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Separation Science and Technology

Publication details, including instructions for authors and subscription information:

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To cite this Article Watcharasing, Sunisa , Chavadej, Sumaeth and Scamehorn, John F.(2008) 'Diesel Oil Removal by Froth Flotation Under Low Interfacial Tension Conditions II: Continuous Mode of Operation', *Separation Science and Technology*, 43: 8, 2048 — 2071

To link to this Article: DOI: 10.1080/01496390802064190

URL: <http://dx.doi.org/10.1080/01496390802064190>

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Diesel Oil Removal by Froth Flotation Under Low Interfacial Tension Conditions II: Continuous Mode of Operation

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Abstract: The objective of this study was to investigate the relationship between interfacial tension (IFT) and foam characteristics and the efficiency of diesel oil removal from water in a continuous froth flotation column. The effects of operational parameters, including surfactant concentration, salinity, oil-to-water ratio, foam height, air flow rate, and hydraulic retention time (HRT) on the oil removal were investigated in the continuous mode of a froth flotation operation and compared to batch operation results. Unlike the batch system, for the continuous system used in the present study, having only branched alcohol propoxylate sulfate sodium salt surfactant ($C_{14-15}(PO)_5SO_4Na$) and NaCl present in the solution yielded such poor foam characteristics that a stable froth which overflowed the flotation column could not be produced, so the addition of sodium dodecyl sulfate (SDS) as a froth promoter was used to improve the foam stability. Unlike the batch froth flotation system with only $C_{14-15}(PO)_5SO_4Na$, the continuous froth flotation with the mixture of $C_{14-15}(PO)_5SO_4Na$ and SDS, it was not possible to find a SDS and a NaCl concentration at which both ultralow IFT and good foaming were both achieved. Foam formation, stability, and production rate were found to be crucial parameters to the froth flotation efficiency. The continuous froth flotation system offers a high diesel oil removal of 96% in the single stage unit. Demonstration of efficient operation in the continuous mode in this work is important to the practical application of froth flotation in large scale processing.

Received 27 December 2007; accepted 19 February 2008.

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Keywords: Continuous froth flotation; Diesel oil removal; Foam formation; Foam stability; Microemulsion

INTRODUCTION

Diesel oil is an important transportation fuel because, based upon volume, it possesses a higher power output than gasoline. It is anticipated that diesel oil demand and utilization will still rise substantially in the next few decades (1). Because of its widespread use and appearance in several industrial processes, such as metal manufacture and machining, as well as in petroleum refinery plants, diesel oil is often found in wastewater (2). Hence, it is of interest to develop a high efficiency treatment process with low cost and simplicity of operation for removing diesel oil as well as other oils from wastewater before discharging it into the environment.

Froth flotation is a surfactant-based separation process (3,4,5). It was first used in ore processing, and it has been pointed out to be a promising technique for oily wastewater treatment (4–13). Froth flotation processes are suitable for treating wastewater containing suspended solids as well as oils in both emulsion and dissolved forms since it has several advantages, including rapid operation, low space requirement for equipment set-up, high removal efficiency, flexibility of the application to various pollutants at varying scales, and low operating cost (8).

In a froth flotation operation, a proper type and concentration of a surfactant is first added to oily wastewater, and air is introduced into the system in order to generate fine bubbles. The surfactant added tends to adsorb preferentially at the air/water interface with the hydrophilic part or head groups in the water and the hydrophobic part or tail groups in the air. As a result, oil concentrates at the bubble surfaces while they rise through the solution to form foam or froth at the top of the flotation cell, which is continuously skimmed off. The formation of stable bubble particle aggregates is required in the froth flotation operation in order to achieve high separation efficiency (14).

From our previous work (8), maximum oil removal was found to correspond to the ultralow interfacial tension (IFT) condition when the system is in the Winsor Type III microemulsion region. This is the initial point of our research group to continue studying the relationship between the Winsor Type III microemulsion and the froth flotation efficiency with different types of oils because a microemulsion has superior characteristics such as relatively large interfacial area, high solubilization capacity, and ultralow IFT (8). Later, Chavadej et al. (9) found that the most oil removed during the froth flotation operation came from the excess oil phase rather than from the middle phase in the Winsor Type III microemulsion system.

This proves that it is the ultralow IFT corresponding to the Winsor Type III microemulsion which is responsible for efficient flotation; formation of a third phase (middle phase) under this condition is coincidental to oil removal. Recently, Yanatatsaneejit et al. (10) found that ethylbenzene removal from water by froth flotation was efficient only when both low IFT and good frothing are present. The importance of foam stability was also observed by Carre et al. (15). Moreover, Yanatatsaneejit et al. (11) proposed four sequential steps in the mechanism of oil removal by froth flotation. Firstly, air bubbles are generated through the liquid solution, and oil droplets adhere to the surface of the air bubbles. The second step is the formation of oil films on the surfaces of the air bubbles while the air bubbles are rising through the solution. The third step is the rising of the air bubbles with attached oil films to the top of the solution. The fourth step is the emergence of the air bubbles from the liquid phase to form froth. In both the third and fourth steps, high stability of the oil-film covered air bubbles is necessary. For successful separation, high stability of the froth is needed in order to yield dry foam with high oil content. Foamability or foam formation and foam stability influence the foam production rate, which needs to be sufficient for good separation, no matter how well the oil attaches to the air bubbles rising through the solution. Yanatatsaneejit et al. (12) correlated the performance of batch froth flotation to remove diesel oil from water with the system IFT, foam characteristics, and coalescence time between oil droplets. The results indicate that both IFT and foam characteristics should be optimized to achieve a high efficiency of oil removal in a froth flotation operation. However, the coalescence time between oil droplets is not a significant parameter for a successful froth flotation operation.

As mentioned before, all studies of froth flotation, including our group's previous works (8–12), were operated in a batch mode, whereas large quantities of industrial wastewater are more efficiently treated by continuous, steady-state processes. Hence, we have developed a continuous froth flotation process for treating oily wastewater. In this work, the relationship between the system IFT and foam characteristics and the efficiency of diesel oil removal from the water by continuous froth flotation was investigated using a surfactant mixture of a branched alcohol propoxylate sulfate sodium salt ($C_{14-15}(PO)_5SO_4Na$) and sodium dodecyl sulfate (SDS). The mixed surfactants were employed in order to achieve a low IFT as well as high foamability and high foam stability. The $C_{14-15}(PO)_5SO_4Na$ is needed for ultralow IFT and the SDS is needed as a foam booster. The effects of operational parameters (concentration of surfactant, salinity, oil-to-water ratio, foam height, air flow rate, and hydraulic retention time, HRT) on flotation efficiency were also systematically investigated.

EXPERIMENTAL SECTION

Materials

Two types of surfactants were used in this work; a branched alcohol propoxylate sulfate, sodium salt ($C_{14-15}(PO)_5SO_4Na$), and sodium dodecylsulfate (SDS). The $C_{14-15}(PO)_5SO_4Na$ (Alfoterra) was 28.7% active in liquid form and was supplied by Sasol North America Inc., Texas, USA. It is an extended anionic surfactant having 14–15 carbon atoms and 5 groups of propylene oxide (PO) with sulfate as the hydrophilic group. The SDS, which was obtained from Carlo Erba Reagenti with a purity in the range of 94–98%, is an anionic surfactant with a negatively-charged sulfate head group and an alkyl chain length of twelve carbon units. The diesel oil selected as a model contaminant oil was purchased from PTT Public Co., Ltd (Thailand) and is a mixture of hydrocarbons having carbon numbers predominantly in the range of C9-C20 with having not more than 65% by volume recovered at 240°C and not less than 85% by volume recovered at 350°C (16). Analytical grade sodium chloride (NaCl) with 99% purity was obtained from Labscan Asia Co., Ltd. All chemicals were used as received without further purification. Deionized water was used to prepare all aqueous solutions.

Methodology

This work consisted of three main parts. The first part was to study the equilibrium microemulsion formation of diesel oil with aqueous solutions of varying surfactant concentrations. For the second part, continuous froth flotation experiments were conducted at various surfactant concentrations, NaCl concentrations, oil-to-water ratios, foam heights, air flow rates, and hydraulic retention times (HRT). The last part was to measure foam characteristics.

Microemulsion Formation

Five (5) mL of diesel oil was added to a series of vials containing 5 mL of a surfactant solution having different surfactant concentrations and salinities. After that, each vial was shaken gently by hand for 1 min and then equilibrated in a temperature-controlled incubator (KB400/E2, Binder) at 30°C until the system reached equilibrium. The equilibrium state was considered to be attained when the volume of each phase of the microemulsion system was invariant. The measurement of phase height was conducted by using a cathetometer, model TC-II from Titan Tool

Supply, Inc., attached to a digimatic height gauge, model 192–631, obtained from Mitutoyo, with ± 0.002 mm accuracy. The interfacial tension (IFT) between the diesel oil and the various surfactant solutions was measured using a spinning drop tensiometer (SITE 04, Krüss).

At a very low surfactant concentration, it is difficult to visually observe which microemulsion type is present since the phase volume of any middle phase formed is so small. Therefore, electrolytic conductivity was used to determine the microemulsion type (13, 17). For each condition, the electrolytic conductivity was measured, under gentle stirring with a magnetic stirrer, by using a conductivity meter (CON11& CON110, Eutech Instruments) at room temperature ($26 \pm 1^\circ\text{C}$). Since the aqueous phase contains a certain concentration of sodium chloride, the inversion is easily monitored by a change of two or more orders of magnitude in conductivity (mS/cm or $\mu\text{S}/\text{cm}$) (13). High conductivity indicates a Winsor Type I or III microemulsion while a low value implies a Winsor Type II microemulsion (17). Moreover, the interfacial tension (IFT) between the surfactant solution and the oil phase which were in equilibrium at different conditions was measured using a spinning drop tensiometer (SITE 04, Krüss) in order to localize precisely the microemulsion phase boundary at very low surfactant concentrations. The conductivity and the IFT results were used to plot the phase diagram or conditions where Winsor Type I, II, and III microemulsions exist. When plotted as surfactant concentration vs. salinity (or vice versa), these phase plots are called fish diagrams. The fish diagrams are generally used to determine a minimum surfactant concentration required to form a Winsor Type III microemulsion which is known as the critical microemulsion concentration ($C\mu\text{C}$).

Froth Flotation Experiments

Figure 1 shows a schematic of the continuous froth flotation apparatus used in this study. The apparatus consisted of a glass cylindrical column with 5 cm inside diameter and 120 cm height, and it was operated in continuous mode. Compressed air was first filtered to remove all particles, water, and oil before entering the flotation column. The flow rate of the filtered air was regulated by a mass flow controller (GFC171S, Aalborg). The filtered air was introduced into the bottom of the column through a sinter glass disk with pore diameters of about 16–40 μm . A well-mixed solution, with different surfactant concentrations, was fed continuously at a desired flow rate into the froth flotation column by using a peristaltic pump (Easy-load II, Masterflex). The level of the solution in the column was adjusted by a three-way flexible outlet tube

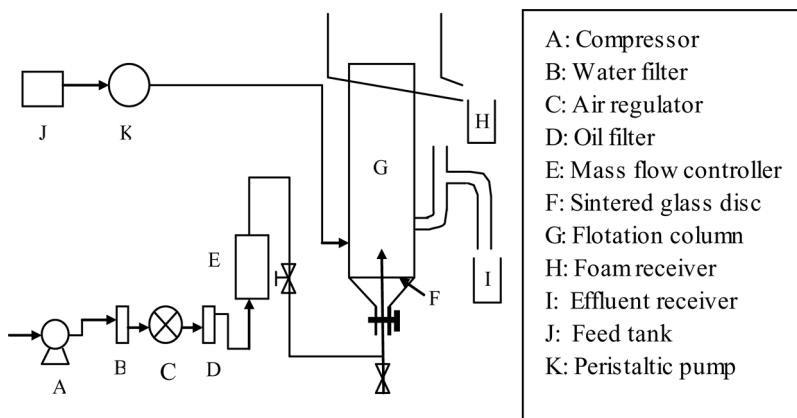


Figure 1. Schematic of the froth flotation apparatus with a continuous mode of operation.

in order to vary the foam height. The air bubbles ascending through the solution in the column generated foam or froth which overflowed from the top of the column and was collected in a foam receiver at 10 minute intervals, and then the collapsed froth was analyzed for diesel oil and surfactant concentrations in the froth. In addition, liquid effluent samples were also collected for the analysis of diesel oil concentration and total surfactant concentration by using the methylene chloride extraction method (18) and the titration method with methylene blue chloride (19), respectively. All froth flotation experiments were carried out at room temperature of $26 \pm 1^\circ\text{C}$. Each experiment was run until the system reached steady state. The steady state was justified when the concentrations of diesel oil in the froth and liquid effluent samples became invariant. The reported data obtained under steady state conditions were averaged from at least three samples from each run to evaluate the process performance.

Measurement of Foam Characteristics

The foam characteristic experiments were independently conducted in a glass cylinder having the same inside diameter as the flotation column. A quantity of 250 mL of the solution sample with different initial oil-to-water ratios and various surfactant and NaCl concentrations was transferred to the column. After that, filtered air at a constant flow rate of 0.1 L/min was introduced into the bottom of the column through a sintered glass disc to generate fine bubbles through the solution. When,

for each run, the maximum foam height was achieved and recorded, the air flow was then terminated. The ratio of maximum foam height to initial solution height is defined as foamability while the time required for the foam volume to collapse to half of the maximum foam height is defined as foam stability ($t_{1/2}$). All experiments were carried out at room temperature ($26 \pm 1^\circ\text{C}$).

RESULTS AND DISCUSSION

In all experiments, the surfactant and NaCl concentrations are expressed in weight percent (wt.%) per volume of the aqueous phase consisting of water, salt, and surfactants (not including oil).

Phase Behavior and IFT

A low or ultralow oil/water IFT can greatly enhance the performance of froth flotation, as mentioned in our previous studies (8–12). The use of extended surfactants can form a microemulsion with a variety of oils without added alcohol at room temperature (20). Hence, $\text{C}_{14-15}(\text{PO})_5\text{SO}_4\text{Na}$ was selected to form micromulsions with diesel oil in the present study. It is of interest to know the minimum surfactant concentration required to exhibit a Winsor Type III microemulsion which is known as the critical microemulsion concentration ($C\mu C$) (21). To find the $C\mu C$, the IFT between diesel oil and the equilibrium surfactant solution having different concentration at 5 wt.% NaCl, which was the optimum salinity providing the minimum IFT as mentioned in our previous work (12), was plotted against the surfactant concentration, as shown in Fig. 2. The plot showed two sharp drops of the IFT. The first sharp decrease in the system IFT corresponds to the adsorption of the surfactant at the oil-water interface, which occurs at a concentration slightly less than the CMC. The second one corresponds to the change in the curvature of the micelles which ends at the point where the first droplet of microemulsion forms, known as the $C\mu C$ (21). The $C\mu C$ value for the $\text{C}_{14-15}(\text{PO})_5\text{SO}_4\text{Na}$ system in this study was found to be about 0.08 wt.% at the optimum salinity of 5 wt.%. Figure 3 presents the surfactant concentration/salinity phase diagram showing the regions where different microemulsion types exist (fish diagram) for the diesel oil/water microemulsion system at an oil-to-water ratio of 1:1. The fish diagram was constructed by using the visual observation at very high surfactant concentrations and the conductivity data at low surfactant concentrations. For a surfactant concentration lower than 0.1 wt.%, the IFT data was used instead. For a given surfactant concentration in the range of

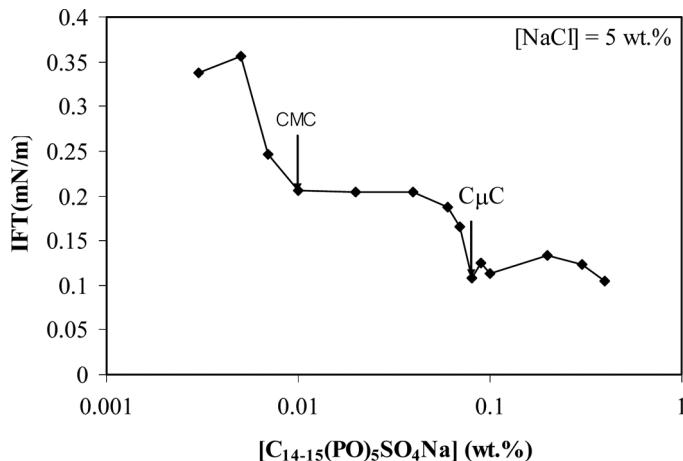


Figure 2. IFT as a function of surfactant concentration at the optimum NaCl concentration of 5 wt.% for a single surfactant system at an oil-to-water volumetric ratio of 1:1 and 30°C.

0.1–10 wt.%, an increase in salinity (known as salt scan) results in a phase transformation from a Winsor Type I to a Type III, then to a Type II microemulsion, as shown in Fig. 3 (22). At a very high

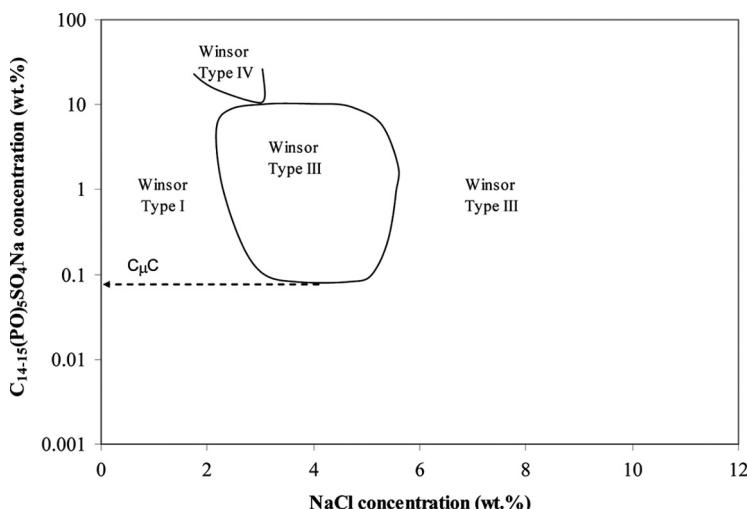


Figure 3. Microemulsion phase diagram (Fish diagram) of single surfactant system ($C_{14-15}(PO)_5SO_4Na$) as a function of salinity at an oil-to-water volumetric ratio of 1:1 and 30°C.

surfactant concentration above 10 wt.%, a single microemulsion phase, known as Winsor Type IV, is present.

A $C_{14-15}(PO)_5SO_4Na$ concentration of 0.08 wt.% or the $C\mu C$ was first selected as a base condition to run the froth flotation experiments. It was found that with $C_{14-15}(PO)_5SO_4Na$ alone, the system was not able to generate stable foam to reach the foam outlet at the top of the column. Hence, SDS was added as a foam booster to improve foam stability. Hence, experiments of microemulsion formation with the mixed surfactants (SDS and $C_{14-15}(PO)_5SO_4Na$) were carried out. For the phase study of the mixed surfactants, the weight ratio between the two surfactants was fixed at the $[C_{14-15}(PO)_5SO_4Na]/[SDS]$ of 1:5 while a total surfactant concentration was varied. An oil-to-water ratio of 1:19 was used instead of 1:1 as is generally used in most phase studies since most real wastewater normally has an oil content much lower than 1:1. Figure 4 shows the two sharp decreases in IFT vs. surfactant concentration, which correspond to the CMC and the $C\mu C$ of the mixed system, which are 0.18 and 0.6 wt.%, respectively. Figure 5 shows the fish diagram of diesel oil with the mixed surfactants at an oil-to-water ratio of 1:19 which was the system to be used in the froth flotation experiments. Again, the fish diagram was constructed by using visual observation, conductivity data and IFT data, as described before. As shown in Fig. 5, for any given total surfactant concentration greater than the $C\mu C$ (0.6 wt.%), the phase transformation from Winsor I to Type III and

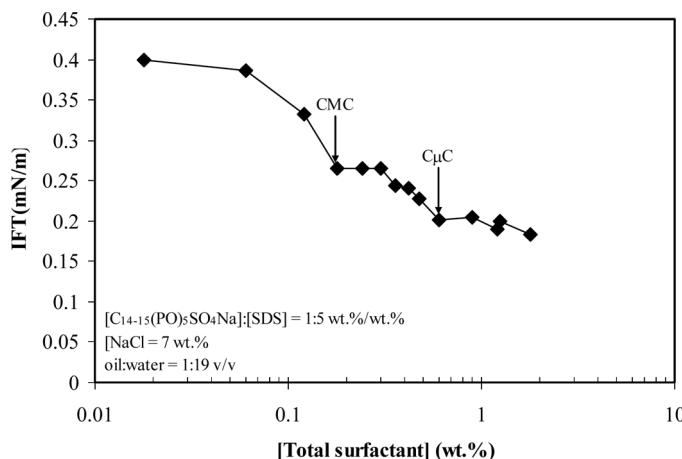


Figure 4. Interfacial tension as a function of total surfactant concentration at optimum NaCl concentration of mixed surfactant system and 30°C of the mixed surfactants.

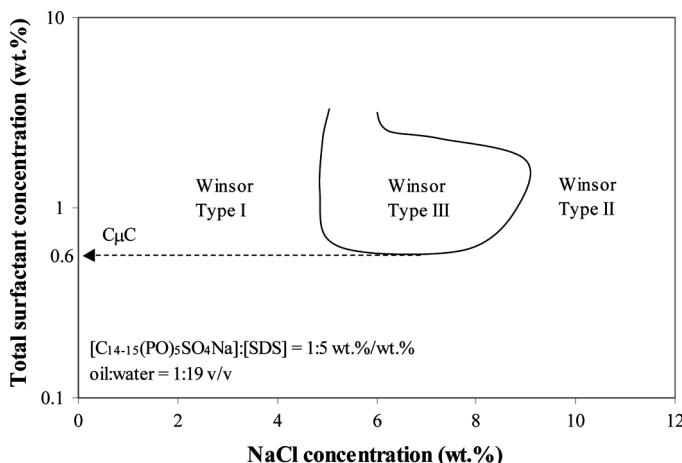


Figure 5. Phase or fish diagram of mixed surfactant system (C₁₄₋₁₅(PO)₅SO₄Na and SDS) at an oil-to-water volumetric ratio of 1:19 and 30°C.

Type II microemulsion occurs with increasing salinity, this progression being known as a salinity scan. The C_μC remains fairly constant over a range of salinities from about 5 to about 8 wt.% NaCl. The C_μC value of the mixed surfactants was found to be 0.6 wt.% which is significantly higher than that of the pure C₁₄₋₁₅(PO)₅SO₄Na system (0.1 wt.%) and the optimal salinity at the C_μC was found to be 7 wt.% NaCl which is also higher than that of the single C₁₄₋₁₅(PO)₅SO₄Na system. Both the higher C_μC and higher optimal salinity for the mixed surfactant system is due to the high hydrophilicity of SDS (high HLB number). Thus, the addition of SDS increases the HLB, so a higher concentration of C₁₄₋₁₅(PO)₅SO₄Na is needed to form a Winsor Type III microemulsion with diesel oil, a highly hydrophobic oil.

For an ionic surfactant system, the addition of salt facilitates the phase transformation from a Winsor Type I microemulsion toward a Winsor Type III and then a Winsor Type II microemulsion (23). In addition, the effect of salinity is important to know because wastewater often contains a significant salt concentration. However, it will be shown that insufficient foam production occurs in the froth flotation column above a NaCl concentration of 4 wt.% for the froth to reach the overhead outlet at a mixed surfactant concentration of 1 wt.%. At this salinity (4 wt.%), a Winsor Type III microemulsion is not formed, consistent with the modest (eg. 1 mN/m) IFT values, as shown in Fig. 6. From Fig. 6, as the NaCl concentration increases from 2 to 4 wt.%, the system IFT decreases modestly. The explanation of the effect of NaCl concentration

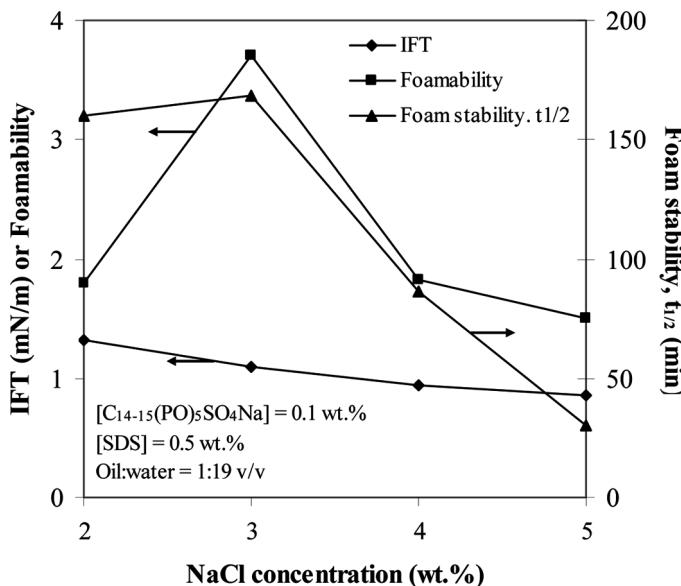


Figure 6. IFT, foamability, and foam stability of the mixed surfactant system as a function of salinity.

on IFT and phase behavior was already discussed in our previous work on ethylbenzene (10).

The effect of NaCl on foam characteristics will be discussed in the next section. From Fig. 6, a NaCl concentration of 3 wt.% produces a reasonably high foamability and foam stability. Therefore, even though the system IFT is not the minimum value, 3 wt.% NaCl was selected to further determine the effect of oil-to-water ratio on the IFT.

Figure 7 illustrates the system IFT as a function of oil-to-water ratio at 0.1 wt.% $C_{14-15}(PO)_5SO_4Na$, 0.5 wt.% SDS and 3 wt.% NaCl. In the studied range of oil-to-water ratio, the system IFT was found to only modestly depend on the oil-to-water ratio. This is probably because each oil-to-water ratio contains almost the same surfactant adsorption density at the oil/water interface, as also hypothesized in our previous work (10). Generally, the oil-to-water ratios in real wastewater streams are much lower and different from those used in traditional phase studies (1:1 volume/volume). This robust feature of the IFT is very useful in the design and operation of a froth flotation unit for treating most industrial wastewaters containing low oil contents. It is important to note that the production of overhead froth constraint prevents attainment of ultralow IFT values.

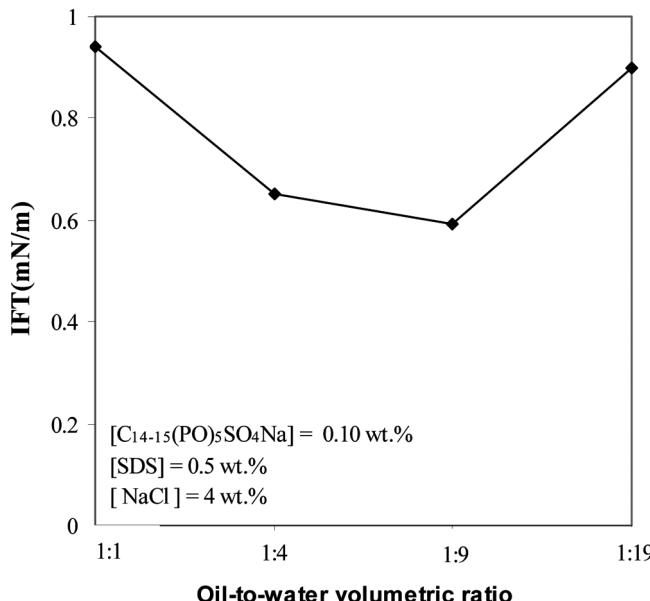


Figure 7. IFT of the mixed surfactant system as a function of oil-to-water volumetric ratio.

Based on the previous results of our batch froth flotation experiments with different types of oils (8–12), it has been pointed out that the oil removal is governed by both IFT and foam characteristics. Therefore, foam characteristics will also be discussed prior to presentation of the froth flotation results.

Foam Characteristics

Some real wastewater which is not well mixed can affect performance of wastewater treatment plants. Unlike the batch mode of operation (12), in a continuous froth flotation unit, agitation of the feed solution is generally needed before being fed into the froth flotation column in order to obtain a uniform composition of the feed solution. Hence, in this study, the effect of premixing on foam characteristics was investigated. For the agitated system, the feed solution was stirred at 2,000 rpm for one hour before being transferred to the froth flotation column. Figure 8 shows foamability and foam stability as a function of $\text{C}_{14-15}(\text{PO})_5\text{SO}_4\text{Na}$ concentration (no SDS) with and without premixing. When the $\text{C}_{14-15}(\text{PO})_5\text{SO}_4\text{Na}$ concentration was less than 0.5 wt.%,

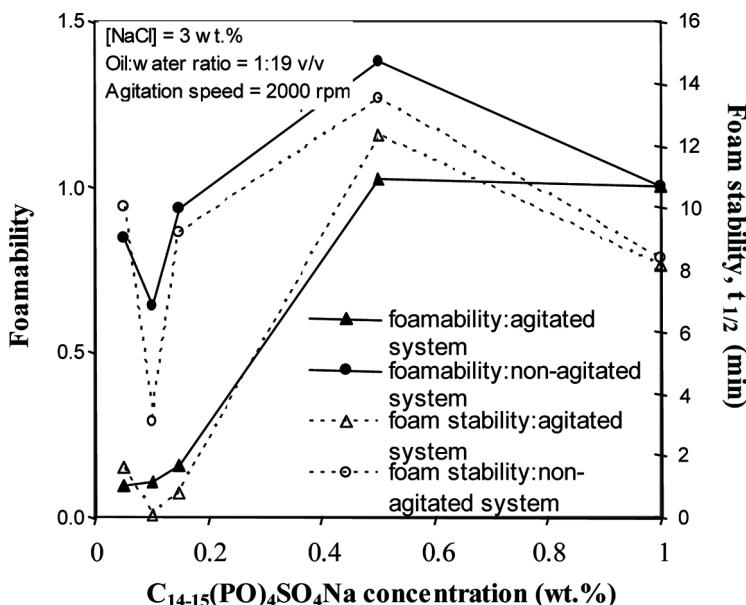


Figure 8. Foamability and foam stability at different $C_{14-15}(\text{PO})_4\text{SO}_4\text{Na}$ concentrations (without added SDS) with and without premixing.

the non-agitated system had higher foam stability and foamability than the agitated system. However, at a $C_{14-15}(\text{PO})_4\text{SO}_4\text{Na}$ concentration greater than 0.5 wt. %, both systems had similar foamability and foam stability. For both systems, with and without agitation, the lowest foamability and foam stability were found at 0.1 wt. % $C_{14-15}(\text{PO})_4\text{SO}_4\text{Na}$, which corresponds to the lowest IFT, as shown in Fig. 2. Based on the present results, the effect of premixing plays an insignificant role on both foamability and foam stability. However, premixing was still needed for running the continuous froth flotation unit to ensure the homogeneity of the feed solution. When, 0.1 wt. % of $C_{14-15}(\text{PO})_4\text{SO}_4\text{Na}$ was selected for running the froth flotation experiments, the froth produced could not reach the outlet at the top of the column. Hence the addition of SDS into the feed solution as a foam booster was used in subsequent froth flotation experiments.

Figure 9 shows foam characteristics and flotation parameters (to be discussed later) as a function of SDS concentration. Both foamability and foam stability tended to increase with increasing SDS concentration. Interestingly, the effect of adding SDS on the foam stability was found to be much more pronounced than that on the foamability. Figure 10 shows the effect of NaCl concentration on foam characteristics and

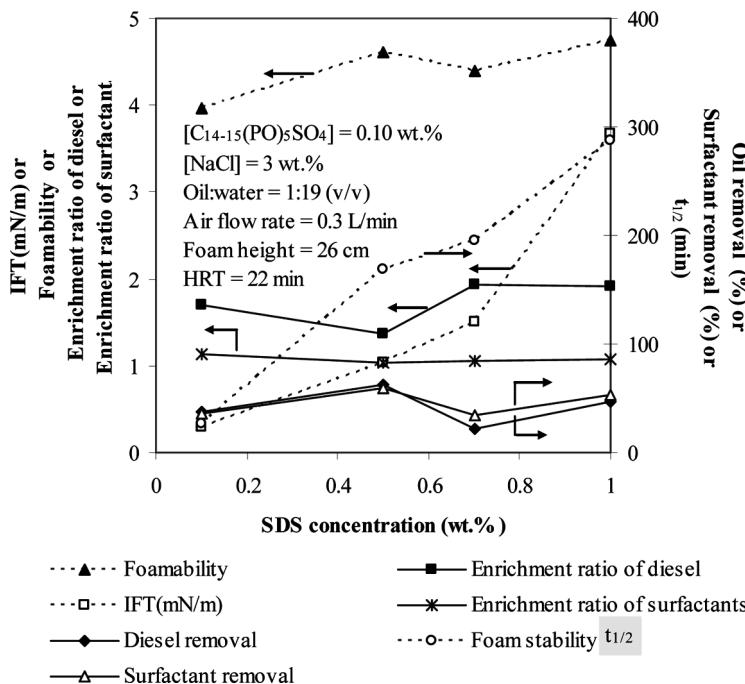


Figure 9. Effect of the addition of SDS on process parameters for continuous froth flotation.

flotation parameters. When the NaCl concentration increased from 2 to 3 wt.%, the foamability increased drastically, but the foam stability increased only slightly. However, both foamability and foam stability decreased substantially when the NaCl concentration further increased from 3 to 5 wt.%. The effect of NaCl on the foam characteristics will be explained latter.

As illustrated in Fig. 11, the effect of oil-to-water ratio on either foamability or foam stability is not pronounced. This is probably because surfactant adsorption at the air/water interface is independent of oil-to-water ratio. Independence of IFT on oil-to-water ratio along with this foam behavior implies that the surfactant concentration in the water phase, inducing adsorption at interfaces, is independent of oil-to-water ratio. The present results are consistent with the ethylbenzene system (14).

Figure 13 illustrates that the foamability increases almost linearly with increasing air flow rate because increasing air flow rate produces a higher quantity of air bubbles passing through the solution. Zouboulis et al. (24) also found that a higher air flow rate caused a larger amount of foam to be created. For an air flow rate lower than 0.25 L/min, the foam

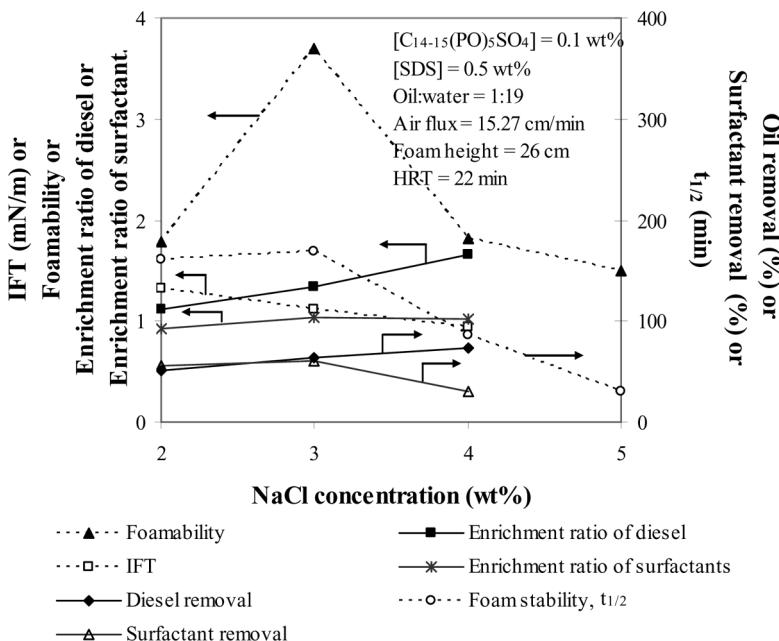


Figure 10. Effect of NaCl concentration on process parameters for continuous froth flotation.

stability was found to be independent of the air flow rate. However, the foam stability of the system decreased significantly with increasing air flow rate from 0.25 to 0.30 L/min because the circulation velocity induced by the bubble swarm rising through the column causes turbulence in the froth/collection zone, leading to foam collapse. Similar results of a batch study were also reported (12). Practically, there is an optimum air flow rate for maximum foam stability.

Froth Flotation Performance

Generally, high oil removal efficiency is a vital requirement for an effective froth flotation operation. If both oil and water are present in the froth with the same proportions as those in the influent, the separation of oil from water does not occur. Hence, for effective separation, the concentration of oil in the overhead froth has to be much higher than that in the feed. Consequently, in this study, both the removal and enrichment ratio of diesel oil are used to evaluate the separation efficiency of the continuous froth flotation system. Diesel oil removal is calculated based

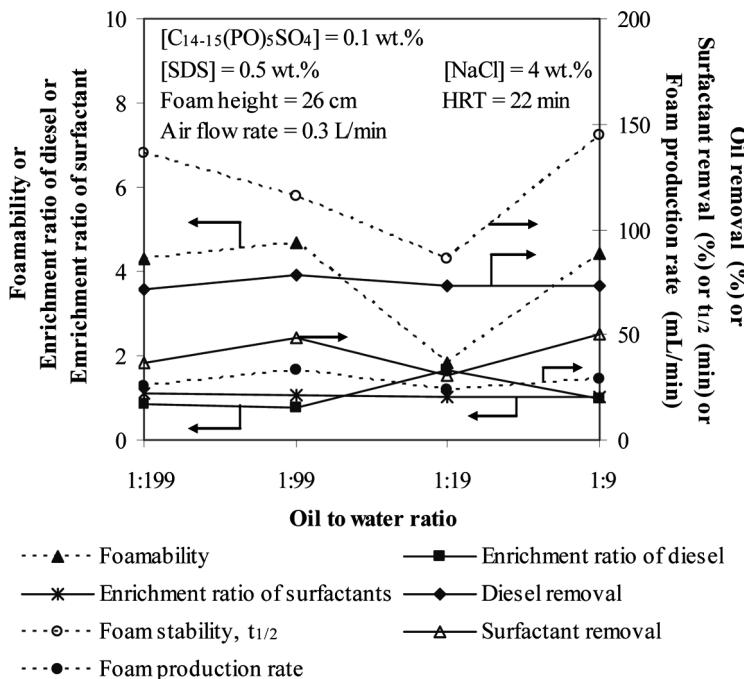


Figure 11. Effect of oil-to-water ratio on process parameters for continuous froth flotation.

on the mass difference of diesel oil in the feed and in the effluent. The enrichment ratio of diesel oil is defined as the ratio of the concentration of diesel oil in the liquid from the overhead froth to that in the feed solution. The higher the enrichment ratio, the better the separation efficiency. From the results of the batch froth flotation study, the optimum concentrations of $C_{14-15}(PO)_5SO_4Na$ and NaCl to achieve the maximum separation were found to be 0.3 and 3 wt.%, respectively (12). However, as already discussed, under these conditions, the continuous froth flotation unit used in this study was not able to produce stable foam to reach the outlet at the top of the column and SDS had to be added as a foam booster to the feed solution to obtain stable froth.

Effect of Added SDS

Figure 9 shows the effect of adding SDS on the process performance of continuous froth flotation at 3 wt.% NaCl. At a fixed $C_{14-15}(PO)_5SO_4Na$ concentration of 0.1 wt.%, which is the $C_{\mu}C$ of the pure

$C_{14-15}(PO)_5SO_4Na$ system, the maximum diesel oil removal was achieved at 0.5 wt.% SDS. From Fig. 5, at a salinity of 3 wt.% NaCl and at a total surfactant concentration of 0.6 wt.%, a Type III microemulsion is not attained. Moreover, at this total surfactant concentration (0.5 wt.% SDS and 0.1 wt.% $C_{14-15}(PO)_5SO_4Na$), the system IFT is modest (about 1 mN/m), as shown in Fig. 9. However, unlike the effect of surfactant concentration in the batch study (12), the trend of diesel oil removal as a function of SDS was found to mirror the effect on foamability. The diesel oil removal increased with increasing IFT, suggesting that maximum diesel oil removal is more influenced by foam characteristics than IFT under these studied conditions. But, as will be discussed in the next section, at this SDS concentration, at a high enough salinity to achieve ultralow IFT, stable froth could not be achieved in the continuous froth flotation unit. Since all flotation experiments corresponded to relatively high IFT values, lack of importance of IFT should not be overemphasized in a continuous operation. As the SDS concentration increased from 0.1 wt.% to 0.5 wt.%, the enrichment ratio of diesel oil slightly decreased. At 0.5 wt.% SDS, the system had the lowest enrichment ratio of diesel oil. This is because SDS can enhance both foamability and foam stability. Consequently, the foam becomes more stable and holds more water. When the SDS concentration further increased to 0.7 wt.% and 1.0 wt.%, the diesel oil enrichment ratio slightly increased. This can be explained by the fact that at very high surfactant concentrations, increasing surfactant concentration leads to increasing both foamability and foam stability, so the oil content in the foam increases. The combined effect of both increasing amounts of diesel oil and water in the foam lamellae leads to an insignificant change in the enrichment ratio of diesel oil with respect to the SDS concentration. Consequently, the enrichment ratio of diesel oil tended to increase slightly with increasing concentration of SDS in the studied range. This result is similar to the ethylbenzene results from our previous work (10). As shown in Fig. 9, the enrichment ratio of surfactants decreases slightly with increasing SDS concentration and the removal of surfactants shows a similar trend to the diesel oil removal. Interestingly, the surfactant enrichment ratio was found to be slightly higher than unity for the studied concentration range of SDS, confirming that the surfactants adsorb preferentially at the air/water interface.

Effect of NaCl Concentration

Figure 10 shows the effect of NaCl concentration on the process parameters of continuous froth flotation operated at 0.1 wt.%

$C_{14-15}(PO)_5SO_4Na$ and 0.5 wt. % SDS. The removal of diesel oil increased slightly with increasing NaCl concentration in the studied range, whereas the system IFT decreased slightly. Both foamability and foam stability firstly increased with increasing NaCl from 2 to 3 wt. % and then decreased with increasing NaCl concentration beyond 3 wt. %, perhaps because increasing NaCl results in more diesel oil being attached to the foam. Increasing the NaCl concentration decreases the repulsive force between the negative-charged heads of the surfactants, potentially leading to higher surfactant adsorption at the surface of the foam lamellae. As a result, both foamability and foam stability increase, which, in turn, increases the diesel oil removal. Maximum diesel oil removal was found at 4 wt. % NaCl. When the NaCl concentration exceeded 4 wt. %, the studied froth flotation system could not generate stable froth to reach the froth outlet at the top of the column because the system possessed poor foamability and foam stability, which is probably due to dramatically decreasing electrostatic repulsion between the charged surfactant monolayers at the two surfaces of the lamellae. Due to this limitation, the Type III microemulsion was not attained in the continuous froth flotation system in this study. An increase in the NaCl concentration from 2 to 4 wt. % increased the enrichment ratio of diesel oil. Similar to the diesel oil removal, the diesel oil enrichment ratio was highest at 4 wt. % NaCl. The present results of the continuous froth flotation system are in good agreement with our previous work in the batch mode (12).

Both the removal and the enrichment ratio of surfactants increased slightly with increasing NaCl concentration from 2 to 3 wt. %. With increasing NaCl concentration beyond 3 wt. %, the removal and the enrichment ratio of surfactants decreased, which correspond to the foamability and foam stability results. Based on these results, 4 wt. % NaCl was selected to use as a base condition to investigate other process parameters.

Effect of Oil-to-Water Ratio

Most available work on froth flotation (10–12) involved an 1:1 oil-to-water ratio. But in real applications, a volumetric ratio of emulsified oil-to-waste water is much lower than 1:1. Consequently, in this work, the effect of oil loading on the performance of froth flotation was investigated by varying the oil-to-water ratio; 1:199, 1:99, 1:19, and 1:9 at 0.1 wt. % $C_{14-15}(PO)_5SO_4Na$, 0.5 wt. % SDS, and 4 wt. % NaCl. Figure 11 shows the effect of oil-to-water ratio on the process performance of continuous froth flotation. Similar to our previous work on batch froth flotation (10,12), the efficiency of the oil removal of the continuous froth

flotation was not affected significantly by changing the oil-to-water ratio in the feed. However, the trend of oil removal was found to correspond to the foam production rate as well as the foamability and the foam stability. Interestingly, the highest enrichment ratio of diesel oil was found to be at a 1:19 oil-to-water, and so this ratio was selected for further investigation. At the oil-to-water ratio of 1:19, the system had the lowest foam production rate as well as the lowest foamability and foam stability, leading to the highest amount of water to be entrained back to the solution. However, changing oil-to-water ratio did not significantly affect either the removal or the enrichment ratio of the surfactants in the studied conditions. The trends of both the removal and the enrichment ratio of the surfactants were found to correspond to the foamability, foam stability and foam production rate of the system. A lower foam production rate indicates that more foam has collapsed, resulting in a higher amount of surfactant to be entrained back into the solution; as a result, the removal and the enrichment ratio of the surfactants decrease.

Effect of Foam Height

Figure 12 illustrates the effect of foam height on all flotation process parameters. The diesel oil removal decreased slightly when the foam height increased because the foam production rate decreased with increasing foam height. The lower the quantity of foam produced, the lower the amount of diesel oil removed. In contrast, the enrichment ratio of diesel oil increased as the foam height increased because the foam produced has a longer holding time to allow more water drainage from the foam. Hence, the foam produced contains a lower amount of water or a higher enrichment ratio of diesel oil. The surfactant removal decreased but the enrichment ratio of surfactants slightly increased as the foam height increased. This is because a high foam height leads to a low foam production rate. The same explanation for the removal and the enrichment ratio of diesel oil can be used to describe those parameters of the surfactant. A foam height of 26 cm was selected for further studies because the system has the highest diesel oil and surfactant removal of the conditions studied.

Effect of Air Flow Rate

Figure 13 shows that diesel oil removal is not significantly affected by increasing the linear air flow rate in the range of 0.15 to 0.20 L/min, while the foamability and the foam production rate of the system increase almost linearly with air flow rate. However, at an air flow rate higher

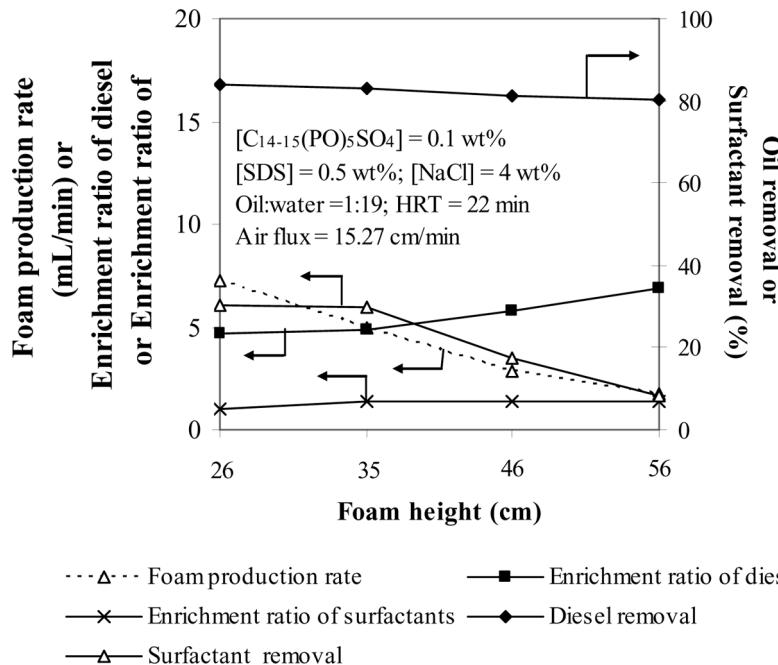


Figure 12. Effect of foam height on process parameters for continuous froth flotation.

than 0.25 L/min, the diesel oil removal decreased markedly with increasing air flow rate, so this condition was selected to investigate the effect of HRT, which will be discussed in the next paragraph. The trend of the diesel oil removal was similar to that of the foam stability. The result indicates that the diesel oil removal is mainly governed by the foam stability of the system, which is different from the batch result where the diesel oil removal was found to correspond to the foamability (12). The difference in the results can be explained in that, for the batch system, all parameters, especially diesel oil and surfactant concentrations, vary during the operation while they are invariant in the continuous system. The higher the air flow rate, the lower the enrichment ratio of diesel oil. This can be explained in that a higher air flow rate simply produces more bubbles passing through the solution, resulting in both higher foamability and foam production rate, and less time for water drainage. Hence, a larger amount of water can be carried with the produced froth to the top of the column, resulting in a decrease in the enrichment ratio of the diesel oil. Unlike the batch froth flotation operation in our previous work (12), the diesel oil enrichment ratio was not significantly affected by

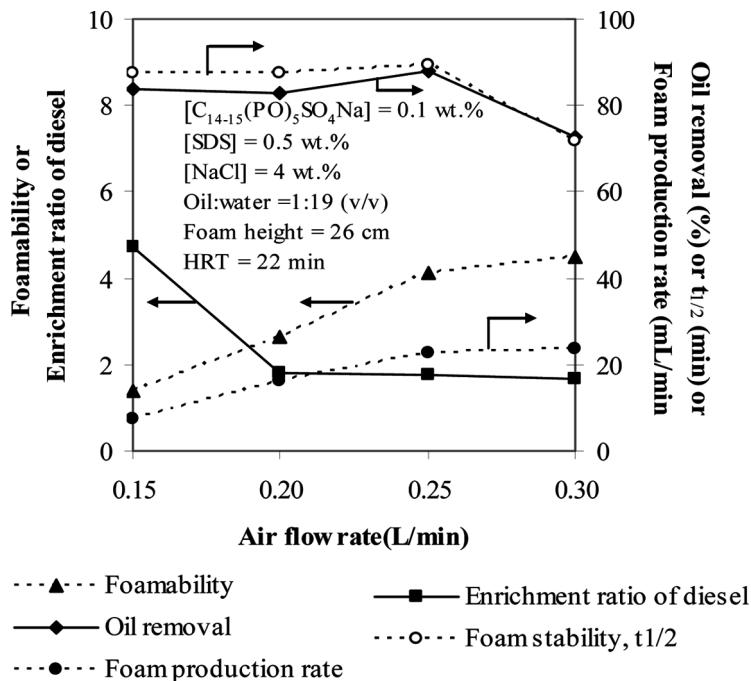


Figure 13. Effect of air flow rate on process parameters for continuous froth flotation.

the air flow rate. For an air flow rate in the range of 0.15 to 0.25 L/min, the surfactant removal was almost constant, but at an air flow rate greater than 0.25 L/min, the surfactant removal decreased with increasing air flow rate. It is interesting to point out that there is a similar trend in the removal of the diesel oil and the surfactants. The same explanation can be used to describe the surfactant removal results. The enrichment ratio of surfactants decreased slightly as the air flow rate increased. It was observed that the higher the air flow rate, the higher the foam production rate and foamability, leading to a higher amount of water to be carried over into the collapsed froth. As a result, the enrichment ratio of surfactants decreases with increasing air flow rate.

Effect of HRT

The term of hydraulic retention time (HRT) is expressed as the holding or residence time of the liquid in the froth flotation column which is

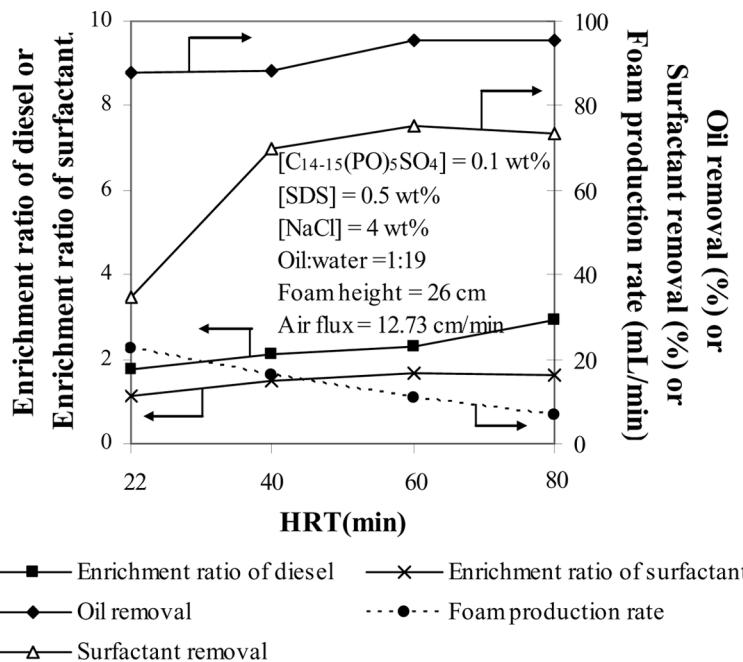


Figure 14. Effect of hydraulic retention ratio (HRT) on process parameters for continuous froth flotation.

calculated from the liquid volume in the column divided by the feed flow rate. Figure 14 shows the effect of HRT on all process parameters of the continuous froth flotation unit operated under the base conditions. The diesel oil removal increased slightly when the HRT increased. This is because a higher HRT represents a longer residence time of diesel oil in the flotation column to be adsorbed onto and coalesced with the rising air bubbles. As a result, a greater amount of diesel oil can be carried by the produced froth to the top of the column, and a higher diesel oil removal is obtained. In this study, the highest diesel oil removal (96%) was achieved at 60 min HRT as compared to 98% for the batch system of our previous study. The enrichment ratio of diesel oil increased slightly with increasing HRT. The foam production rate decreased as the HRT increased because the total amount of surfactant entering the flotation column decreases with increasing HRT. The surfactant removal increased substantially with increasing HRT from 22 to 40 min, and the surfactant removal reached a plateau when the HRT was greater than 40 min. The same explanation for the enrichment ratio of diesel oil can be used to describe the enrichment ratio of surfactants.

ACKNOWLEDGEMENTS

The Thailand Research Fund is acknowledged for providing a Royal Golden Jubilee Ph.D. fellowship for Ms. Sunisa Watcharasing. The expenses for this research were mainly supported by The Advanced Research Scholar Grant from the Thailand Research Fund and the Research Unit of Applied Surfactants for Separation and Pollution Control under The Ratchadapisek Somphot Fund, Chulalongkorn University. The National Excellence Center for Petroleum, Petrochemicals and Advanced Materials under The Ministry of Education is also acknowledged for providing all research facilities. Sasol North America Inc., Texas, USA, is acknowledged for providing the extended surfactant used in this research. Moreover, support was also received from the industrial sponsors of The Institute for Applied Surfactant Research, University of Oklahoma including Akzo Nobel, Clorox, Conoco/Phillips, Church and Dwight, Dow, Ecolab, Halliburton, Huntsman, Oxiteno, Procter & Gamble, Sasol North America, Shell Chemical, and Unilever.

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