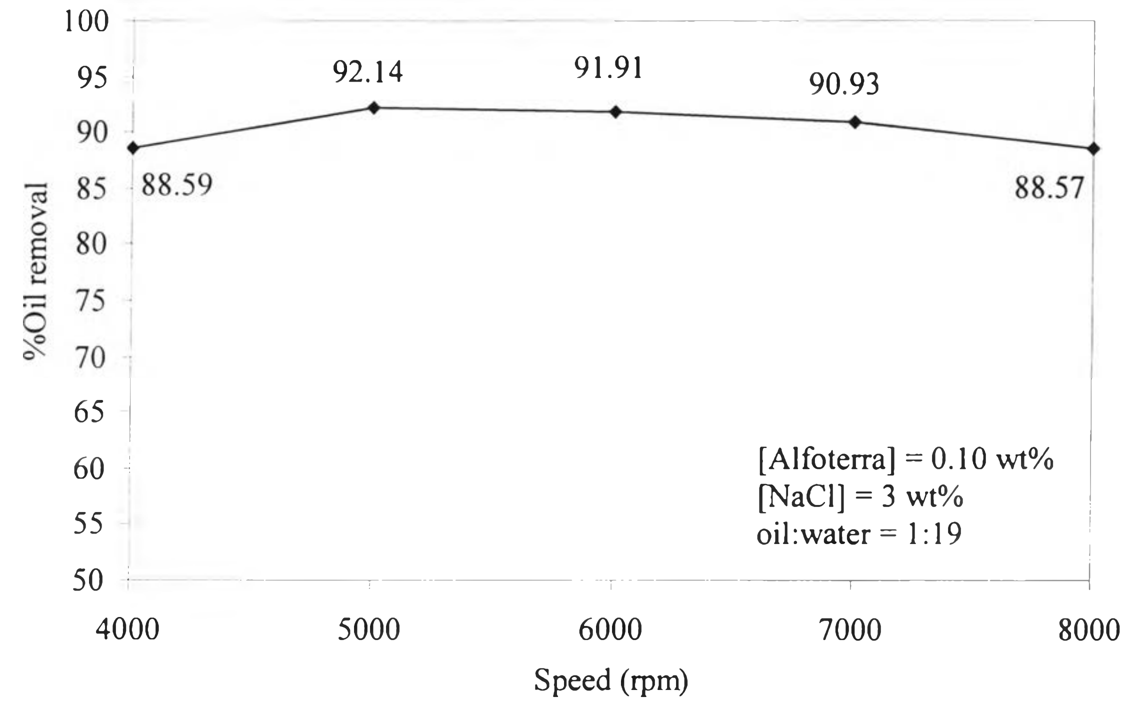

Figure 4.4 Removal efficiency of diesel oil at different stirring speed: [Alfoterra] = 0.10 wt%, [NaCl] = 3 wt%, oil:water ratio = 1:19.

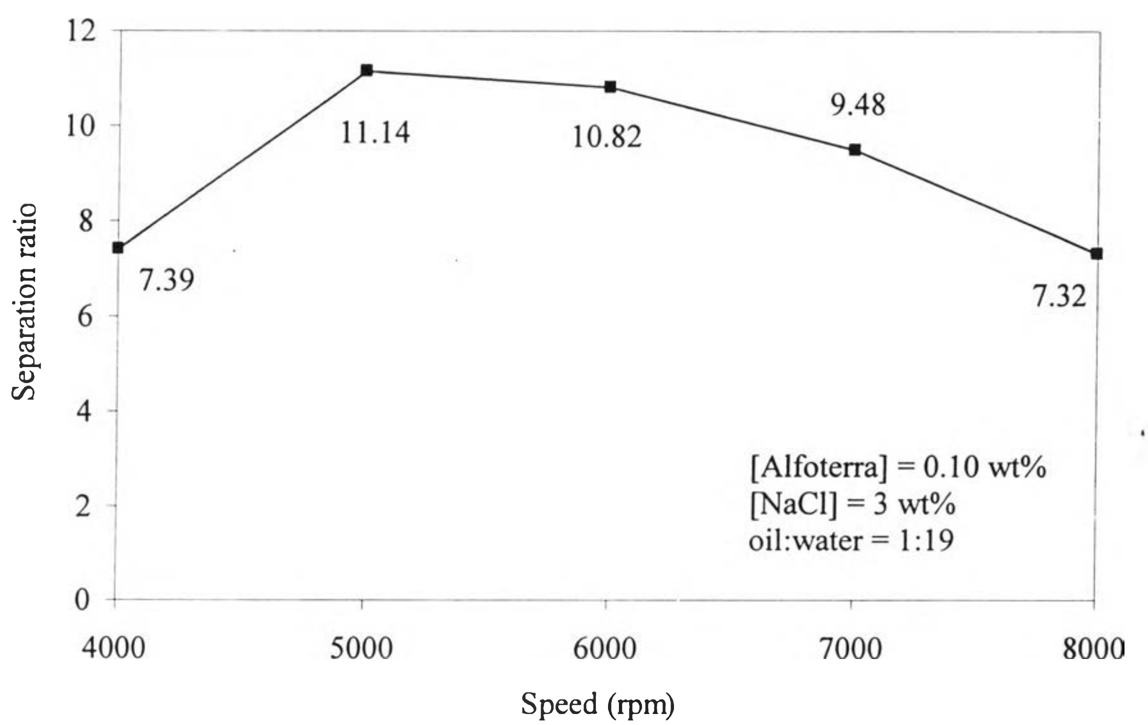

Figure 4.5 Separation ratio of diesel oil at different stirring speed: [Alfoterra] = 0.10 wt%, [NaCl] = 3 wt%, oil:water ratio = 1:19.

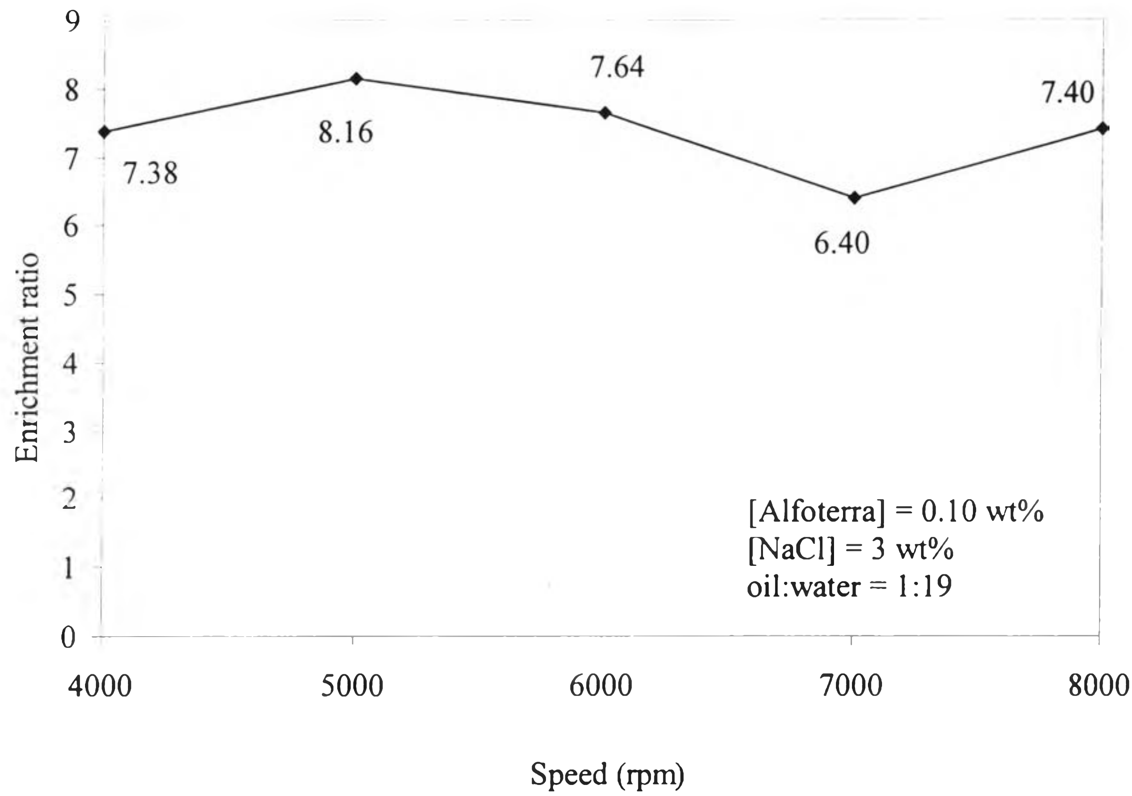

Figure 4.6 Enrichment ratio of diesel oil at different stirring speed: [Alfoterra] = 0.10 wt%, [NaCl] = 3 wt%, oil:water ratio = 1:19.

4.2.2 Effect of Stirring Time on Performance of CGAs in Diesel Removal

The effect of stirring time of homogenizer on CGA stability and gas hold up is shown in Figures 4.7 and 4.8. When increasing stirring time from 2 to 15, the stability and gas hold up increase. Save and Pangarkar (1994) reported that at lower surfactant concentration, with increasing time of stirring, the rate of dispersion was probably higher than the rate of coalescence thus resulting in higher stability. Figure 4.9 illustrates the effect of stirring time on oil removal. The highest percent oil removal locates at the stirring time of 5 min and it has the same trend of separation ratio as shown in Figure 4.10. Enrichment ratio is also high as shown in Figure 4.11. Hence, the stirring speed of 5000 rpm and stirring time of 5 min was chosen as the optimum condition.

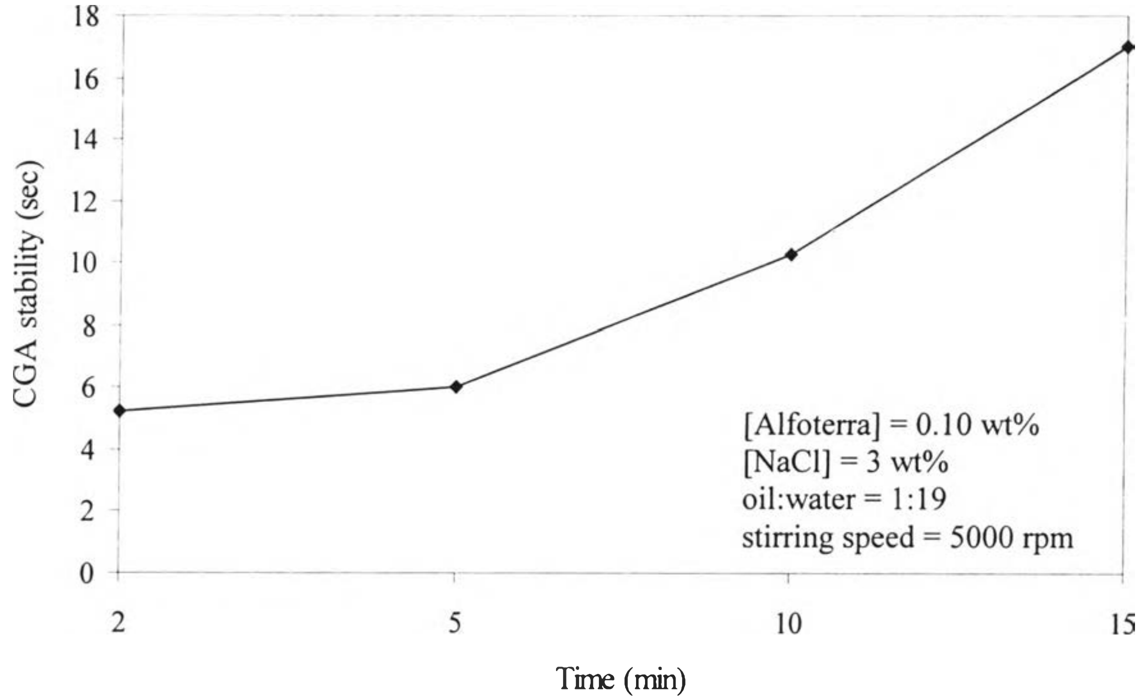

Figure 4.7 Colloidal gas aphron stability at different stirring time: [Alfoterra] = 0.10 wt%, [NaCl] = 3 wt%, oil:water ratio = 1:19, stirring speed = 5000 rpm.

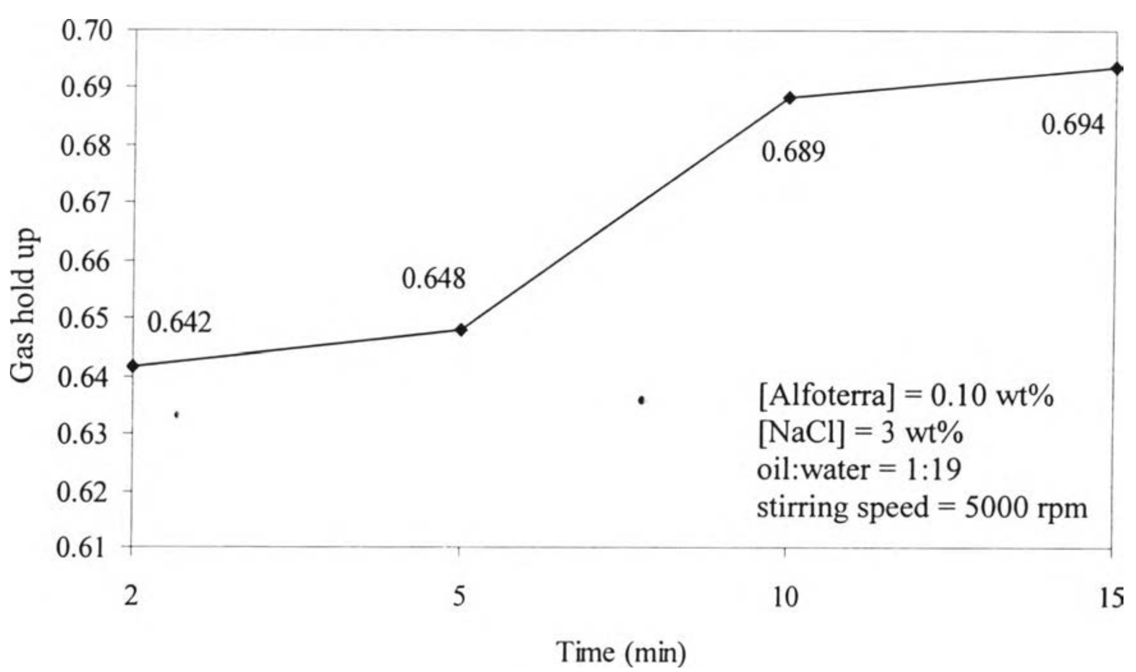

Figure 4.8 Gas hold up at different stirring time: [Alfoterra] = 0.10 wt%, [NaCl] = 3 wt%, oil:water ratio = 1:19, stirring speed = 5000 rpm.

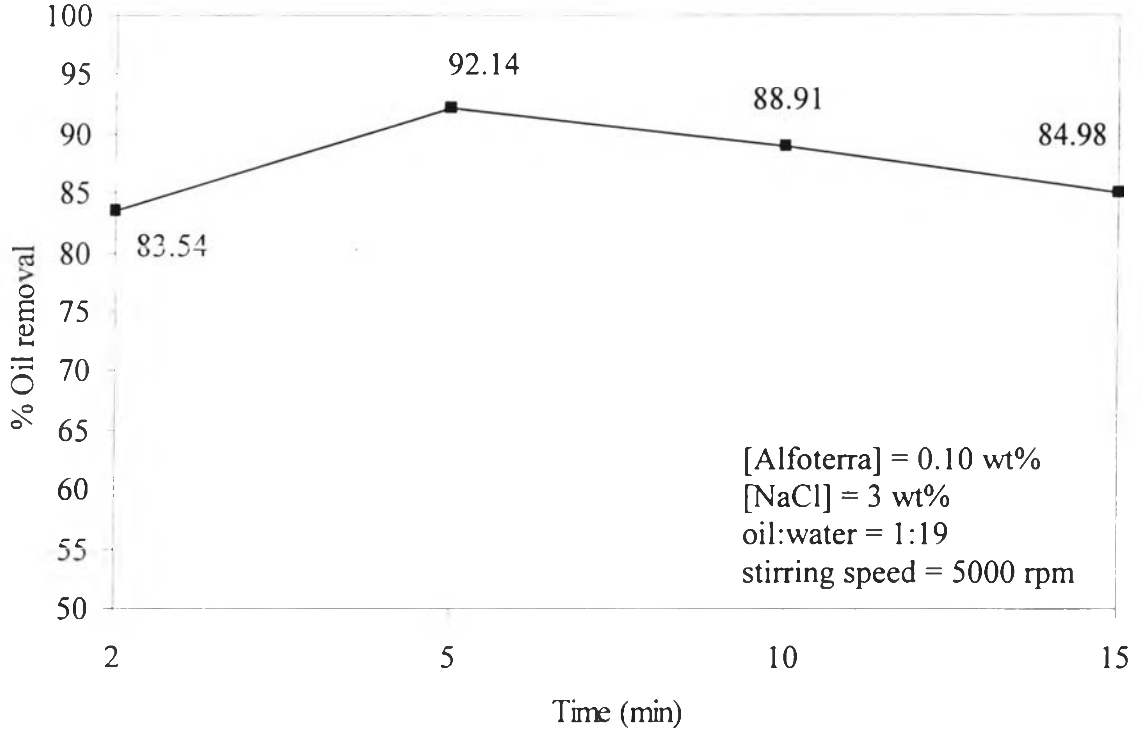

Figure 4.9 Removal efficiency of diesel oil at different stirring time: [Alfoterra] = 0.10 wt%, [NaCl] = 3 wt%, oil:water ratio = 1:19, stirring speed = 5000 rpm.

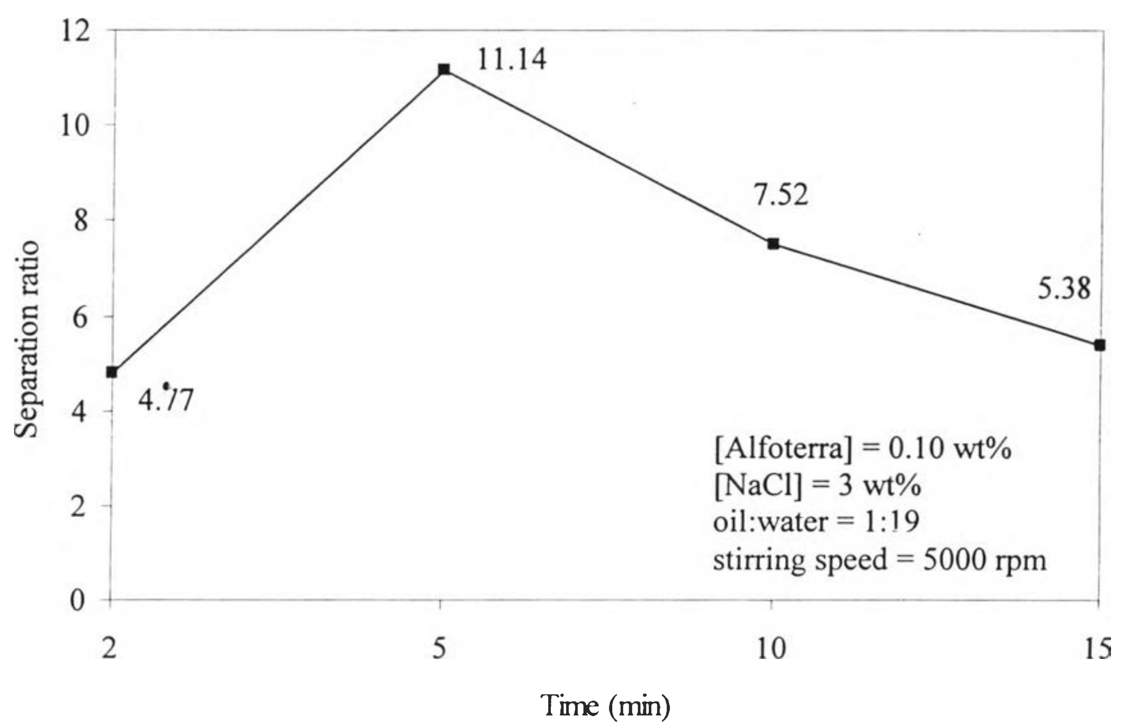

Figure 4.10 Separation ratio of diesel oil at different stirring time: [Alfoterra] = 0.10 wt%, [NaCl] = 3 wt%, oil:water ratio = 1:19, stirring speed = 5000 rpm.

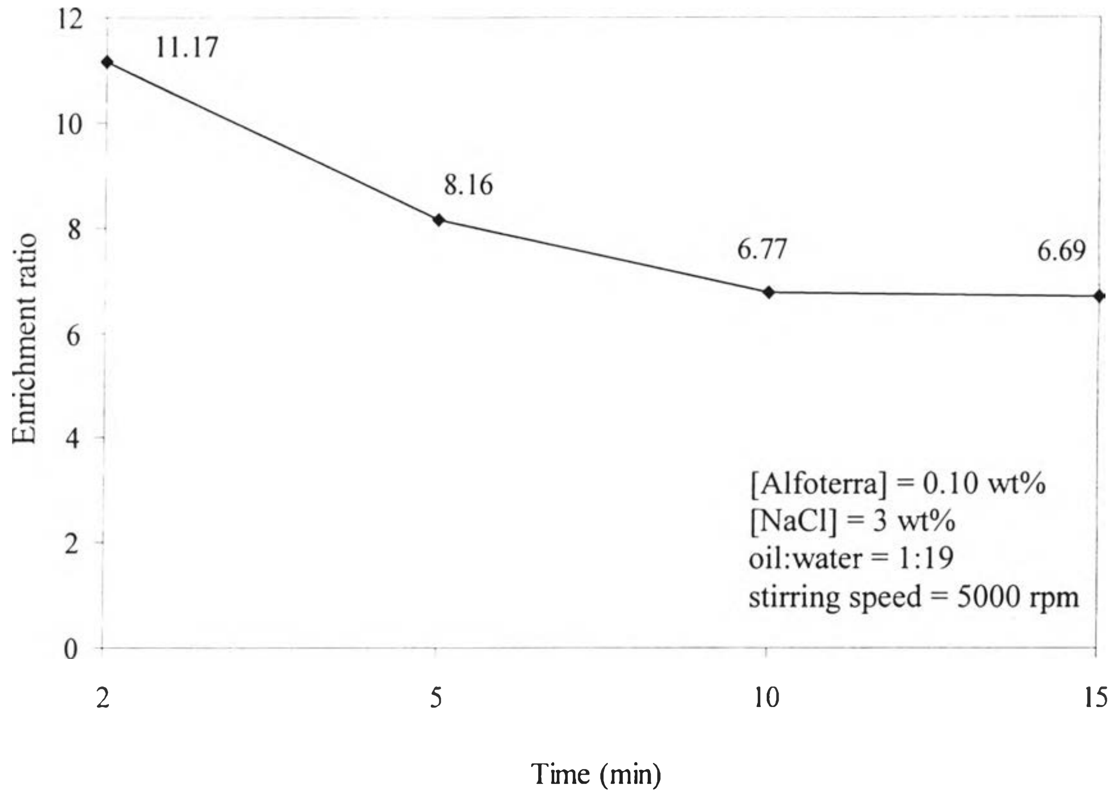

Figure 4.11 Enrichment ratio of diesel oil at different stirring time: [Alfoterra] = 0.10 wt%, [NaCl] = 3 wt%, oil:water ratio = 1:19, stirring speed = 5000 rpm.

4.2.3 Effect of Surfactant Concentration on Performance of CGAs in Diesel Removal

Figures 4.12 and 4.13 show that the CGA stability and gas hold up increase with increasing surfactant concentration. These results are consistent with those reported by Chaphalkar *et al.* (1993). andJauregi *et al.* (1997). As the concentration of surfactant increases, either in the CGAs shell or in the bulk liquid phase, repulsive and stabilizing forces between aphrons are likely to increase. Consequently, it will delay the coalescence of aphrons. Moreover, larger amount of aphrons should be formed at higher surfactant concentration.

The effect of surfactant concentration was studied at the levels of 0.05, 0.1, 0.15, and 0.5 wt%. The effect of surfactant concentration on oil removal is shown in Figure 4.14. The highest percent oil removal presents at the surfactant concentration of 0.1 wt% and it has the same trend of separation ratio as shown in Figure 4.15. In Figure 4.16, every surfactant concentration also has high enrichment ratio. Hence, the stirring speed of 5000 rpm, stirring time of 5 min, and surfactant concentration of 0.1 wt% was chosen as the optimum condition.

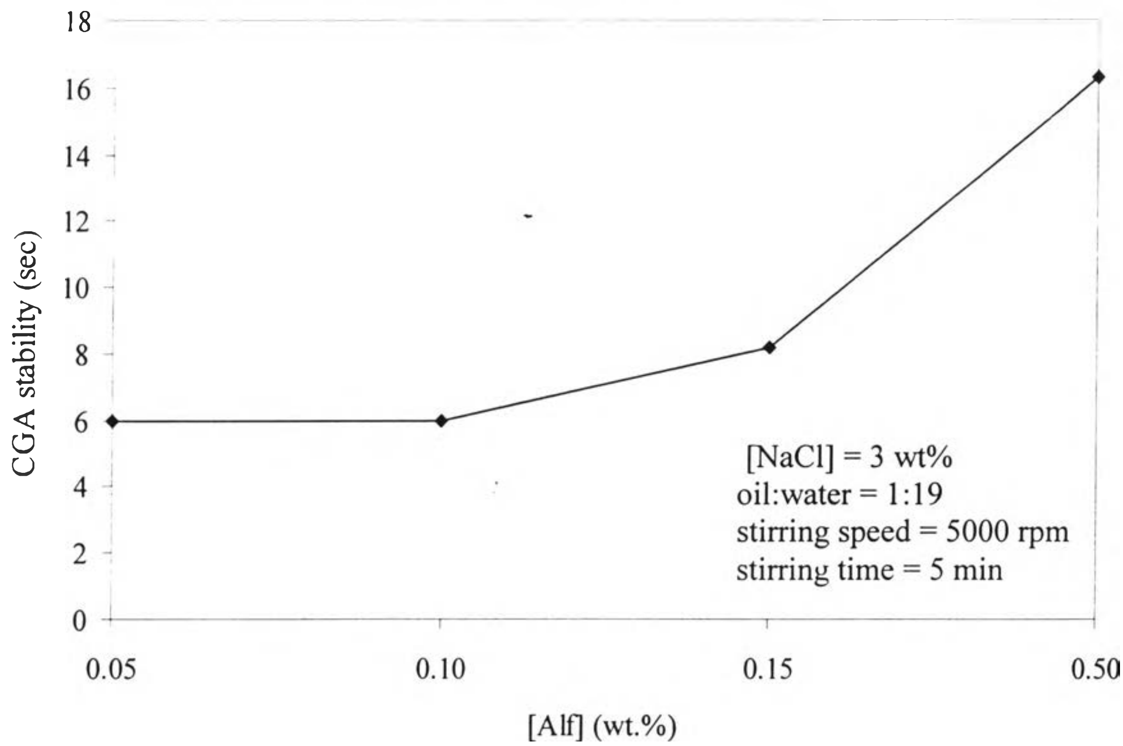

Figure 4.12 Colloidal gas aphron stability at different surfactant concentration: [NaCl] = 3 wt%, oil:water ratio = 1:19, stirring speed = 5000 rpm, stirring time = 5 min.

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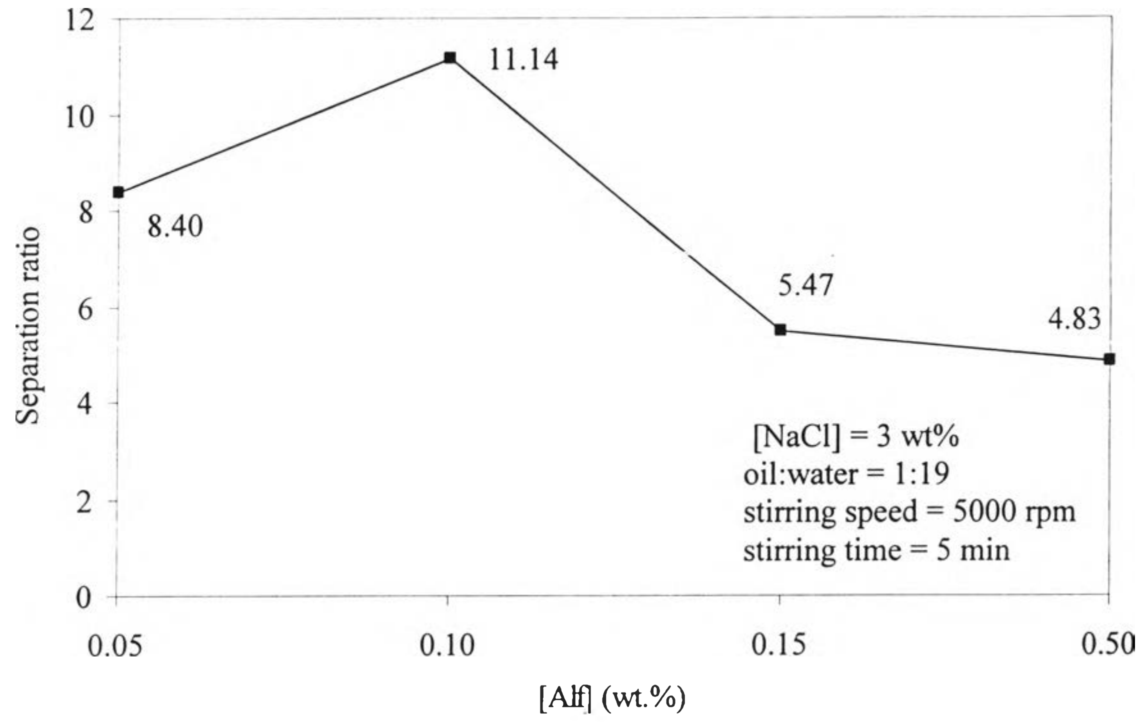

Figure 4.15 Separation ratio of diesel oil at different surfactant concentration: [NaCl] = 3 wt%, stirring speed = 5000 rpm, stirring time = 5 min.

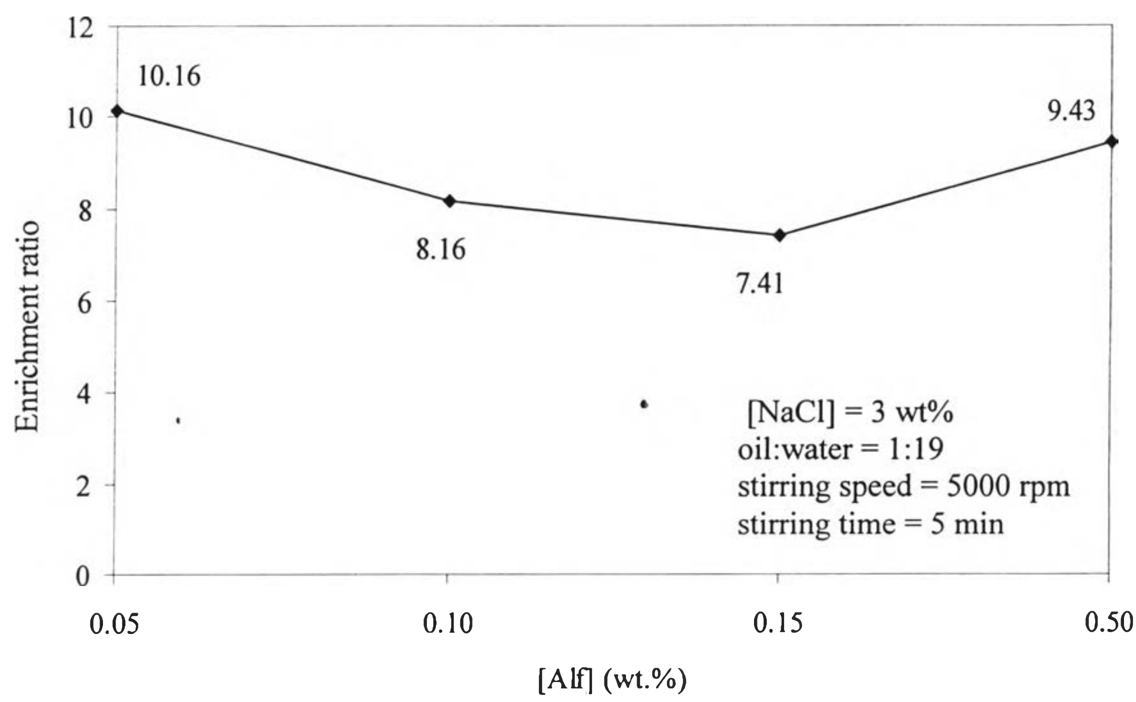

Figure 4.16 Enrichment ratio of diesel oil at different surfactant concentration: [NaCl] = 3 wt%, stirring speed = 5000 rpm, stirring time = 5 min.

4.2.4 Effect of NaCl Concentration on Performance of CGAs in Diesel Removal

As shown in Figures 4.17 and 4.18, an increase in NaCl concentration from 2 to 6 wt%, the CGA stability and gas hold up decrease because the basis of electrostatic interactions which play an important role in the stability of this type of dispersion. There are repulsive electrostatic interactions between the negatively charged aphrons and these interactions stabilize the system. The addition of salts or electrolytes has an effect on the electrostatic interactions. Increasing the concentration of salt (NaCl) causes these interactions to be suppressed leading to the formation of a less stable dispersion (Jauregi *et al.*, 1997).

The effect NaCl concentration on oil removal is shown in Figure 4.19. The highest percent oil removal presents at the NaCl concentration of 3 wt% and in Figure 4.20, it has the same trend of separation ratio. Enrichment ratio increases when NaCl concentration increases as shown in Figure 4.21.

Hence, the stirring speed of 5000 rpm, stirring time of 5 min, surfactant concentration of 0.1 wt%, and NaCl concentration of 3 wt% was chosen as the optimum condition in the experiment.

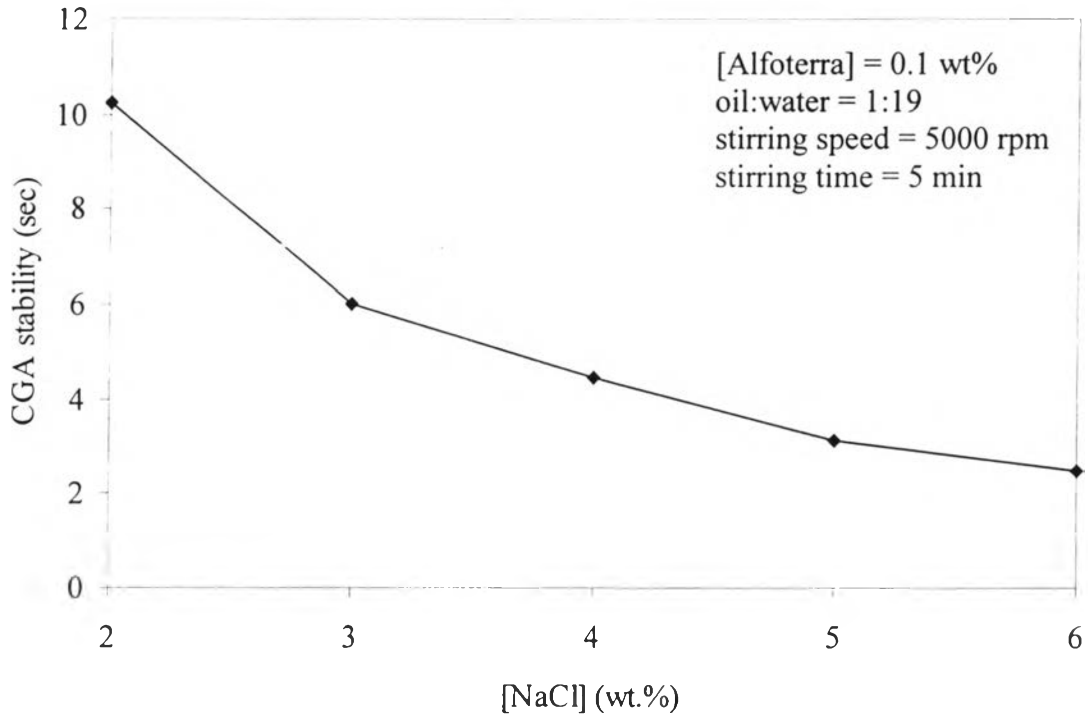

Figure 4.17 Colloidal gas aphron stability at different NaCl concentration: [Alfoterra] = 0.10 wt%, stirring speed = 5000 rpm, stirring time = 5 min.

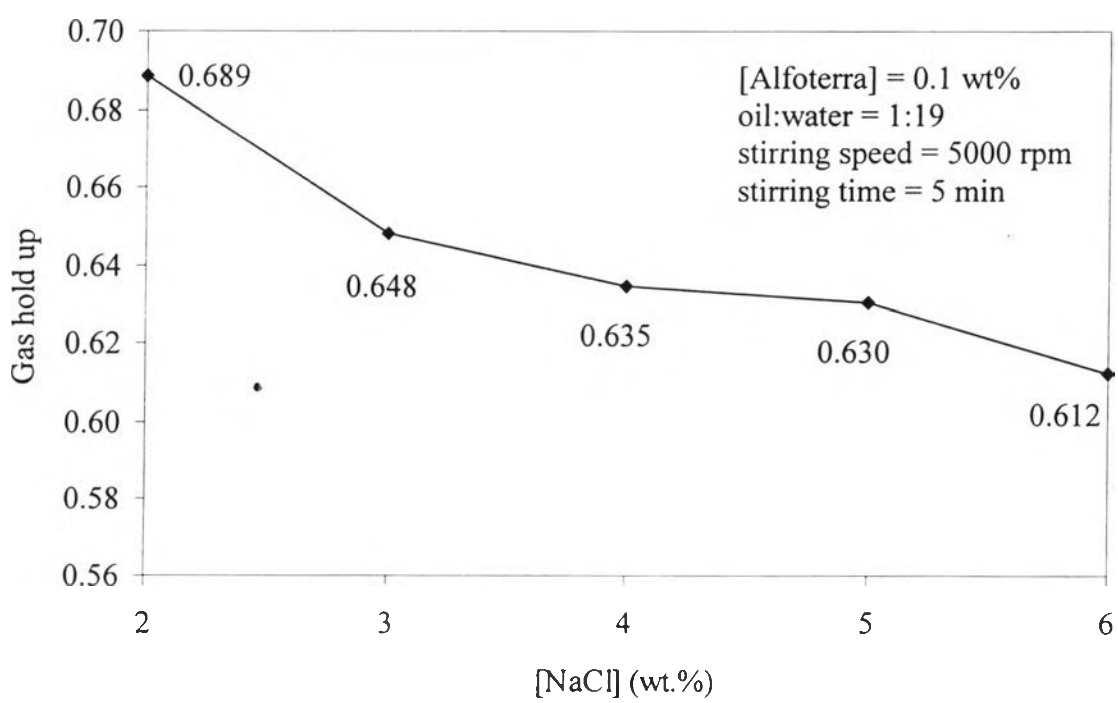

Figure 4.18 Gas hold up at different NaCl concentration: [Alfoterra] = 0.10 wt%, stirring speed = 5000 rpm, stirring time = 5 min.

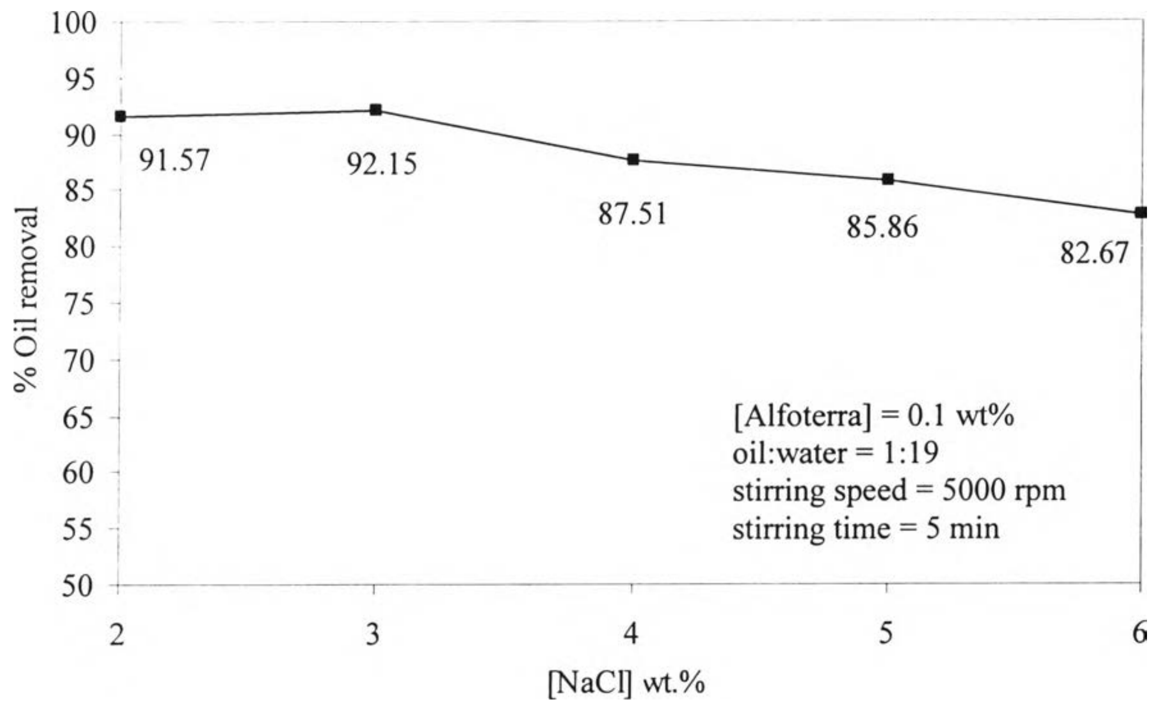

Figure 4.19 Removal efficiency of diesel oil at different NaCl concentration: [Alfoterra] = 0.10 wt%, stirring speed = 5000 rpm, stirring time = 5 min.

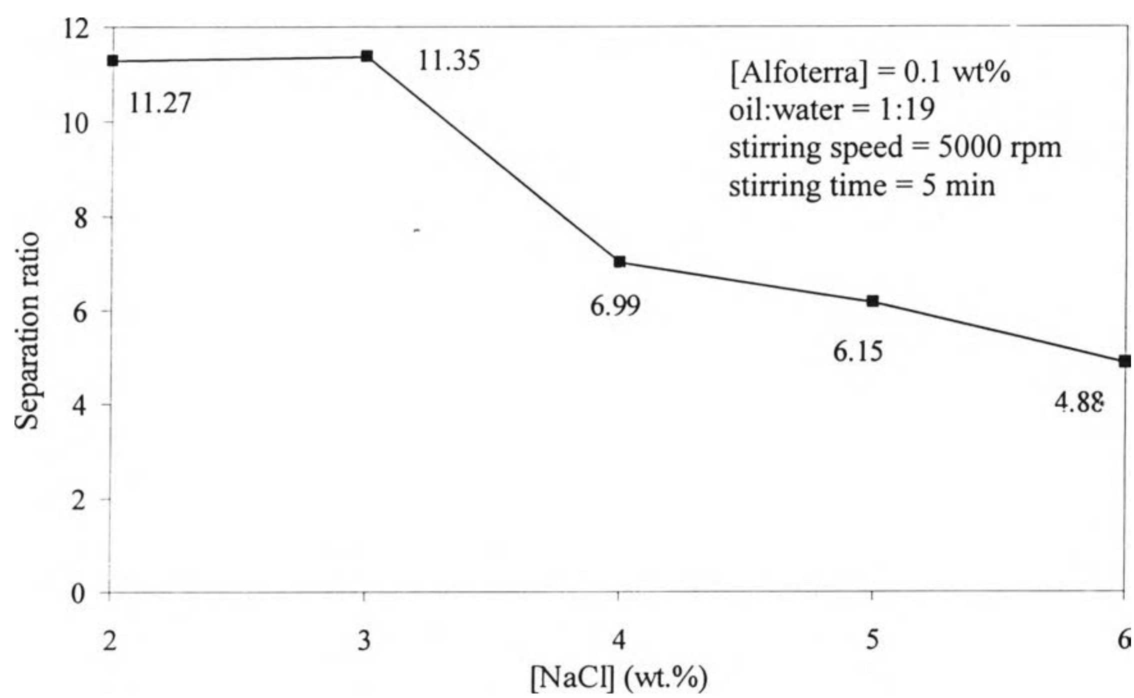

Figure 4.20 Separation ratio of diesel oil at different NaCl concentration: [Alfoterra] = 0.10 wt%, stirring speed = 5000 rpm, stirring time = 5 min.

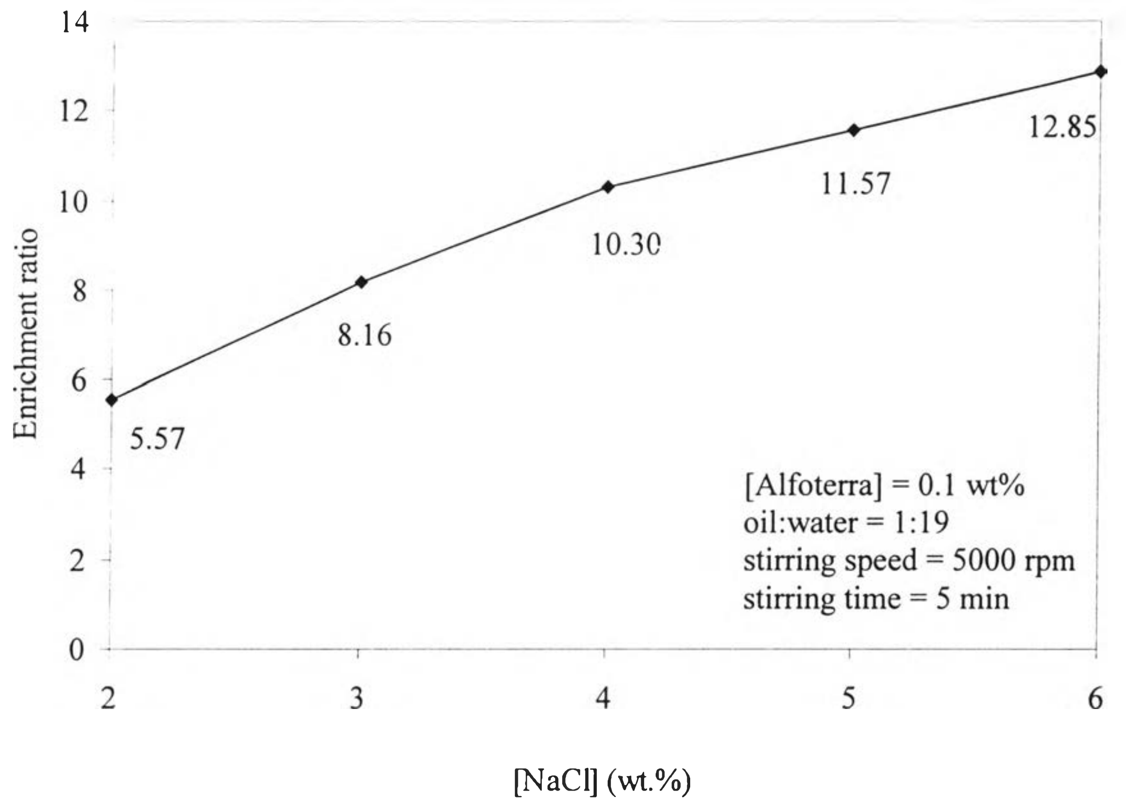

Figure 4.21 Enrichment ratio of diesel oil at different NaCl concentration: [Alfoterra] = 0.10 wt%, oil:water ratio = 1:19, stirring speed = 5000 rpm, stirring time = 5 min.

4.3 Froth Flotation Experiments

In this study, oil removal and enrichment ratio are considered as significant parameters for the performance of froth flotation. Moreover, the surfactant removal, foam wetness, and foam flow rate were also determined. In order to treat wastewater, not only emulsified oil but also surfactants used to treat wastewater are present in the treated water in very low concentrations.

High oil removal efficiency is a vital requirement for an effective froth flotation process, but it is not the sole factor to be considered. If oil and water are present in the froth in the same proportional as in an influent solution, the selectivity and separation of oil and water do not occur. Hence, for effective separation, the concentration of oil in the overhead froth should be higher than that in the feed.

Consequently, the separation efficiency is indicated by the enrichment ratio in this study. The enrichment ratio is defined as the ratio of concentration of oil in the overhead froth to that in the feed. In order to achieve the separation, the enrichment ratio must be greater than one. Moreover, the higher the enrichment ratio, the higher the separation is achieved.

From the study of CGAs in diesel removal, the optimum condition in the experiment is the stirring speed of 5000 rpm, stirring time of 5 min, surfactant concentration of 0.1 wt%, and NaCl concentration of 3 wt%. So, this condition was selected for the froth flotation experiments.

4.3.1 Effect of Air Flow Rate on Performance of Froth Flotation

Air flow rate is one of the potentially important parameters in forth flotation operation since it is a key factor to occur liquid hold-up. The system with 0.1 wt% of Alfoterra and 3 wt% of NaCl was selected to determine the relationship between the air flow rate and froth flotation performance.

Figure 4.22 shows dynamic oil removal efficiency of non-equilibrium system at different air flow rates. Oil removal is not significantly affected by the air flow rate. Figure 4.23 shows total cumulative oil removal at different air flow rates, 0.20, 0.25, 0.30, and 0.35 l/min. It was found that the oil removal increases with increasing the air flow rate until it reaches the maximum value at the air flow rate of 0.3 l/min. When the air flow rate increases further, the decreasing oil removal occurs because higher air flow rate results in more bubbles passing through the solution, resulting in more oil, surfactant, and water in foam. But, the circulating velocity, which is induced by excess bubble produced at higher air flow rate simply swarm rising through the column, increases the turbulence at the froth collection zone interface, and some oil and water are entrained back in to the solution. This result is consistent with that of Wittayapanyanon (2003).

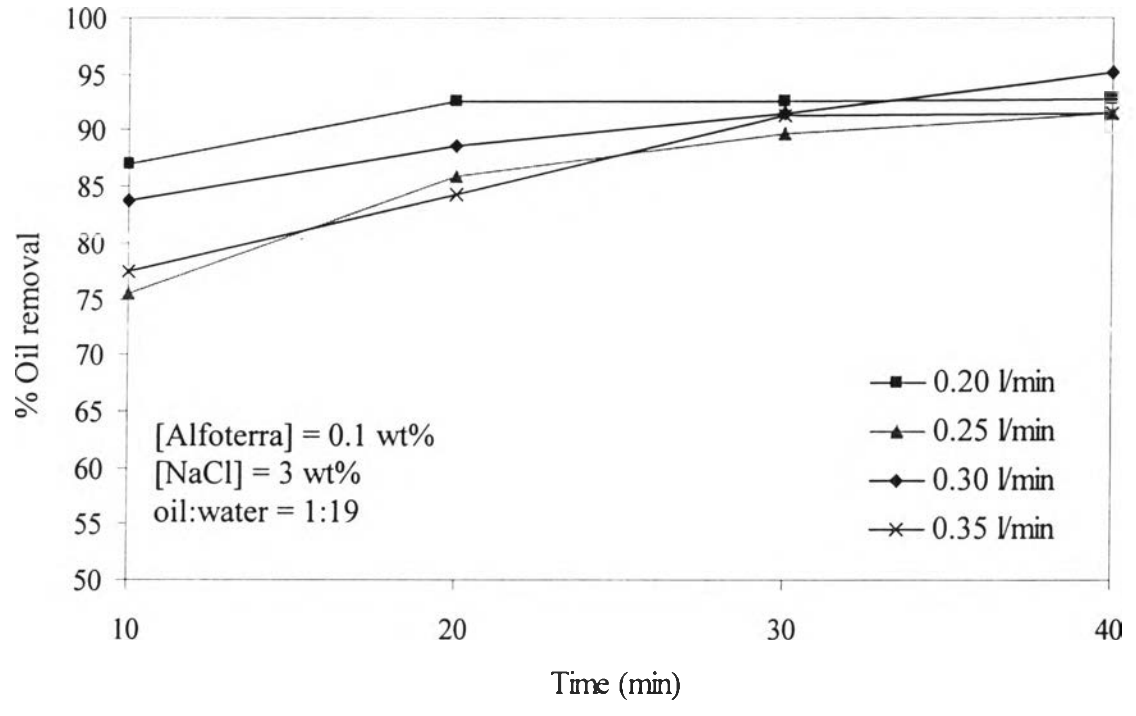

Figure 4.22 Dynamic oil removal efficiency of non-equilibrium system at different air flow rates: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

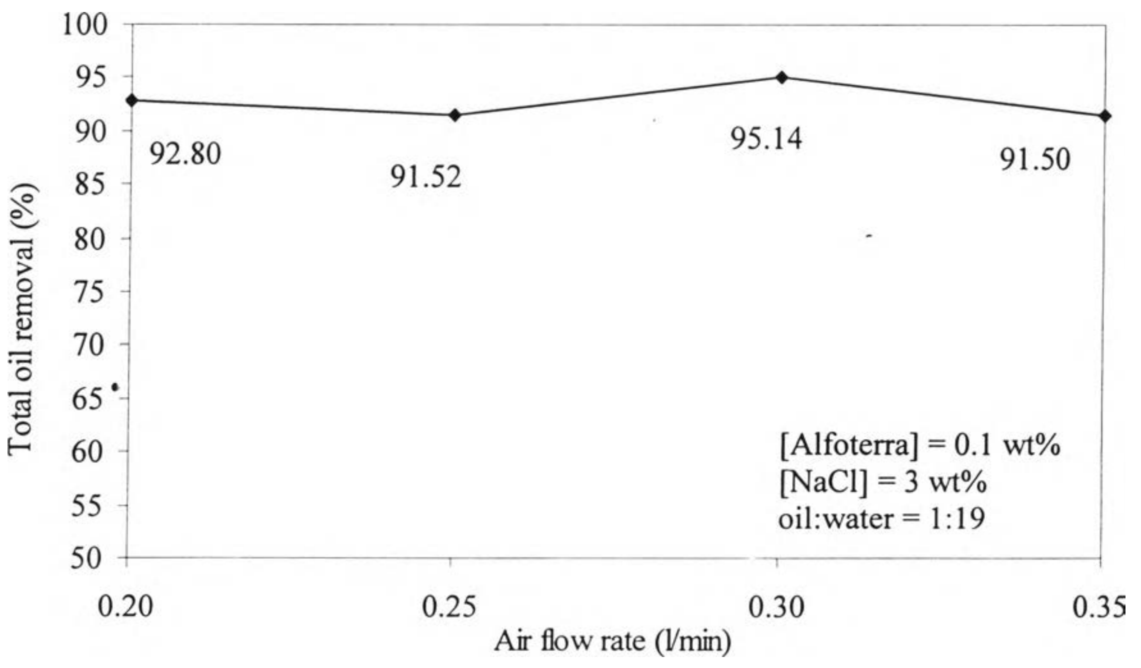

Figure 4.23 Total oil removal efficiency of non-equilibrium system at different air flow rates: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

The effect of air flow rate on the enrichment ratio of oil is shown in Figure 4.24. Because a higher air flow rate simply produces more bubbles passing through the solution resulting in wetter foam so the enrichment ratio of oil decreases.

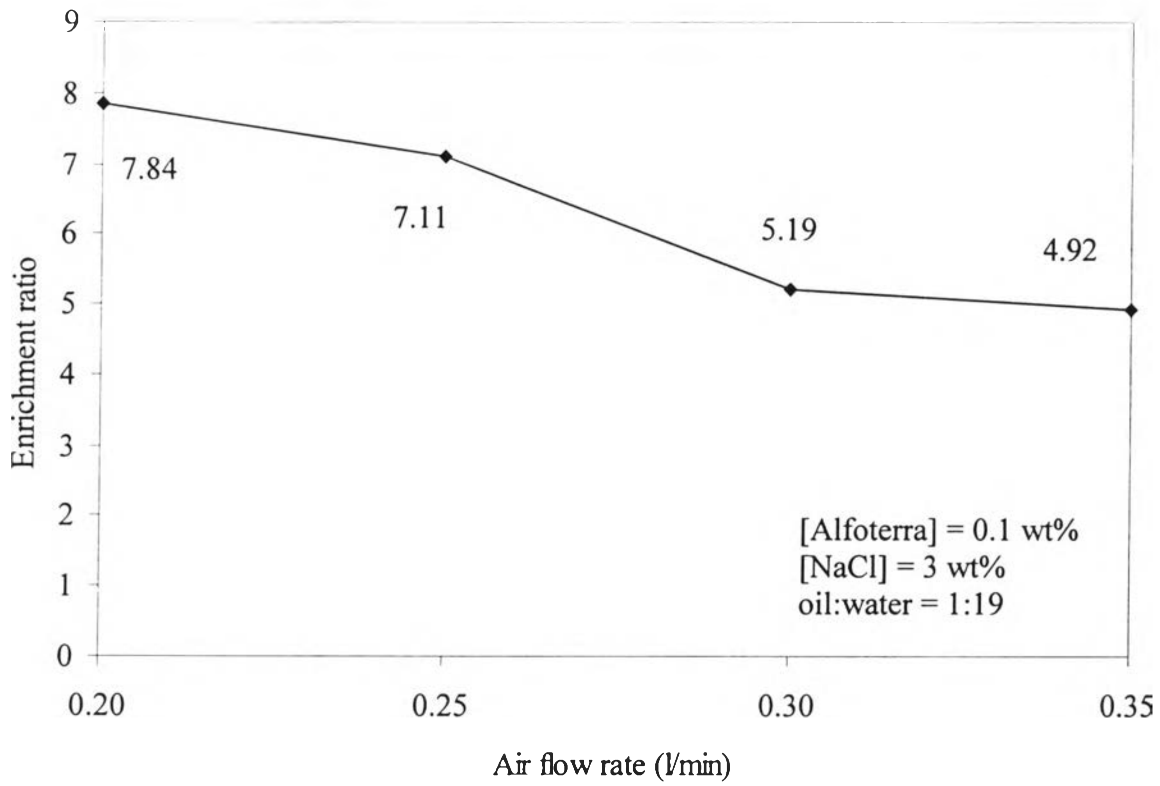

Figure 4.24 Enrichment ratio of diesel oil in non-equilibrium system at different air flow rates: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

Figure 4.25 illustrates the foam wetness at different air flow rates. The higher air flow rate, the higher foam wetness is obtained. This is because a higher air flow rate leading to a higher foam flow rate will become more diluted and so oil in the froth is more diluted leading to a low enrichment ratio of oil, so the wetness of foam is high.

As shown in Figure 4.26, increasing air flow rate promotes foam flow rate. This is because increasing air flow rate leads to more bubble passing through the solution and so the foam flow rate should increase with increasing air flow rate.

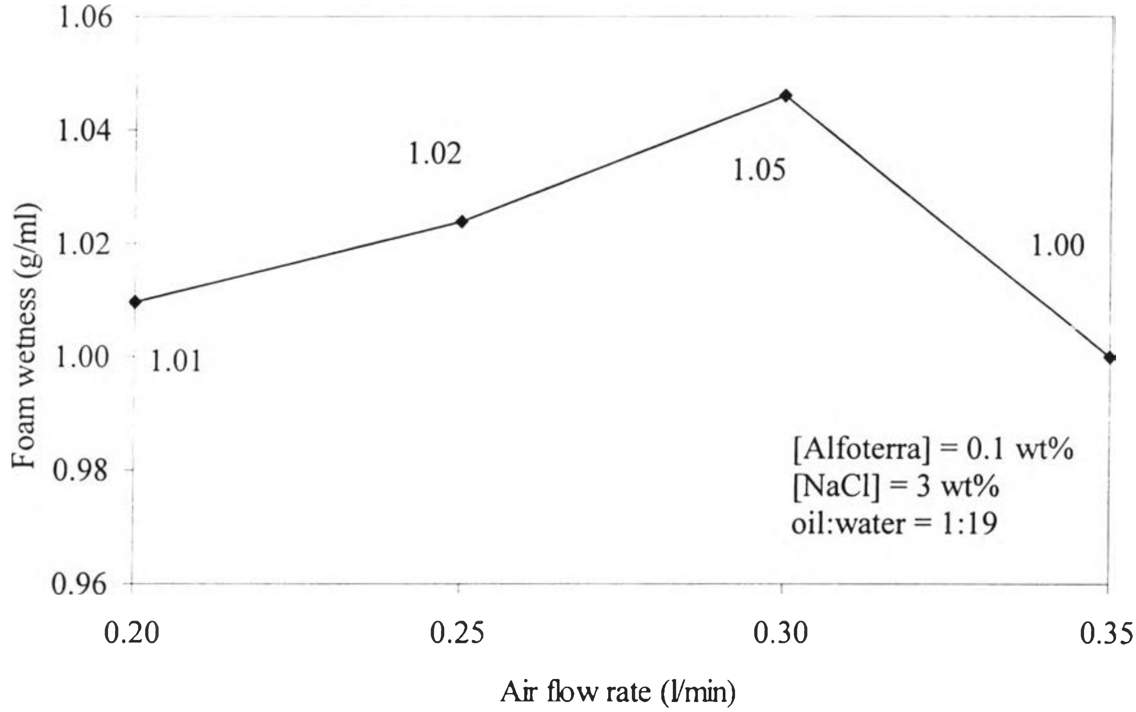

Figure 4.25 Foam wetness of non-equilibrium system at different air flow rates: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

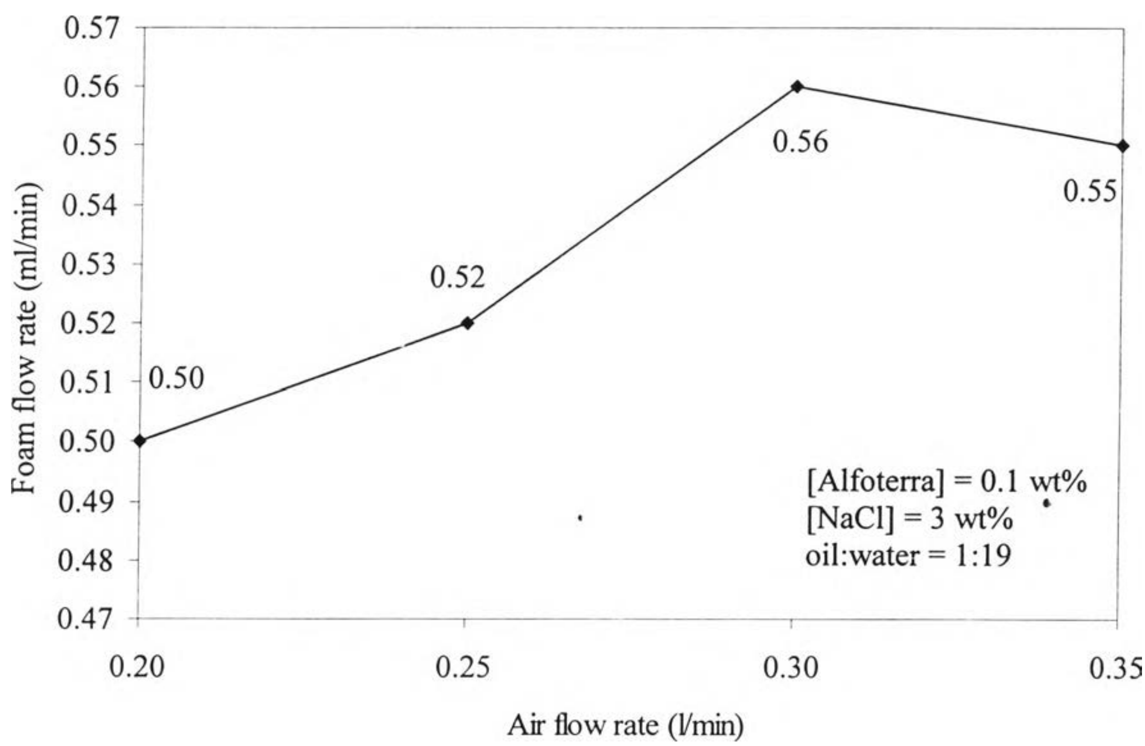

Figure 4.26 Foam flow rate of non-equilibrium system at different air flow rates: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

The effect of air flow rate on the surfactant removal is shown in Figure 4.27. Increasing the air flow rate results in an increase in the surfactant removal. This can be explained by using the combined effects of the foam ability in Figure 4.28 and the foam stability in Figure 4.29.

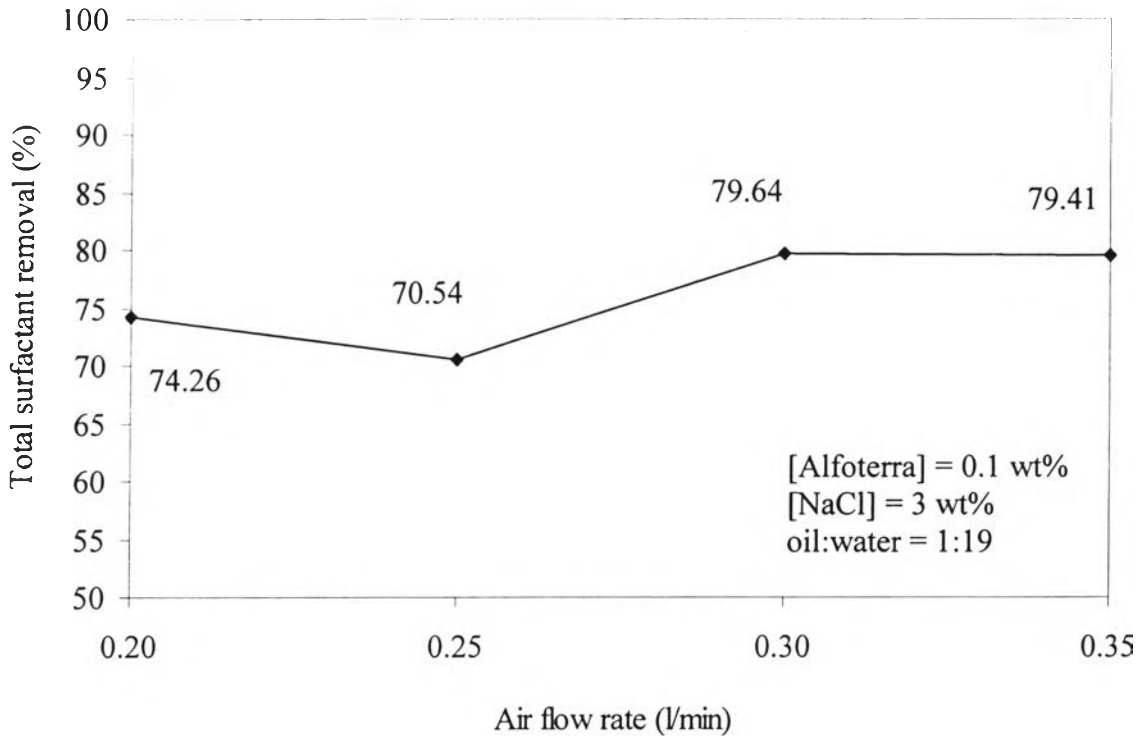

Figure 4.27 Total surfactant removal efficiency of non-equilibrium system at different air flow rates: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

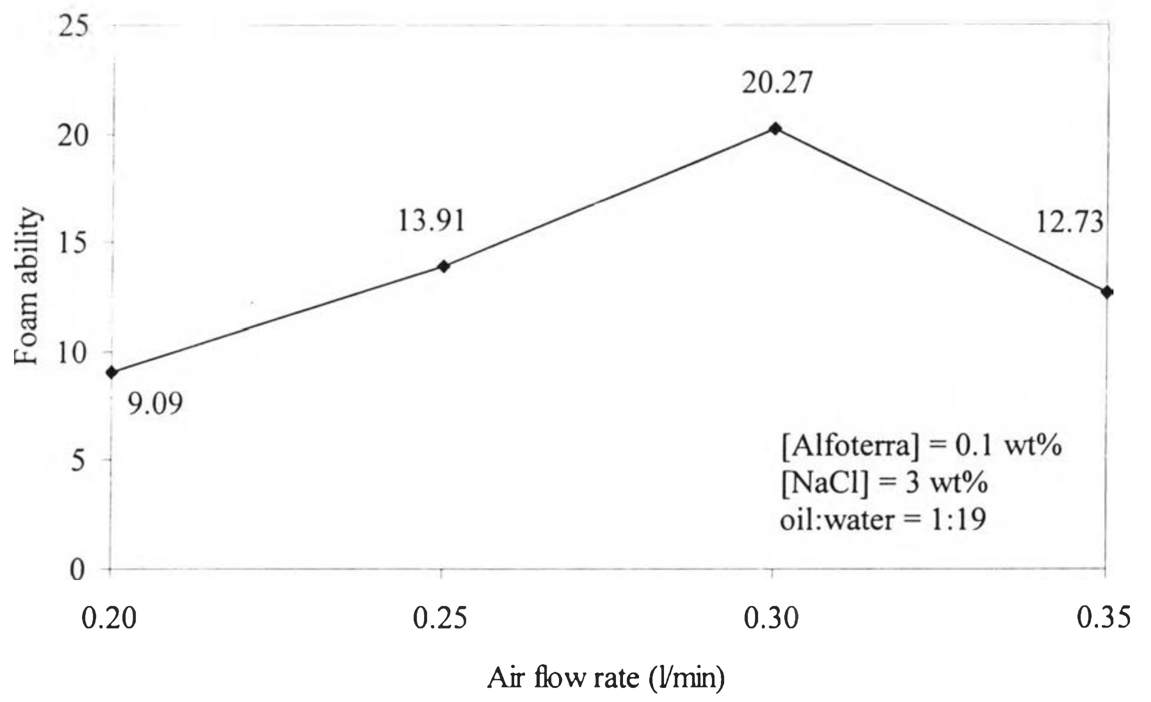

Figure 4.28 Foam ability of non-equilibrium system at different air flow rates: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

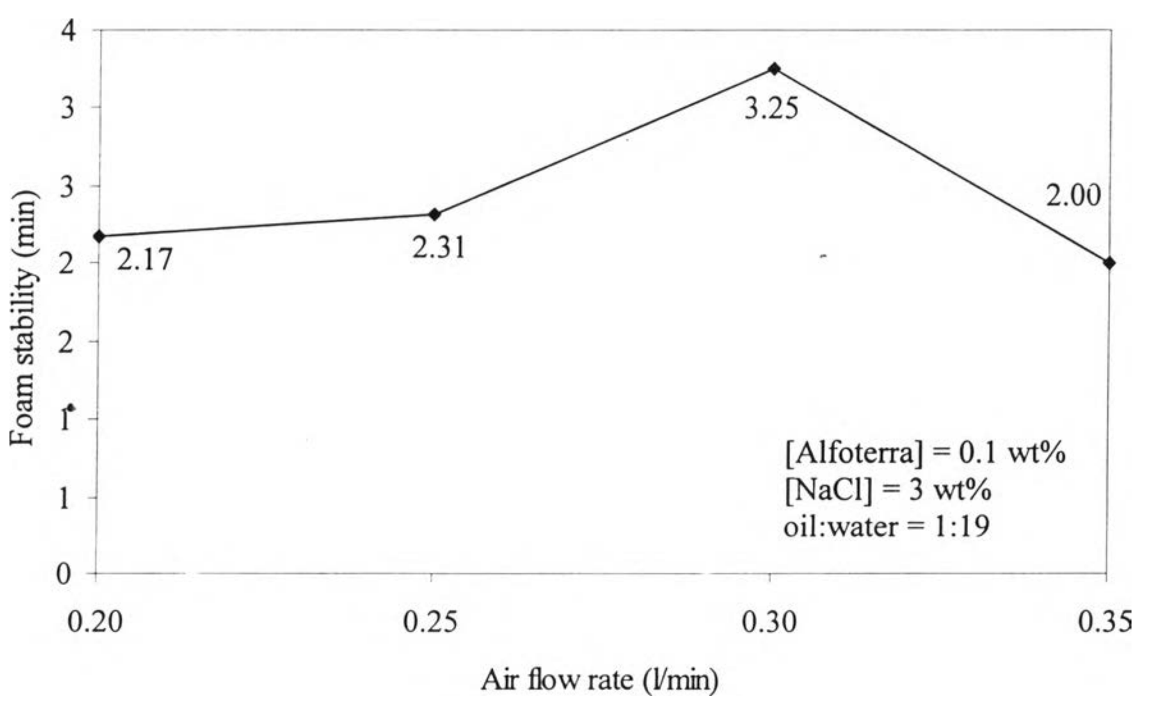

Figure 4.29 Foam stability of non-equilibrium system at different air flow rates: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

4.3.2 Effect of CGAs on Performance of Froth Flotation

From the study of CGAs in diesel removal, the results show that CGAs can use in diesel removal. The objective of this study was to investigate the effect of CGAs on froth flotation performance. The suitable condition for CGAs formation for froth flotation experiment is the stirring speed of 5000 rpm, stirring time of 5 min, surfactant concentration of 0.1 wt%, and NaCl concentration of 3 wt%.

Figures 4.30 and 4.31 show dynamic oil removal efficiency and total oil removal of non-equilibrium system with CGAs. The result shows that oil removal is not significantly affected by the air flow rate and also has the same trend as the non-equilibrium system. However, comparison of the total oil removal between the two systems shows that the non-equilibrium system with CGAs gives higher oil removal than that in the non-equilibrium system as shown in Figure 4.32. This is because the system with CGAs has higher foam ability and foam stability as shown in Figures 4.33 and 4.34.

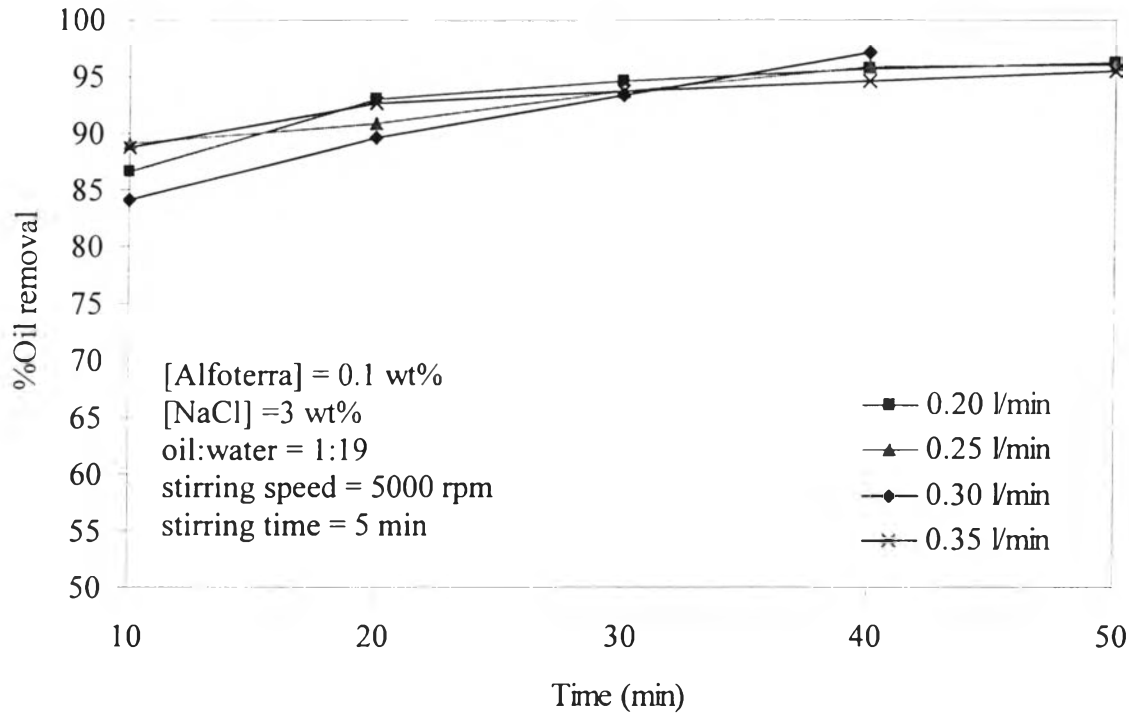

Figure 4.30 Dynamic oil removal efficiency of non-equilibrium system with CGAs: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

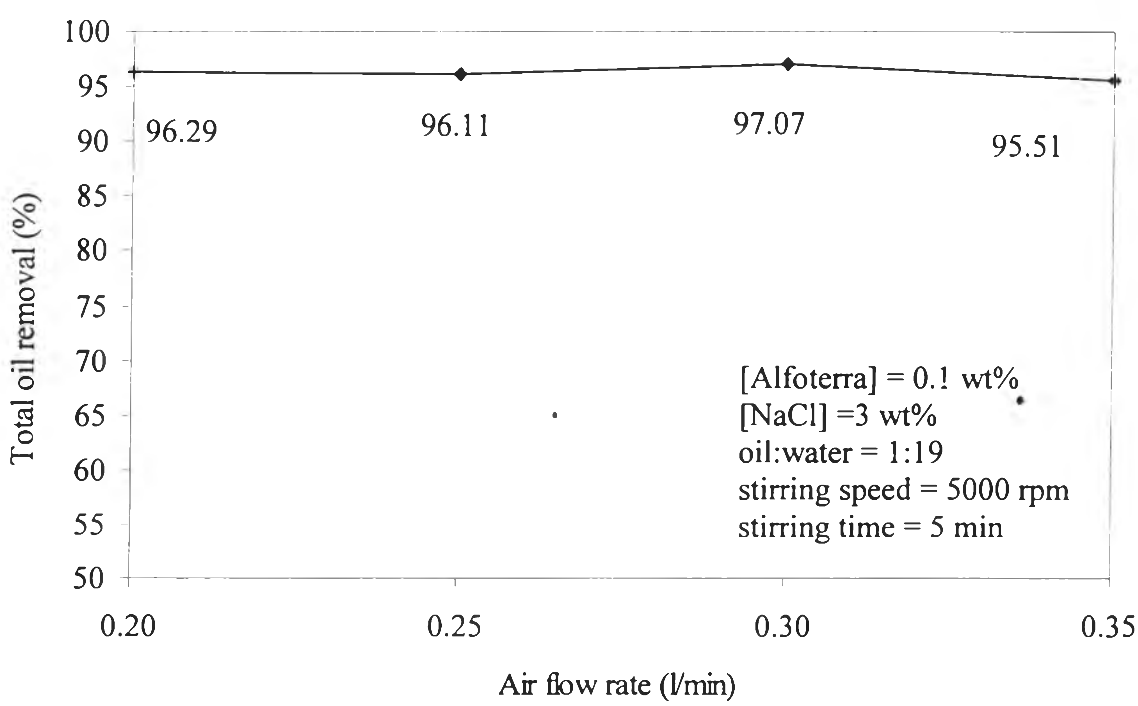

Figure 4.31 Total oil removal efficiency of non-equilibrium system with CGAs: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

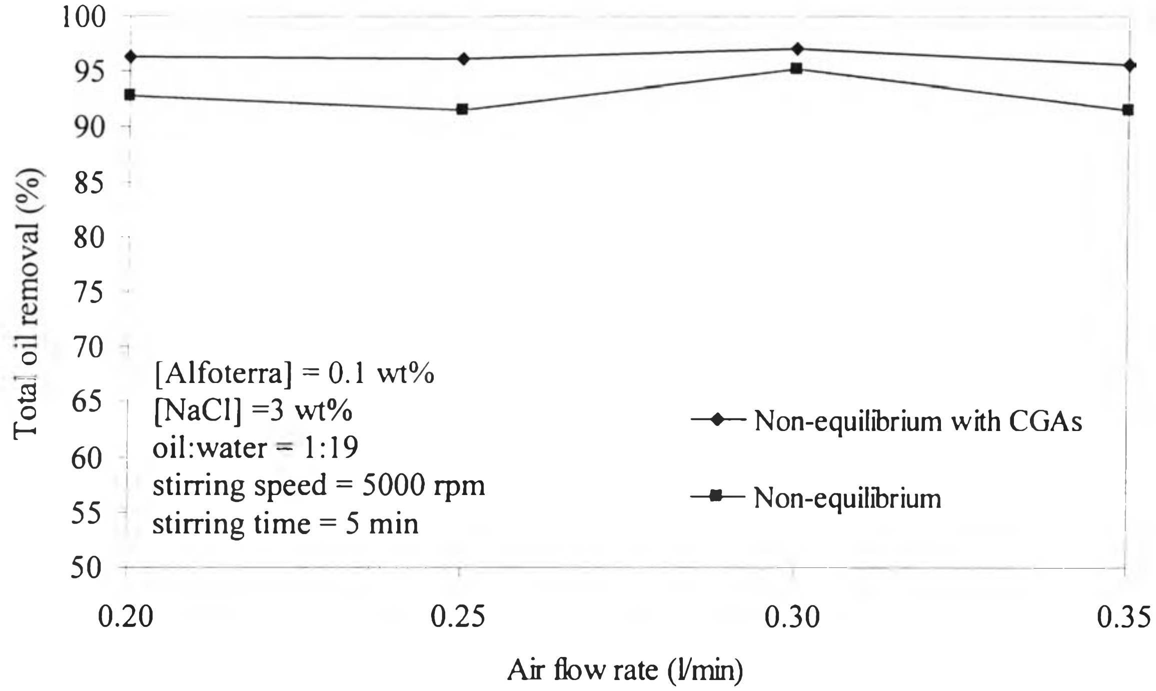

Figure 4.32 The comparison of total oil removal between non-equilibrium system and non-equilibrium system with CGAs: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

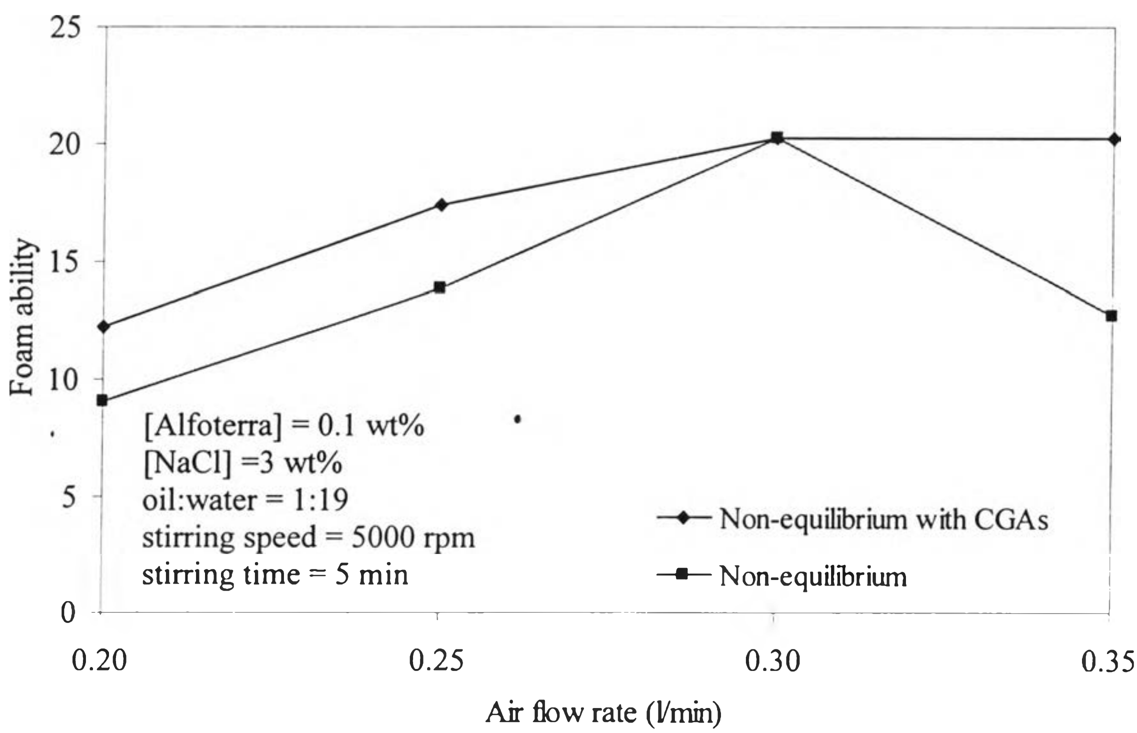

Figure 4.33 The comparison of foam ability between non-equilibrium system and non-equilibrium system with CGAs: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%.

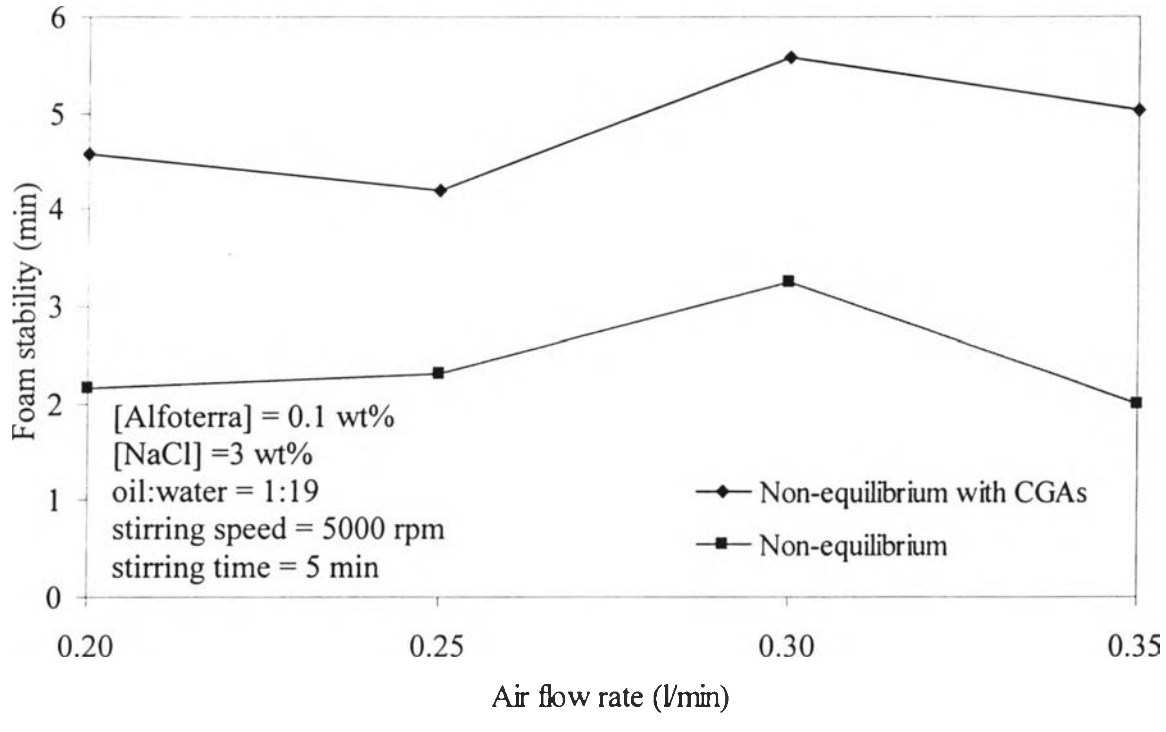

Figure 4.34 The comparison foam stability between non-equilibrium system and non-equilibrium system with CGAs: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%.

The effect of CGAs on total surfactant removal is shown in Figure 4.35. The result shows that the non-equilibrium system with CGAs gives higher surfactant removal than that in the non-equilibrium system corresponding to the total oil removal. This can be explained by the effect of foam ability and foam stability.

Figure 4.36 shows comparison of enrichment ratio of diesel oil between the non-equilibrium and non-equilibrium systems with CGAs. It was found that the non-equilibrium system with CGAs gives lower enrichment ratio than that in the non-equilibrium system. This is because the non-equilibrium system has lower foam flow rate and foam wetness as shown in Figures 4.37 and 4.38. At a lower foam flow rate, foam becomes more concentrated and so oil in the froth is more concentrated leading to a high enrichment ratio of oil, so the wetness of foam is low.

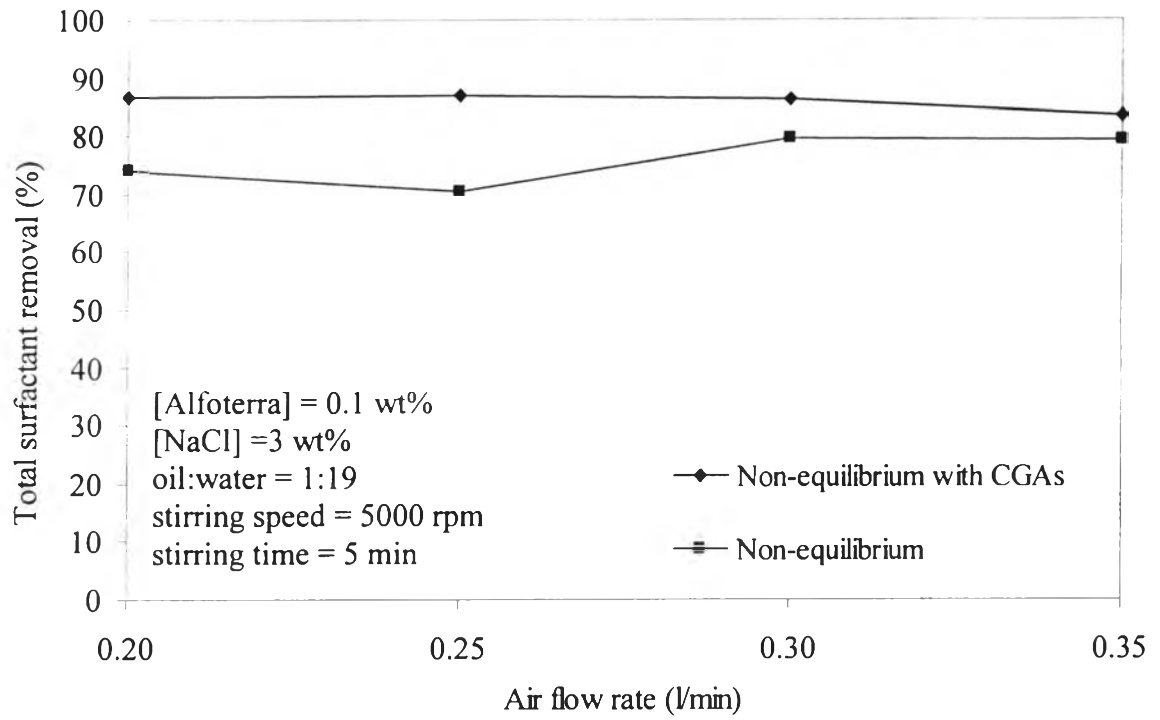

Figure 4.35 The comparison of total surfactant removal between non-equilibrium system and non-equilibrium system with CGAs: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

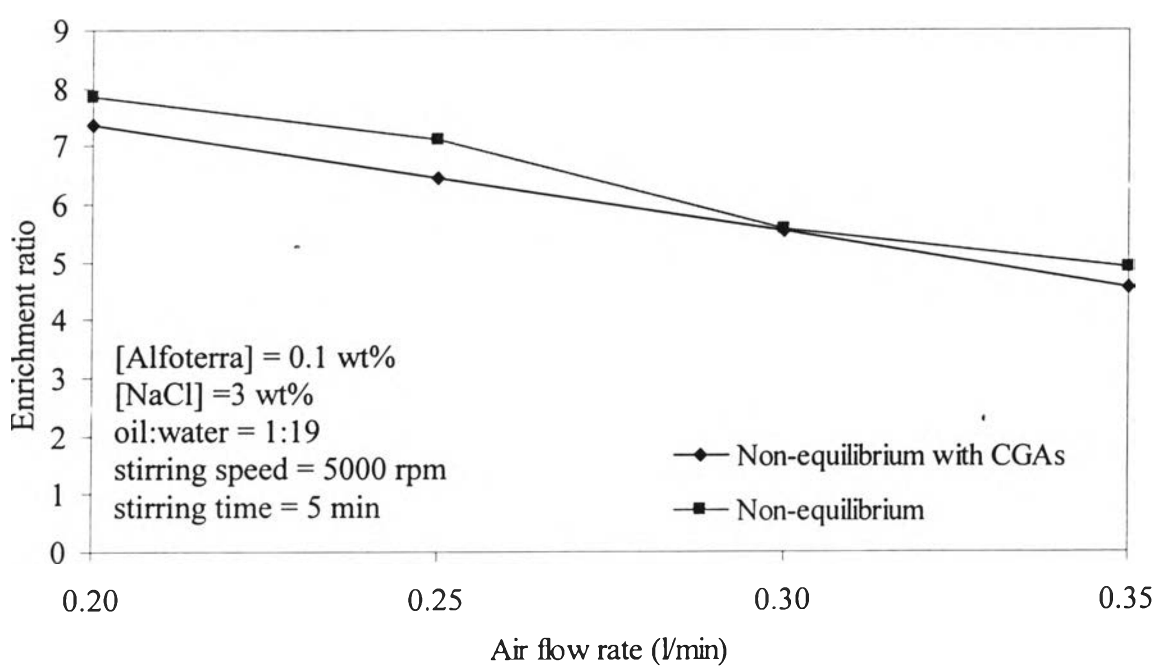

Figure 4.36 The comparison of enrichment ratio between non-equilibrium system and non-equilibrium system with CGAs: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

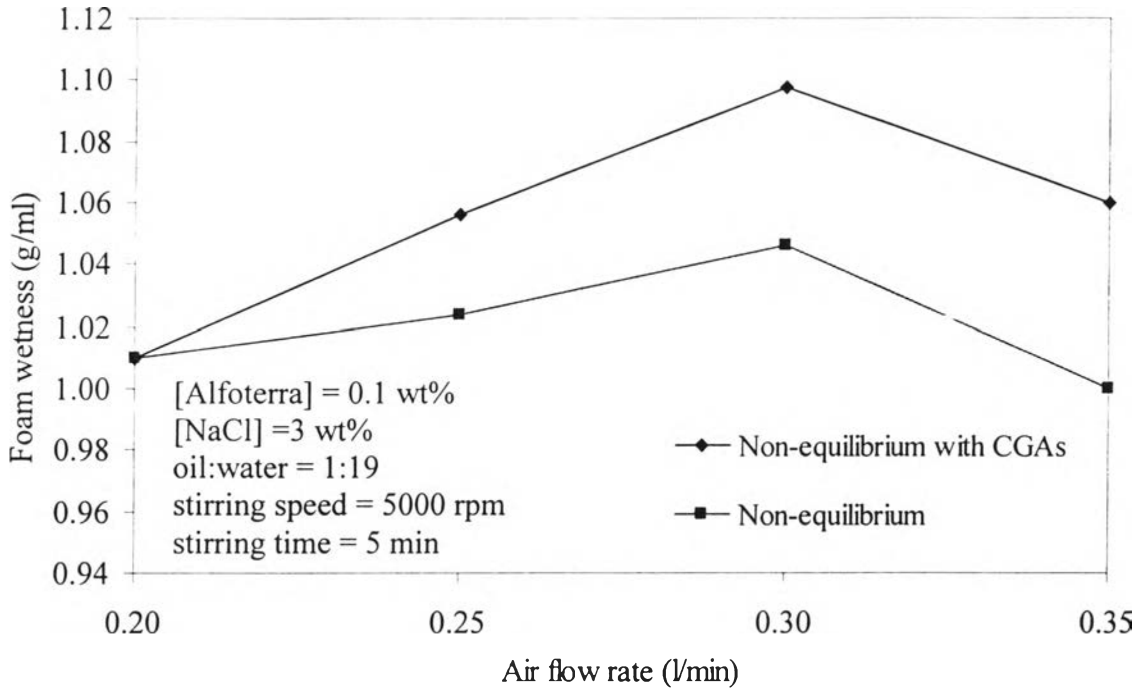

Figure 4.37 The comparison of foam wetness between non-equilibrium system and non-equilibrium system with CGAs: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

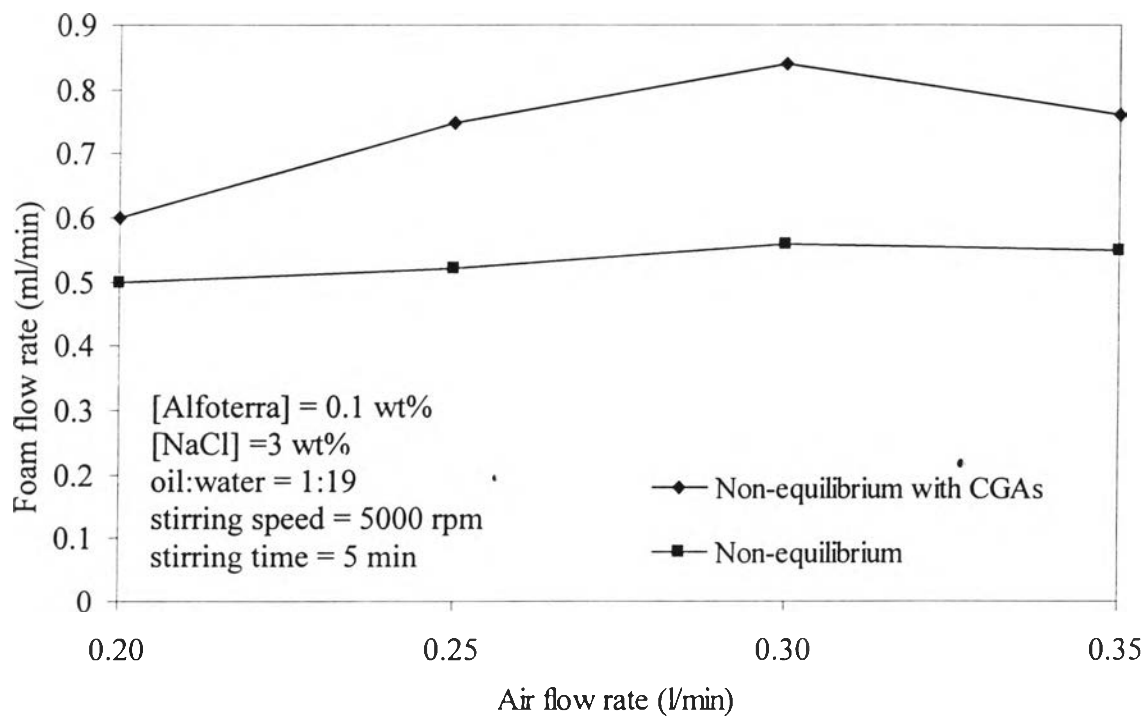

Figure 4.38 The comparison of foam flow rate between non-equilibrium system and non-equilibrium system with CGAs: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

4.3.3 Effect of Equilibration Time on Performance of Froth Flotation

The equilibration time of microemulsion is one of interesting factors in froth flotation operation. To study the effect of equilibration time, the system with 0.1 wt% of Alfoterra and 3 wt% of NaCl with oil to water ratio of 1:19 was selected for froth flotation experiments. Three systems were considered: the non-equilibrium with CGAs system where the solution occur CGAs with stirring speed of 5000 rpm and stirring time of 5 min before flotation experiments; the non-equilibrium system where the solution was immediately transferred to flotation; and equilibrium system which were equilibrated in an incubator at 30^0c for a month.

As shown in Figure 4.39, comparison of the total oil removal of the three systems shows that non-equilibrium system with CGAs gives the highest oil removal and the lowest oil removal was obtained with the equilibrium system.

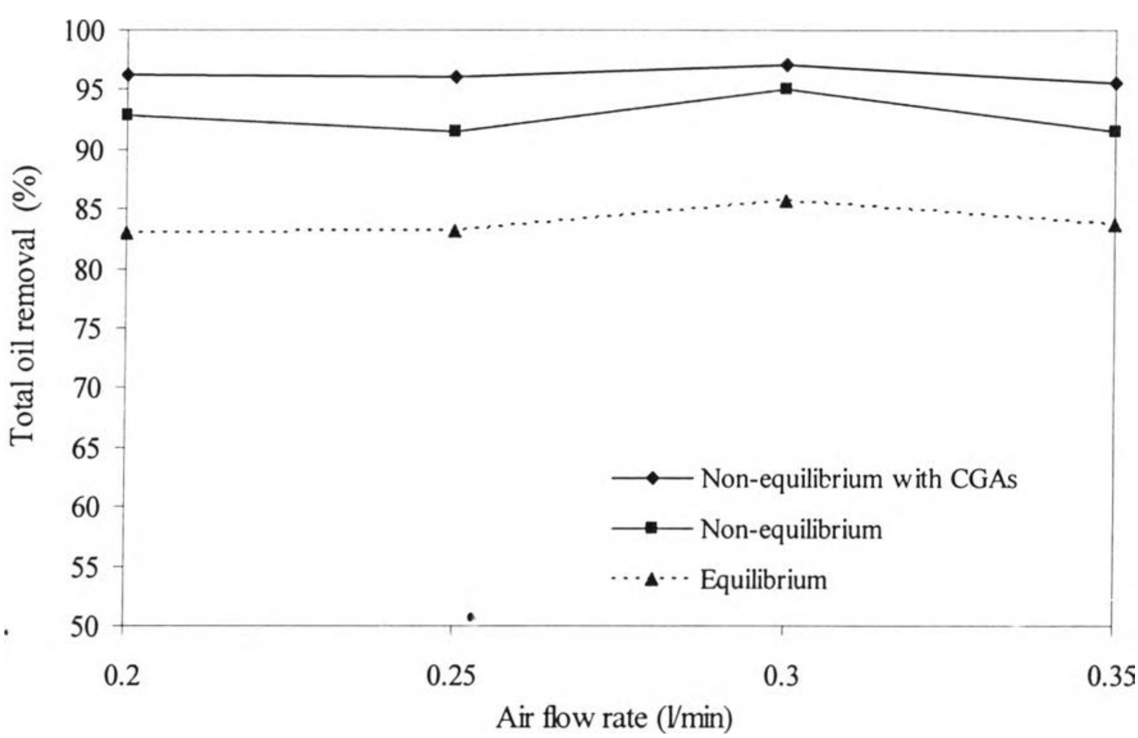

Figure 4.39 The comparison of total oil removal at different systems: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

This can be explained by comparison of total surfactant removal as shown in Figure 4.40. The surfactant removal in the non-equilibrium with CGAs system is higher than those of the non-equilibrium and equilibrium systems. This is because in the equilibrium system, a large fraction of surfactant is present in a bicontinuous structure in the middle phase compared to the other two systems. The surfactant molecules in the bicontinuous structure are not well transferred to the foam, so the surfactant removal in overhead froth is much lower for equilibrium than the non-equilibrium system with CGAs and non-equilibrium system.

In addition, a large fraction of surfactant in a bicontinuous structure in the middle phase of the equilibrium system affect to the lowest foam flow rate, foam wetness, and enrichment ratio as shown in Figures 4.41, 4.42, and 4.43, respectively.

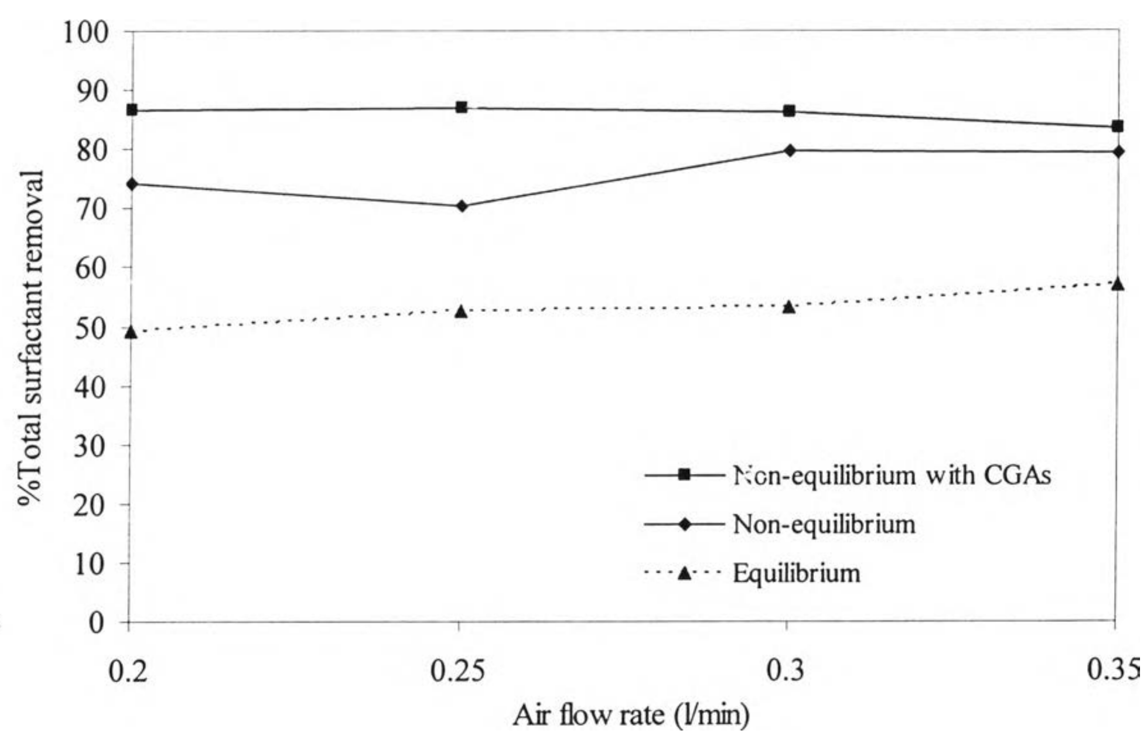

Figure 4.40 The comparison of total surfactant removal at different systems: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

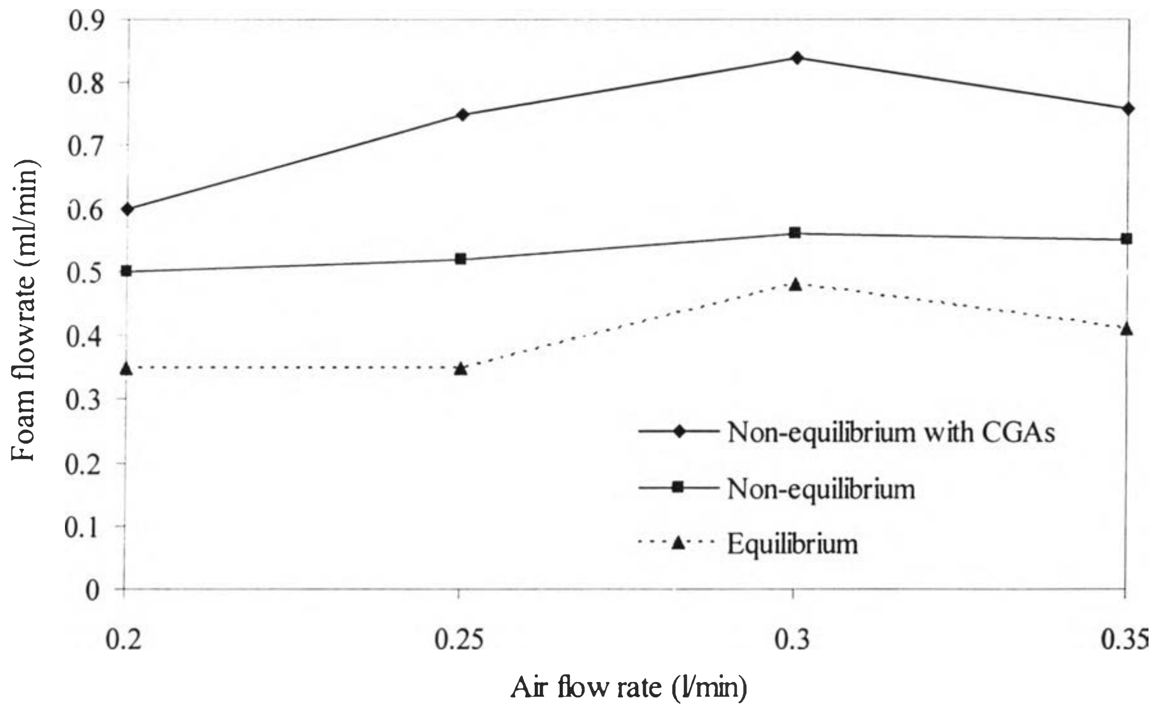

Figure 4.41 The comparison of foam flow rate at different systems with CGAs: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

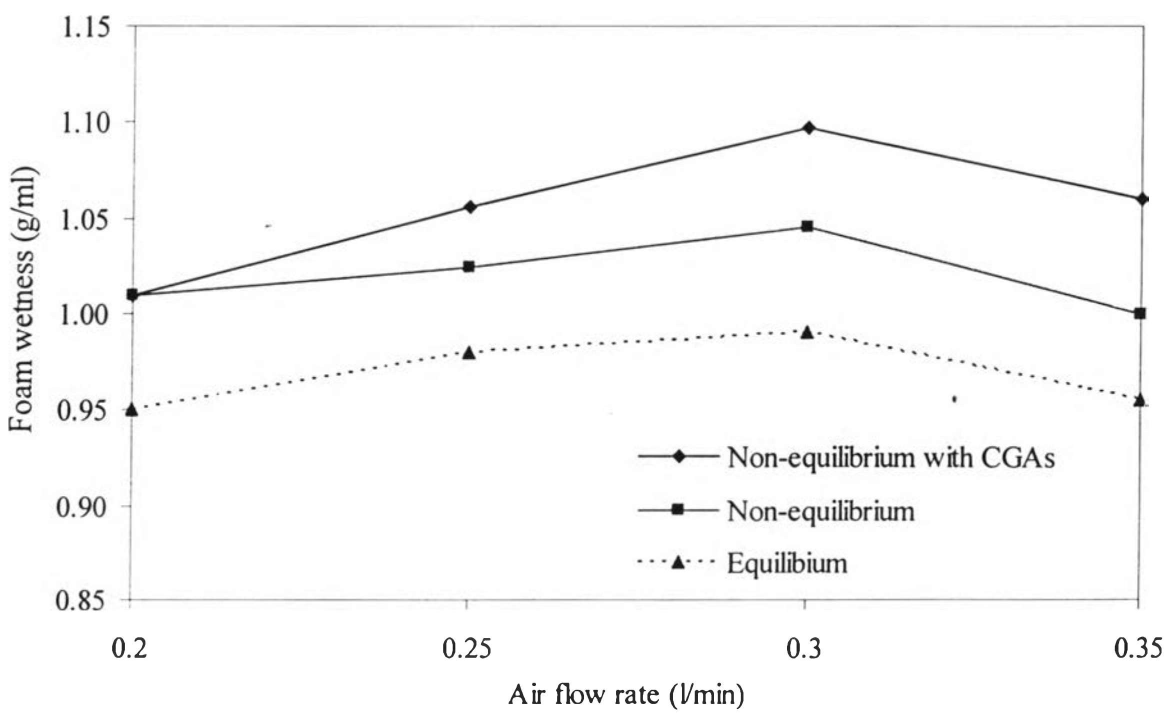

Figure 4.42 The comparison of foam wetness at different systems with CGAs: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

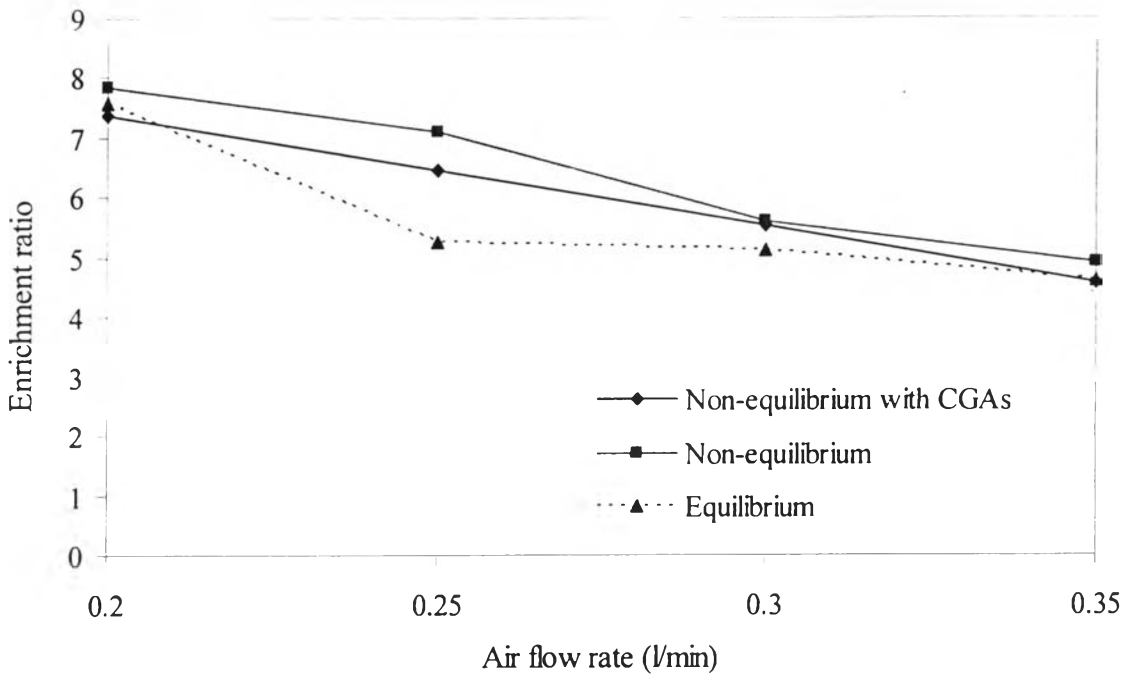

Figure 4.43 The comparison of enrichment ratio at different systems with CGAs: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

Figures 4.44 and 4.45 shows the effect of equilibration time of microemulsion on foam ability and foam stability. It was found that the foam ability and foam stability of the equilibrium system are much lower than those of the non-equilibrium system with CGAs and non-equilibrium system which have the same trend as the total oil removal. These can be explained by the effect of surfactant removal.

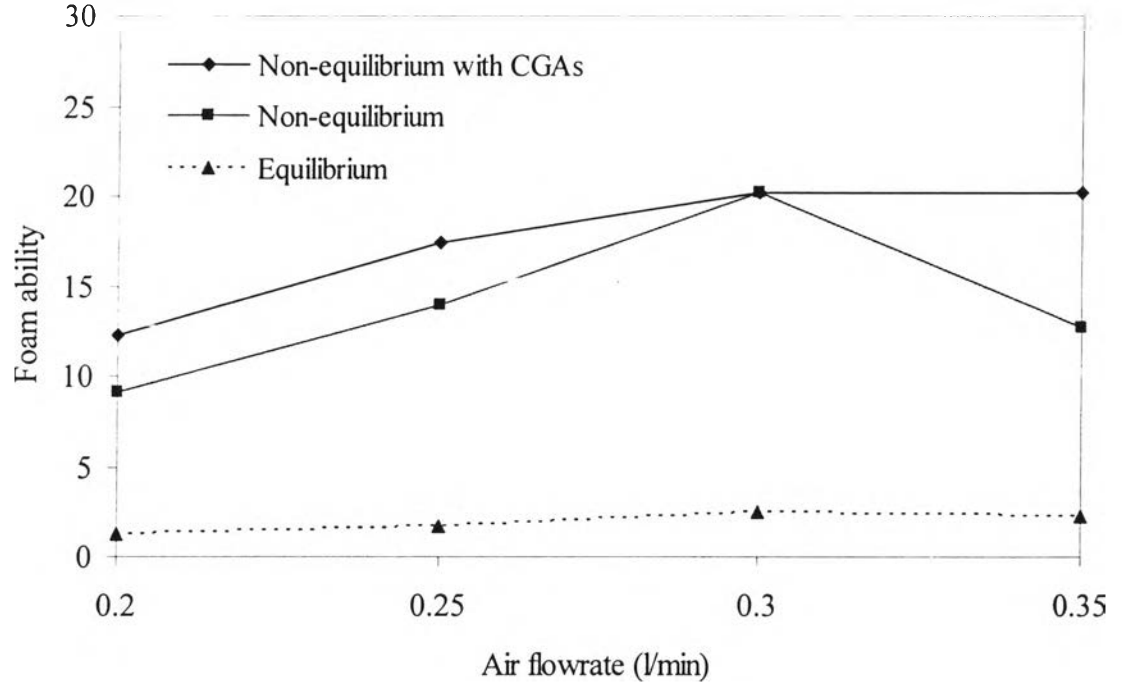

Figure 4.44 The comparison of foam ability at different systems with CGAs: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.

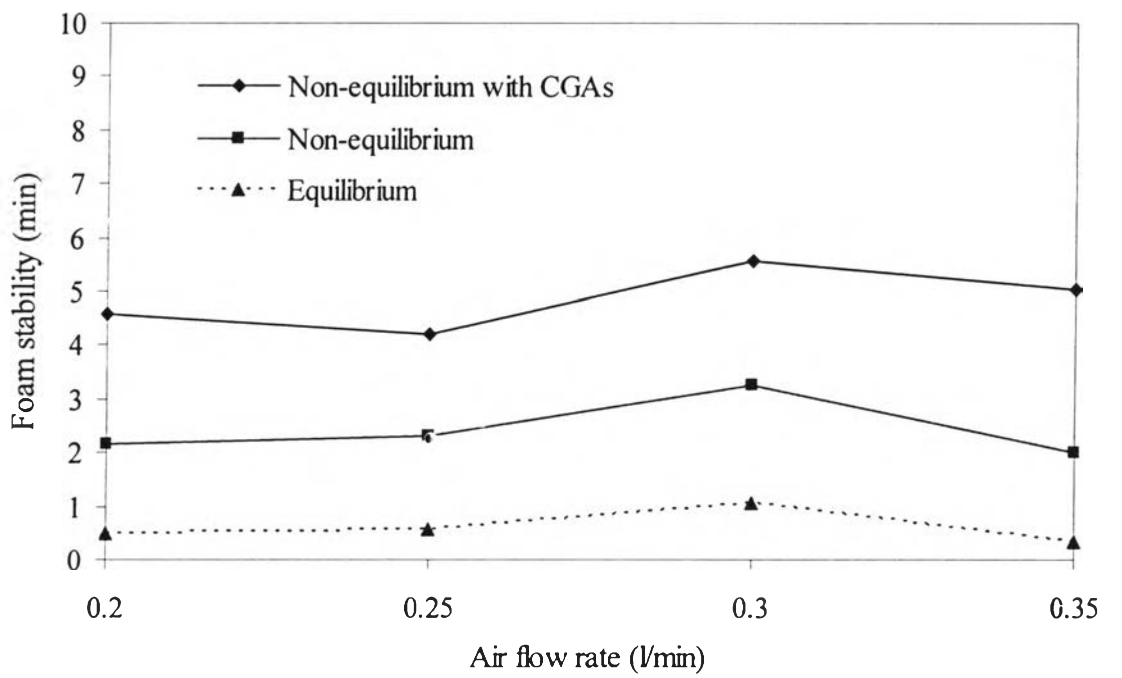

Figure 4.45 The comparison of foam stability at different systems with CGAs: [Alfoterra] = 0.10 wt%, [NaCl] =3 wt%, oil:water ratio = 1:19.