REFERENCES

1. Adamson, W. (1990) Physical Chemistry of Surfaces. New York: Wiley.

2. Boonyasuwat, S., Chavadej, S., Malakul, P., and Scahmehorn, J.F. (2003) Anionic and cationic surfactant recovery from water using a multistage foam fractionator. Chemical Engineering Journal, 93, 241-252.

3. Carleson, T. E. (1989) Surfactant-Based Separation Processes. New York: Marcel Dekker.

5. Grieves, R. B. and Wood, R.K. (1964) Continuous Foam Fractionation: The effect of Operating Variables on Separation. American Institute of Chemical Engineers, 10, 456.

6. Kinoshita, T., Akita, S., Ozawa,S., Nii, S., Kawaizumi, F., Takahashi, K. (2003) A study on Gold(III) Recovery Via Foam Separation with Nonionic Surfactant in Batch Mode. Journal of Materials Characterization and Engineering, 2, 71-82.

7. Kumpabooth, K. (1996) Surfactant Recovery from Water using Foam Fractionation. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.

8. Okamoto, Y. and Chou, E. J. (1979) Handbook of Separation Techniques for Chemical Engineering. New York: Mcgraw-Hill.

9. Porter, M.R. (1994) Handbook of Surfactants, 2nd edition, New York: Chapman & Hal.

10. Rosen, M.J. (1988) Surfactant and Interfacial Phenomena, 2nd edition, New York: Wiley.

11. Scamehorn, J.F., Christiam, S.D., and Ellington, R.T. (1989) Surfactant-Based Separation Processes. NewYork: Marcel Dekker.

13. Sebba, F. (1987) Foam and Biliquid Foam-Aphrons New York: Wiley.

14. Thrapiwattananon, N. , Scahmehon, J. F., Osuwan, S., and Harwell, J. H. (1996) Surfactant Recovery from Water Using Foam Fractionation. Separation Science Technology, 31, 1259.

APPENDIX A

DATA

Experimental results for all multi-stage foam fractionation runs at 3 stages

Influent concentration (% of CMC)	Foam height (cm)	Foam wetness (g/L)				Foam production rate (mL/min)			
		Air flow rate (L/min)				Air flow rate (L/min)			
		30	50	80	100	30	50	80	100
25	30	3.51	2.77	35.55	29.58				
	60	0.72	1.43	2.55	4.01		3.4		
	90	a	a	a	3.59				
50	30	3.04	4.03	33.74	38.02		10.4		
	60	2.14	2.66	4.11	22.00	1.4	4.7	20.0	37.3
	90	a	2.48	3.37	19.45		1.2		
75	30	3.77	17.99	60.43	69.44				
	60	2.87	3.67	4.98	38.46		5.5		
	90	a	2.53	3.93	30.09				
100	30	3.90	26.46	67.77	66.90				
	60	2.89	4.63	30.31	58.76		6.0		
	90	a	4.21	26.66	40.04				

a - the froth could not reach overhead pipe

Interstage CPC Concentration at feed flow rate of 50 mL/min, feed concentration of 50% of CMC (0.161 g/L)

	CPC concentration (g/L)		
	Air flow rate (L/min)		
	30	50	100
Foam Height (cm)			
90	20.09	12.58	1.97
60	8.63	7.19	1.66
30	6.76	4.43	1.12
Tray			
1st (Top)	5.02	3.88	1.06
2nd	3.05	2.41	1.06
3rd	2.76	2.04	1.03
Last Tray (Bottom)	0.404	0.786	0.987
Drain	0.0168	0.0249	0.0991

Operational Zone

	Air Flow Rate (l/min)			
	25	50	80	100
Min feed flow rate	20	20	25	30
Max feed flow rate	120	100	80	50
Min feed flow rate	15	15	20	20
Max feed flow rate	110	95	70	45
Min feed flow rate	8	10	10	10
Max feed flow rate	90	90	60	35
Pure Water	120	120	120	120

Air Flow Rate

CPC

	Air Flowrate (L/Min)						Air Flowrate (L/Min)				
	30	40	50	80	100		30	40	50	80	100
C_f	7.084	5.796	5.152	2.093	1.61	F_f	0.45	0.55	0.6	1.35	1.7
C_i	0.161	0.161	0.161	0.161	0.161	F_i	20	20	20	20	20
C_e	0.02	0.022	0.025	0.025	0.033	F_e	19.55	19.45	19.4	18.5	18.3

SDS

	Air Flowrate (L/Min)						Air Flowrate (L/Min)				
	30	40	50	80	100		30	40	50	80	100
C_f	23.06	20.754	17.295	4.612	2.8825	F_f	0.7	0.75	0.8	3	4.5
C_i	1.153	1.153	1.153	1.153	1.153	F_i	20	20	20	20	20
C_e	0.38	0.4	0.42	0.45	0.45	F_e	19.3	19.25	19.2	17	15.5

PSM

	Air Flowrate (L/Min)						Air Flowrate (L/Min)				
	30	40	50	80	100		30	40	50	80	100
C_f	7.29675E-05	7.297E-05	0.00005405	1.622E-05	1.351E-05	F_f	0.25	0.5	0.55	1.5	1.6
C_i	2.7025E-06	2.703E-06	2.7025E-06	2.703E-06	2.703E-06	F_i	20	20	20	20	20
C_e	0.0000007	0.000001	0.000001	0.000001	0.000001	F_e	19.75	19.5	19.45	18.5	18.4

Foam Height

CPC

	Foam Height (cm)					Foam Height (cm)		
	30	60	90			30	60	90
C_F	1.121	5.152	7.38	F_F		2	0.6	0.4
C_i	0.161	0.161	0.161	F_i		20	20	20
C_e	0.14	0.025	0.01	F_e		18	19.4	19.6

SDS

	Foam Height (cm)					Foam Height (cm)		
	30	60	90			30	60	90
C_F	3.2	17.295	28.7	F_F		2.5	0.8	0.5
C_i	1.153	1.153	1.153	F_i		20	20	20
C_e	0.98	0.42	0.3	F_e		17.5	19.2	19.5

PSM

	Foam Height (cm)					Foam Height (cm)		
	30	60	90			30	60	90
C_F	0.000042	5.41E-05	0.000082	F_F		3	0.55	0.5
C_i	2.7025E-06	2.7E-06	2.7025E-06	F_i		20	20	20
C_e	0.000003	0.000001	0.00000081	F_e		17	19.45	19.5

Feed Concentration

CPC

	Feed Conc (% of CMC)						Feed Conc (% of CMC)				
	25	50	75	85	100		25	50	75	85	100
C_F	8.98	5.152	2.13	1.11	0.6	F_F	0.5	0.6	2.5	3.5	5
C_i	0.161	0.161	0.161	0.161	0.161	F_i	20	20	20	20	20
C_e	0.012	0.025	0.03	0.035	0.04	F_e	19.5	19.4	17.5	16.5	15

SDS

	Feed Conc (% of CMC)						Feed Conc (% of CMC)				
	25	50	75	85	100		25	50	75	85	100
C_F	20.5	17.295	12.5	6.3	2.5	F_F	0.7	0.8	1.5	3.2	3.5
C_i	1.153	1.153	1.153	1.153	1.153	F_i	20	20	20	20	20
C_e	0.3	0.42	0.5	0.55	0.65	F_e	19.3	19.2	18.5	16.8	16.5

PSM

	Feed Conc (% of CMC)						Feed Conc (% of CMC)				
	25	50	75	85	100		25	50	75	85	100
C_F	0.000076	7.2968E-05	0.000059	0.0000155	0.000014	F_F	0.35	0.45	0.55	1.6	2.9
C_i	2.7E-06	2.7025E-06	2.7E-06	2.703E-06	2.7E-06	F_i	20	20	20	20	20
C_e	7E-07	0.000001	0.000001	0.000001	1.5E-06	F_e	19.65	19.55	19.45	18.4	17.1

Number of Trays

CPC

	Number of Trays					Number of Trays			
	1	2	3	4		1	2	3	4
C_F	0.644	2.576	5.152	5.635	F_F	0.1	0.3	0.6	0.8
C_i	0.161	0.161	0.161	0.161	F_i	20	20	20	20
C_e	0.1	0.095	0.03	0.02	F_e	19.9	19.7	19.4	19.2

SDS

	Number of Trays					Number of Trays			
	1	2	3	4		1	2	3	4
C_F	1.7295	8.071	17.295	19.601	F_F	0.3	0.5	0.8	1.2
C_i	1.153	1.153	1.153	1.153	F_i	20	20	20	20
C_e	0.9	0.7	0.4	0.2	F_e	19.7	19.5	19.2	18.8

PSM

	Number of Trays					Number of Trays			
	1	2	3	4		1	2	3	4
C_F	2.97275E-06	1.08E-05	5.946E-05	7.567E-05	F_F	0.15	0.45	0.55	0.8
C_i	2.7025E-06	2.7E-06	2.703E-06	2.703E-06	F_i	20	20	20	20
C_e	0.000000009	9E-09	9E-09	9E-09	F_e	19.85	19.55	19.45	19.2

APPENDIX B

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Surfactant Recovery from Water Using a Multistage Foam Fractionator: Part I Effects of Air Flow Rate, Foam Height, Feed Flow Rate and Number of Stages

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Abstract: Surfactants can be present at low concentrations in wastewater from many industries, such as papermaking or detergent manufacture. The surfactant must sometimes be reduced in concentration in order to meet environmental standards before discharging these wastewaters to the environment. Also, recovery of the surfactant for reuse is sometimes economical and desirable. Foam fractionation has been shown to be an effective method of removing anionic and cationic surfactants from water in a single stage in our previous work. In this study, the recovery of a cationic surfactant (cetylpyridinium chloride or CPC) from water by multistage foam fractionation in a bubble-cap trayed column was investigated with one to four stages operated in steady-state mode for surfactant concentrations less than or equal to the critical micelle concentration. In comparison with a single-stage foam fractionator, CPC was found to be removed from water by the multistage foam fractionator much more effectively. Both enrichment ratio and surfactant removal fraction increase with increasing feed flow rate, foam height, and number of stages, but they decrease with increasing CPC feed concentration and air flow rate. This study has demonstrated that the multistage foam fractionator used in this study can achieve almost quantitative

removal of the surfactant with high enrichment ratio and short residence time. Multi-stage foam fractionation is demonstrated to be an extremely effective method of reducing surfactant concentrations from low to even lower concentrations in wastewater.

INTRODUCTION

Surfactants are widely used in many industries and paper plants such as consumer product manufacture, pulp processing, and ore separation. As environmental regulations tighten, there is increasing concern about reducing the surfactant concentration in effluent streams. Foam fractionation and flotation are surfactant-based separations that can remove pollutants from wastewater and groundwater (1, 2). In addition to satisfying environmental regulations, the value of the surfactant being emitted sometimes makes recovery operations more economical. An alternative approach to the bio-degradation of the surfactant is the direct treatment of the rinsing waters by physical separation that would allow for the reuse of both water and surfactant. Several wastewaters which typically contain very low surfactant concentrations, around or below the critical micelle concentration (CMC), may be treated to separate surfactants economically by using the foam fractionation technique.

Foam fractionation is one member of a group of processes known as adsorptive bubble separation techniques, which isolate species based on surface activity (3). Foam fractionation processes have been used to concentrate and remove surface-active agents from aqueous solutions (4, 5). Foam fractionation is based on the selective adsorption of solutes at the gas-liquid interface, which is generated by a rising ensemble of bubbles through the solution. This ensemble of bubbles forms a foam bed (on top of the liquid pool) which preferentially contains the surface-active solutes (6, 7). The water which forms at the surface is allowed to drain due to gravitational force and the foam is eventually collapsed to form a concentrated liquid that can be recycled in the production process. Foam fractionation as a separation technique for homogeneous liquid mixtures has high efficiency at low concentrations, unlike many conventional methods of separation. Foam provides the most efficient means for the generation of the surface layer (8). There are the limits to this surfactant concentration since adequate foamability is required to reach the top of the column to achieve any separation.

There are two modes of foam fractionation; simple mode (batchwise or continuous); and higher mode with enriching and/or stripping (9–11). The foam fractionation column can also be classified into two categories; single-stage and multistage. Several studies have also been done to investi-gate recovery of the surfactant itself using foam fractionation and to examine the effects of various parameters on the separation efficiency of

surfactants and proteins (3, 12). However most of these studies have used either batch or continuous mode in single-stage flotation columns (3, 5, 13), whereas the use of multistage pilot plants has seldom been reported (14–16). Many variables are considered to have a significant effect upon removal efficiency, such as height of foam-liquid interface, air flow rate, sparger geometry, and feed concentration. The performance of foam fractionation is strongly influenced by the rate and extent of drainage of interstitial fluid and the effects of added electrolyte and temperature have received attention for three types of surfactants (anionic, cationic, and nonionic) using a single-stage foam fractionation (3–5). Previous work has been reported on multistage foam fractionation but not for operation in a continuous mode (10, 14, 17).

The stability of the foam as an isolated system, free from thermal or mechanical perturbation, depends dominantly on its resistance to gravitational drainage (18). The foam stability is related to the surfactant concentration of the foaming solution (19). At higher temperatures (typically >35°C), coalescence dominates and the foam rapidly becomes unstable (20). In the present work, a multistage foam fractionator was constructed and designed in a continuous, steady-state mode. The removal of a cationic surfactant from water at feed concentrations at or below the CMC was studied. The effect of air flow rate, foam height, surfactant feed concentration, and the number of stages on the separation efficiency was measured. Auxilliary properties such as foam wetness, foam formation, and foam stability were also measured to aid in interpretation of the column results. Foam wetness can also help interpret the results of separation efficiency (21).

Foam fractionation is quite similar to an air stripping operation, except the air being passed through the liquid is producing a foam which passes to the tray above it rather than stripping a volatile organic solute from the liquid and passing that into the tray above it. In a multistage foam fractionator, on any given tray, the foam produced has a much higher surfactant concentration than that in the bulk liquid phase. The foam is carried over to the next highest tray by passing through bubble caps and then the foam collapses or is dissolved back into the bulk liquid phase in the next highest tray. As a result, the surfactant concentration increases progressively in the upward direction. In the present study, we choose a multitray design with bubble caps on the trays as is commonly used in stripping or distillation. Foam fractionation column studies using bubble cap plates reported plate efficiencies of up to 30% (22, 23). The foam fractionation column can handle high throughput by employing a large cross-sectional area in counterflow mode (24, 25). Mathematical model based on the Langmir adsorption isotherm and liquid holdup was verified with experimental data for two types of surfactants, octylphenol polyethoxylate (Triton X-100), and cetyl pyridium chloride (CPC) (26). A use of the effect of perforated plates in a foam fractionation column with external reflux was found to reduce the liquid holdup in foam, resulting in increasing enrichment ratio of poly(vinyl alcohol) (27). One of the specific

objectives of this study was to demonstrate that the multistage foam fraction-
ation system could operate without problems like excessive pressure drop
or flooding and to compare the separation efficiency to that expected from
single-stage results. Since our goal is removal of surfactant itself from
water rather than using surfactant as a separating agent to remove something
else, conditions can be substantially different in our study than previous foam
fractionation studies; for example, lower surfactant concentrations.

In this Part I of a series, we investigate important operational parameters
affecting cationic surfactant removal from water. In future parts, we will
also report on the comparative foam fractionation of cationic, anionic, and
nonionic surfactants, and modeling a multistage foam fractionator.

EXPERIMENTAL

Materials

Cetylpyridinium chloride or n-hexadecylpyridinium chloride or CPC (99+%
pure, Zealand Chemical), a cationic surfactant, was used as received. Freshly
deionized water was used in all experiments.

Methods

A schematic diagram of the multistage foam fractionation unit used in this study
is illustrated in Fig. 1. The multistage foam fractionation column was comprised
of a jacketed stainless steel cylinder having a jacket diameter of 30 cm, an
internal column diameter of 20 cm, and tray spacing of 15 cm. Each tray had
16 bubble caps with a weir height of 5 cm and a cap diameter of 2.5 cm.
A sample port was located at the base of each tray for taking liquid samples.
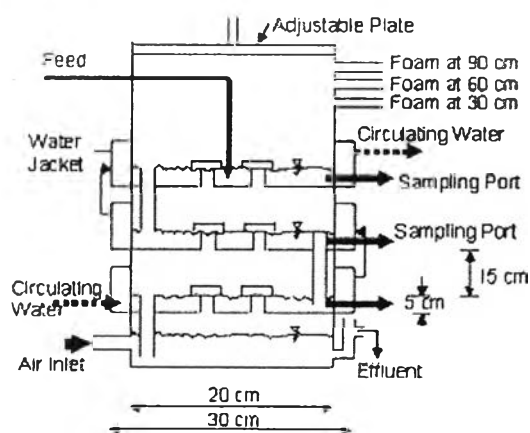
Figure 1. Diagram of multistage foam fractionation column with three trays.

There was a glass window for each tray for visual observation. Three foam heights of 30, 60, and 90 cm from the top tray of the column were studied. Figure 2 illustrates the process flow diagram for the experimental pilot plant.

The foam fractionation was performed in continuous flow operation with aqueous solution containing different surfactant concentrations. The surfactant feed solution was continuously pumped by a peristaltic pump at flow rates in a range of 25–200 mL/min (0.7215–5.77 L/min m^2) and entered the column at the top position of the highest tray. The pressurized air flow rate was measured by a rotameter over a range of 30–100 L/min (STP) and was introduced to the bottom of the column. The pressure drop across each tray averaged 4.5 cm of water. The column operating temperature was held constant at 25°C by using a cooling-heating circulating bath to circulate water through the water jacket around the column. After a designated time interval, the foamate at the top of the solution was collected at three different heights (30, 60, and 90 cm) from the top of the column. The foam collected was frozen, thawed, and then weighted to measure the mass and volume of the collapsed foamate at room temperature over a period of about 20 h to determine the time to achieve steady state. Samples of the feed solution, the collapsed foamate, and the effluent were analyzed for surfactant concentration. In each experiment, foam wetness (gram of collapsed foam solution/L of foam) was measured. The column was thoroughly cleaned with distilled water before starting a new run. All of the experiments were performed at least three times to ensure reproducibility of the results, and the mean values are reported with a precision of ± 2.5%.

The foam fractionation was studied under steady-state conditions. To attain steady state, the experiment was carried out for a minimum of 20 h,
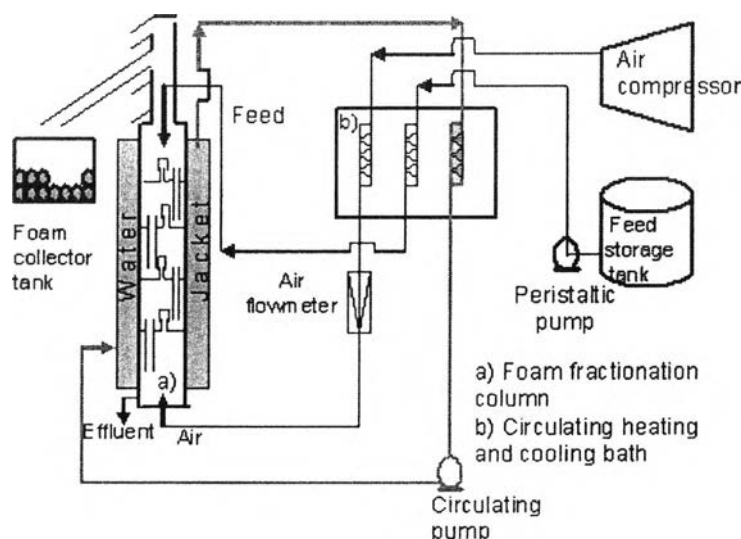
Figure 2. Schematic diagram of experimental multistage foam fractionation system.

which was found to be adequate for the multistage foam fractionator to reach steady state as compared to only 6 h reported in the previous study for a single-stage unit. Steady state was ensured when all measured parameters were invariant with time. In each experiment, foam wetness (gram of foam solution/L of foam), volumetric foam flow rate production (mL/min) and the surfactant concentration (g/L) in the collapsed foam solution, the feed solution, and the effluent were measured. The concentration of CPC was measured by a UV-Visible spectrophotometer at 260 nm (Perkin Elmer, Lambda 10). The CMC of the surfactant was determined from the concentration where the surface tension vs. surfactant concentration showed an abrupt change in the slope. The measurement of surface tension of solutions containing different CPC concentrations was carried out by using a Du-Nouy ring tensiometer (Kruss, K10T).

Independent experiments to measure foamability and foam stability were conducted by using a glass column having an internal diameter of 5 cm and a height of 100 cm. A quantity of 250 mL of solution containing different CPC concentrations was poured into the column and then the solution was sparged with a constant air flow rate of 0.35 L/min. The foam height was measured as a function of time until the maximum foam height was reached at 90 cm; this indicates the foamability of the system. To quantify foam stability, the air introduced into the column was turned off, and the foam height vs. time was then monitored. All experiments were at room temperature (25 to 27°C).

Under base conditions, the foam fractionation system was found to reach steady state within approximately 20 h where the surfactant concentrations measured on each tray were relatively constant. Key parameters used to characterize the separation efficiency are the removal fraction and the enrichment ratio as defined below:

$$\text{Removal fraction} = (C_i - C_e)/C_i \qquad (1)$$

$$\text{Enrichment ratio} = C_f / C_i \qquad (2)$$

where C_i and C_e are surfactant concentrations (mg/L) in the influent and effluent streams, respectively, and C_f is the surfactant concentration (mg/L) in the collapsed foam (liquid after foam breaks). It was found that the mass balance for surfactant closed within at least 90% for all runs.

RESULTS AND DISCUSSION

To operate a foam fractionator successfully, one has to consider two important operational constraints: foam formation and flooding. A sufficient air flow rate is needed to produce foam which can reach the foam outlet of the top stage. Figure 3 shows the minimum air flow rate required to generate foam for three different foam heights. Liquid flooding in a stage depends on the liquid flow rate and the air flow rate. Figure 4 depicts the plot between the air flow
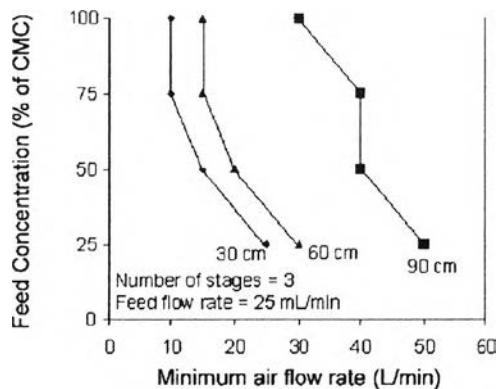
Figure 3. Minimum air flow rate required for foam production at different foam heights.

rate and the maximum liquid feed flow rate for each stage corresponding to flooding for a feed concentration of 50% of the CMC (1CMC = 0.322 g/L). Figure 5 combines the minimum air flow rate to produce foam with flooding conditions to yield the operating zone for the column or range of possible conditions for column operation at 50% of the CMC. Similar operating condition boundaries were generated at other surfactant concentrations.

Foamability and Foam Stability

Figures 6 and 7 show foamability and foam stability, respectively, as a function of CPC concentration. For the studied range of CPC concentrations, the maximum foam height is nearly independent of CPC concentration.
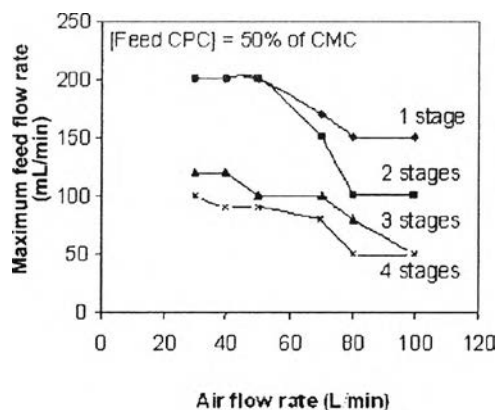
Figure 4. The maximum liquid feed flow rate corresponding to liquid flooding at different stage numbers and different air flow rates.
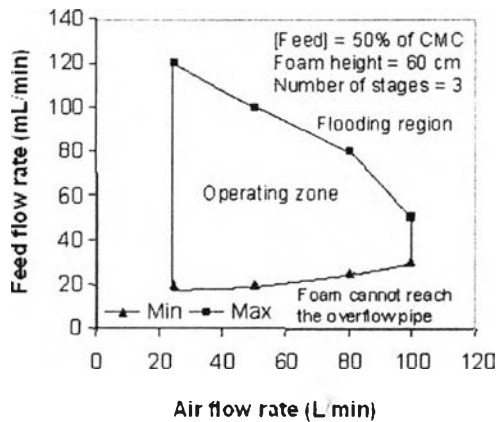
Figure 5. Flooding points and operating zone of the foam fractionation column.

However, it takes a shorter time to reach any given maximum height as the CPC concentration increases. The foam formed over a fluid with a higher concentration is characterized by smaller, more stable bubbles of less than 1 mm in diameter. An increase in CPC concentration increases the time required for complete collapse of foam, indicating that increasing CPC concentration also enhances foam stability.

Effect of Air Flow Rate

The effects of the air flow rate on the enrichment ratio and removal fraction are shown in Fig. 8. The results indicate that for any given CPC concentration in the feed, increasing the air flow rate increases the foam production rate (as seen in Table 1), reduces the enrichment ratio, and reduces the removal fraction.
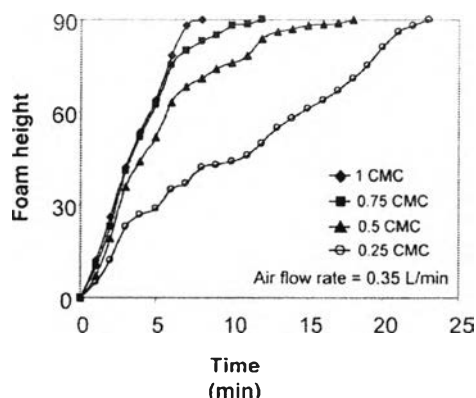
Figure 6. Foamability as a function of time.

Surfactant Recovery from Water Using a Multistage Foam Fractionator   1843
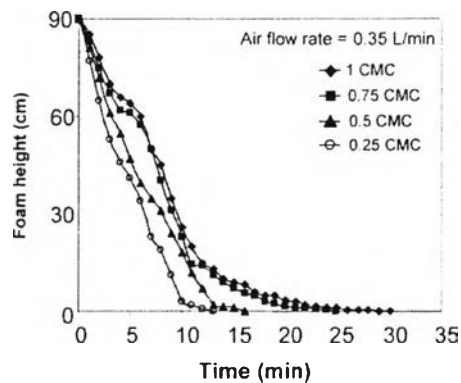
Figure 7.   Foam height as a function of time after air flow discontinued.

The enrichment ratio is higher and the foam is dryer (or lower foam wetness as shown in Table 1) at lower air flow rates because the higher residence time of bubbles in the rising foam permits drainage of water in the lamellae, leaving dry foam with a higher surfactant concentration. This is due to a substantial fraction
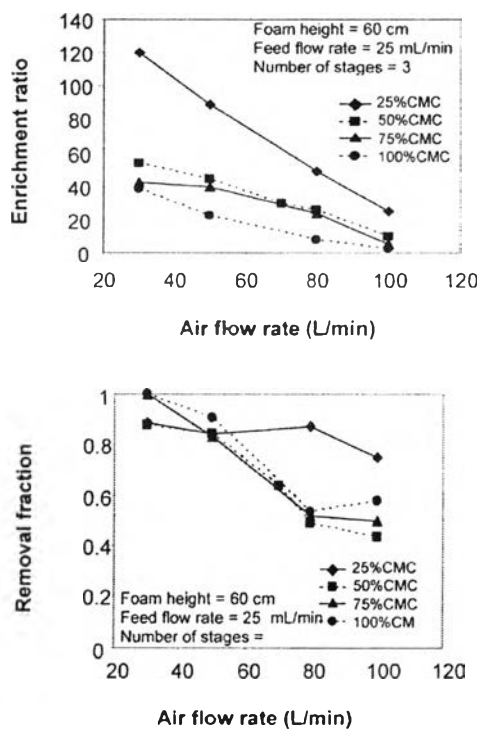

Figure 8.   The effect of air flow rate on enrichment ratio and removal fraction of surfactant at a foam height of 60 cm and different feed concentrations.

Table 1. Experimental results for all foam fractionation runs (using three stages)

Influent concentration (% of CMC)	Foam height (cm)	Foam wetness (g/L): Air flow rate (L/min)				Foam production rate (mL/min): Air flow rate (L/min)			
		30	50	80	100	30	50	80	100
25	30	3.51	2.77	35.55	29.58				
	60	0.72	1.43	2.55	4.01		3.4		
	90	a	a	a	3.59				
50	30	3.04	4.03	33.74	38.02		10.4		
	60	2.14	2.66	4.11	22.00	1.4	4.7	20.0	37.3
	90	a	2.48	3.37	19.45		1.2		
75	30	3.77	17.99	60.43	69.44				
	60	2.87	3.67	4.98	38.46		5.5		
	90	a	2.53	3.93	30.09				
100	30	3.90	26.46	67.77	66.90				
	60	2.89	4.63	30.31	58.76		6.0		
	90	a	4.21	26.66	40.44				

a—The froth could not reach overhead pipe.

of the surfactant in the foam being adsorbed at the air-water interface rather than in the lamellae liquid which drains off. An increase in air flow rate results in a higher volumetric rate of foam and a wetter foam, thus leading to a lower enrichment ratio of CPC. An increase in air flow rate tends to break the foam (visual observation through the glass plate at each column) as well as to produce wetter foam as shown in Table 1. The decrease in enrichment ratio with increasing air flow rate is expected, but the decrease in removal fraction is not. Possible explanations are that the air has such a short residence time in the liquid that less surfactant adsorbs on the bubble surface and ultimately, at the foam lamellae air/water interface; air bubble, and/or foam bubble sizes may be larger when air flow rates are higher, resulting in a reduced surfactant adsorption at the air/water surface and lower removal rates. Also re-entry of the adsorbed surfactant into the solution followed by bubble coalescence and breakage can explain the effect of air flow rate (9, 28). Table 2 also shows a lower CPC concentration profile on the top tray, in the foamate and in interstage tray liquid with higher air flow rate. This result is consistent with a turbulence effect causing a reduction in the enrichment ratio and higher foam wetness since swirling of liquid inside the column causes disruption of separation when the air flow rate is too high. The observed effect of air flow rate is in good agreement with other studies (5, 9).

Effect of Foam Height

As can be seen from Fig. 9 and Table 1, for any given feed CPC concentration, air and feed flow rate, the removal fraction and the enrichment ratio of CPC

Table 2. Interstage CPC concentration at feed flow rate of 50 mL/min, feed concentration of 50% of CMC (0.161 g/L)

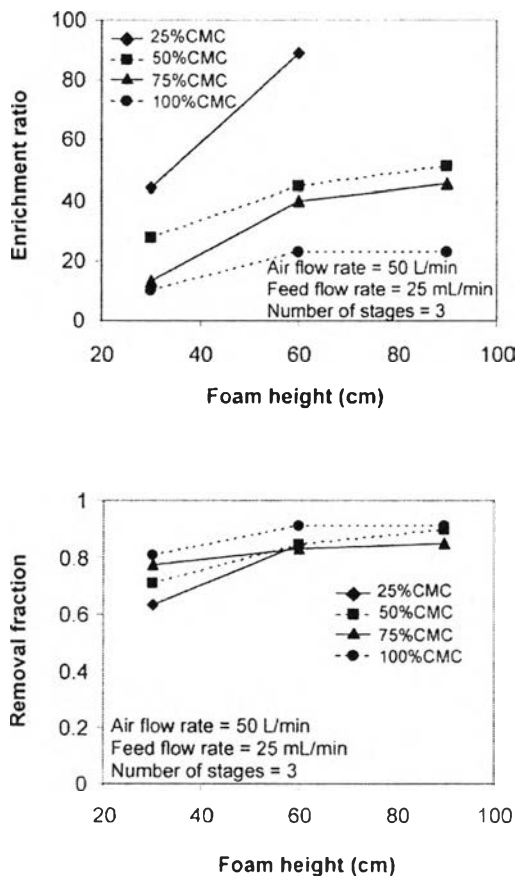|	CPC concentration (g/L): air flow rate (L/min)		
	30	50	100
Foam height (cm)			
90	20.09	12.58	1.97
60	8.63	7.19	1.66
30	6.76	4.43	1.12
Tray			
1st (top)	5.02	3.88	1.06
2nd	3.05	2.41	1.06
3rd	2.76	2.04	1.03
Last tray (bottom)	0.404	0.786	0.987
Drain	0.0168	0.0249	0.0991

Figure 9.   The effect of foam height on enrichment ratio and removal fraction of sur-
factant at an air flow rate of 50 L/min and different feed concentrations.

both increase with increasing foam height (of the top tray) with one exception
datum for removal fraction. The foam exiting from the 30-cm-high port
entrains more liquid content than that from the higher 60-cm port. An
increase in foam height leads to a longer foam residence time, which allows
more drainage of the liquid in the films. This accounts for the significantly
enhanced enrichment ratio observed for the foam collected from a greater
height. The data presented in Table 1 show the enrichment ratio at the
90 cm-port cannot be measured for some experimental conditions since the
system was operated below the minimum air flow rates for foam production
from the top of the column.

The drainage of foam results from competition between gravitational
forces and the capillary pressure in channels separating adjacent bubbles.
The drainage-capillary effects imply that the top of the foam becomes dry

while the bottom of the foam remains wet. A dry foam is composed of poly-hedral bubbles meeting at thin edges, while wet foams are composed of spherical bubbles which can sometimes move freely (29). In order to quantify the foam height effect, the foam wetness has been measured as shown in Table 1. This supports the enrichment ratio data indicating that the dryer foams correspond to a greater foam height and longer residence time for drainage to reduce the water content of the foam. The dilution of the adsorbed surfactant by foam lamellae liquid is lower as foam height increases, which in turn leads to higher enrichment ratio. It is not obvious why increased foam height leads to an increase in removal fraction.

Effect of Liquid Feed Flow Rate

The effect of the liquid feed flow rate on enrichment ratio and removal efficiency for CPC is shown in Fig. 10. For varying feed concentration less than 50% of CMC, an increase in the flow rate of the liquid feed results in an increase in the enrichment ratio, while the removal fraction increases and reaches approximately unity (quantitative removal) under these studied conditions. As a higher flow rate of liquid enters the column, the interfacial turbulence eddies swirling upward occur possibly causing internal reflux with subsequent increase in the enrichment ratio and surfactant recovery (30). Turbulence disrupts the stable bubbles, the total foam height decreases sharply, then the bubbles move up slowly or are carried down by drainage liquid. The top layer void fraction is higher because the large gas bubbles carry less liquid to the top which leads to enhanced enrichment (28). The increasing enrichment ratio with increasing liquid feed flow rate at the operating feed concentration below the CMC was considered as an unexpected result and is probably due to observed instabilities of films below the CMC as visually observed due to disrupting of bubbles. These improvements in performance with increasing liquid flow rate is limited by the minimum flow rate required to reach the flooding condition (Fig. 5). Interestingly, at higher feed concentrations close to the CMC, both enrich-ment ratio and removal fraction of CPC are almost constant with increasing feed flow rate. The explanation of the effect of feed concentration will be discussed next.

Effect of Feed Concentration

The effect of the influent CPC concentration at different feed flow rates is shown in Fig. 11. For any given feed flow rate, an increase in CPC concen-tration leads to a decrease in the enrichment ratio but does not affect the removal fraction significantly. An increasing CPC concentration results in
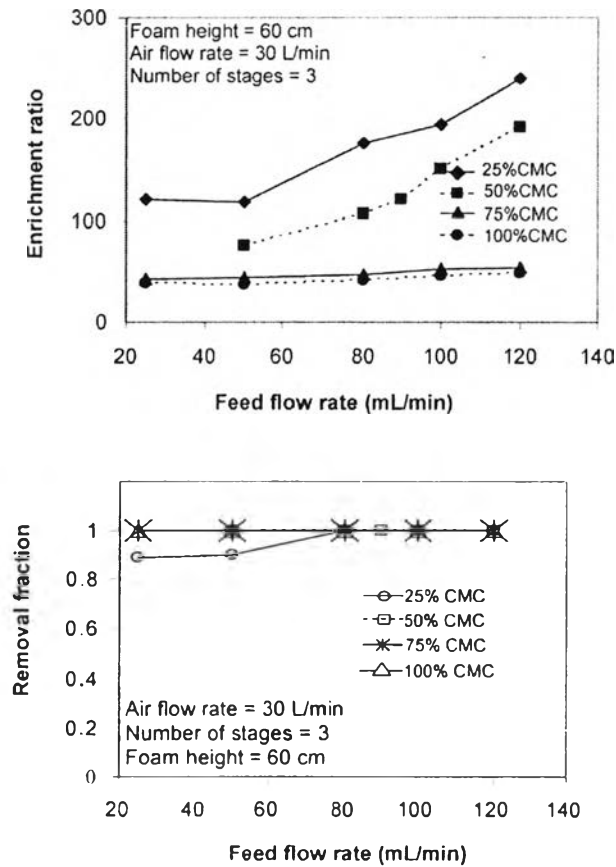
Figure 10. The effect of feed flow rate on enrichment ratio and removal fraction of surfactant at a foam height of 60 cm and different feed concentrations.

increased foamability and foam stability (Figs. 6 and 7) and increased wetness (Table 1). As CPC concentration increases, increasing wetness and foam stability (less drainage of water from the foam) explains the lower enrichment ratio and increasing foam production rate. The wetness of the foam increases with increasing surfactant concentration as shown in Table 1. For increasing feed inlet concentration, the volumetric foam production rate is found to increase (Table 1), resulting in a subtle change in the liquid overflow between stages inside the column. In previous studies, increasing feed inlet concentration caused volumetric foam production rate to increase (5, 31, 32). An important result here is that higher enrichment ratio in multistage foam fractionation occurs at lower surfactant concentrations, although this improvement would be limited by a minimum surfactant concentration for enough foaming to generate overhead froth.
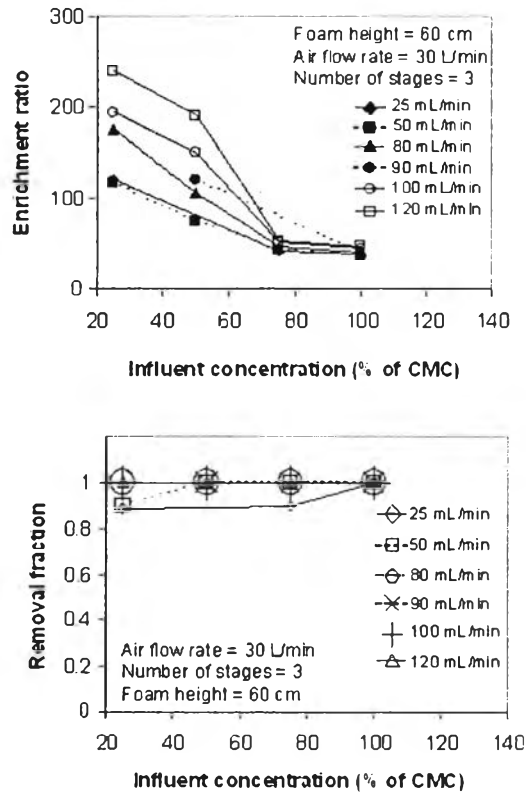
Figure 11.   The effect of surfactant influent concentration on enrichment ratio and removal fraction of surfactant at different feed flow rates.

Effect of Number of Stages

Figure 12 shows the effect of the number of stages on CPC separation efficiency. It was found that for any given feed flow rate and air flow rate, the total removal fraction and enrichment ratio both increased with increasing number of stages. This is understandable, since an increase in number of stages directly increases the surface area for gas-liquid contact as well as residence time leading to a greater surfactant mass transport from the aqueous phase to the foam phase; hence the advantage for reaching higher enrichment ratio and yielding greater removal fraction. The CPC concentration profile across the column as shown in Table 2 also confirms the effect of the number of stages. However, there is little improvement in the separation performance by adding a fourth stage as shown in Fig. 12.

In the attempt to further explain the effect of the number of stages, the experimental results are replotted to show the separation performance; see Fig. 13 as a function of number of stages at a constant residence time of 277 min. The effect
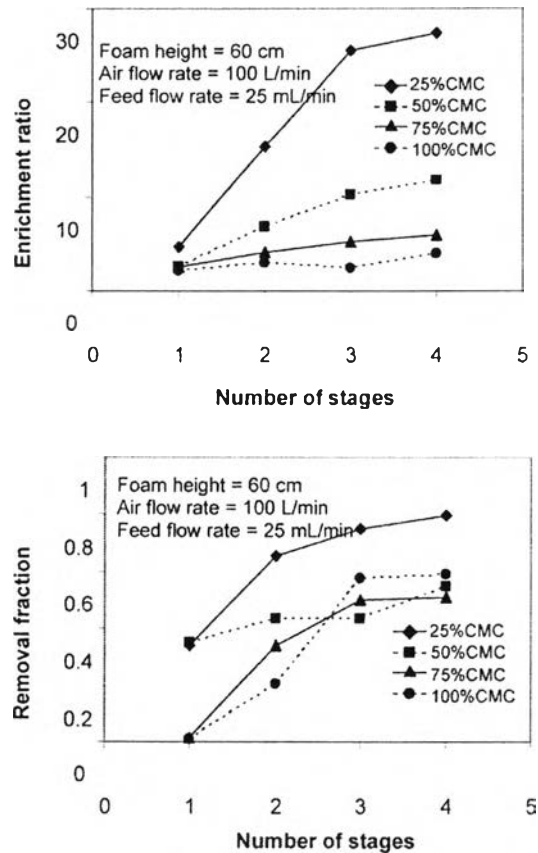
Figure 12.   The effect of number of stages on enrichment ratio and removal fraction of CPC at different feed concentrations.

of number of stages and of increasing residence time are separated here since residence time normally increases as the number of stages increases if flow rates are constant. At a constant residence time, both the enrichment ratio and the removal fraction increase with increasing number of stages, probably due to increasing air/water interfacial area with increasing number of stages. This result confirms that an increase in the number of stages results in improving both the enrichment ratio and the surfactant removal fraction since the surface area of gas-liquid contact is increased with increasing number of stages.

CONCLUSIONS

The highest value of enrichment ratio of approximately 240 and almost complete removal could be obtained for the inlet stream containing CPC at
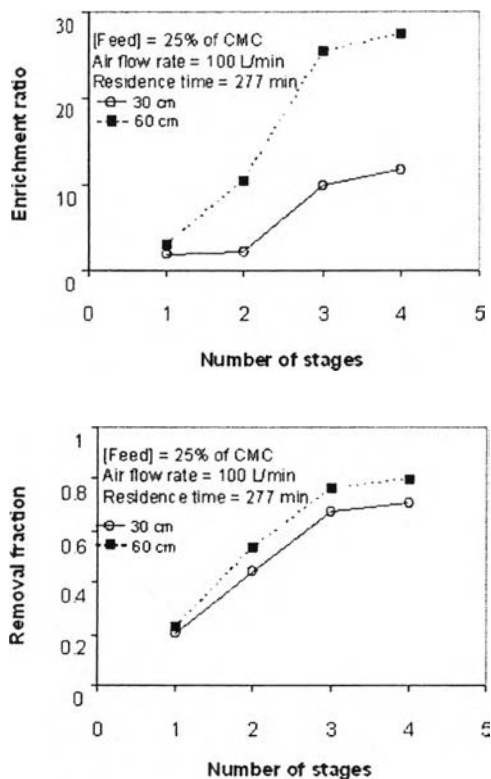
Figure 13. The effect of number of stages on enrichment ratio and removal fraction of CPC at different foam heights.

the concentration of 25% of CMC with a liquid residence time of 82 min. This observed enrichment ratio was much higher than that of the previous work using a single-stage unit where an enrichment ratio of 21.5 at a liquid residence time of 375 min was observed (5). The specific air velocity, foam height, and number of stages in operation of a multistage fractionation column affect the removal degree and the enrichment ratio. In this multistage operation, the performance of the fractionator was increased substantially with increasing number of stages up to three stages but a fourth stage improved performance only marginally. An increase in the air flow over the range studied decreases the enrichment ratio and decreases removal of CPC. A greater foam height produces a higher enrichment ratio and higher CPC removal. The enrichment ratio decreases while the surfactant removal increases as feed CPC concentration increases. A multistage unit is superior to a single-stage foam fractionator, in terms of a higher enrichment ratio and shorter residence time.

ACKNOWLEDGMENTS

REFERENCES

1. Scamehorn, J.F. and Harwell, J.H. (1989) *Surfactant-Based Separation Processes*; Marcel Dekker, Inc.: New York.
2. Scamehorn, J.F. and Harwell, J.H. (2000) *Surfactant-Based Separations Science and Technology*; American Chemical Society Symposium: Series 740; Washington, D.C..
3. Christopher, L.E., Kim, S.H., Bummer, P.M., and Jay, M. (2000) Scintigraphic measurement of liquid hold up in foam fractionation columns. *J. Colloid Interface Sci.*, 227 (1): 24–31.
4. Kumpabooth, K., Scamehorn, J.F., Osuwan, S., and Harwell, J.H. (1999) Surfactant recovery from water using foam fractionation: effect of temperature and added salt. *Separ. Sci. Technol.*, 34 (2): 157–172.
5. Tharapiwattananon, N., Scamehorn, J.H., Osuwan, S., Harwell, J.H., and Haller, K.J. (1996) Surfactant recovery from water using foam fractionation. *Separ. Sci. Technol.*, 31 (9): 1233–1258.
6. Narsimhan, G. and Ruckenstein, E. (1986) Hydrodynamics, enrichment, and collapse in foams. *Langmuir*, 2 (2): 230–238.
7. Yu, Q., Fei, W., Xia, L., and Wang, J. (1992) Evaluation of mass transfer coefficients from single-drop models in pulse sieve-plate extraction columns. In *Separation and Purification Technology*, 1st Ed.; Norman, N.L. and Joseph, M.C., eds.; Marcel Dekker, Inc.: New York, 213–218.
8. Xiao-Fang, W. and Hui-Zhou, L. (2000) Relationship between foaming properties and solution properties of protein/nonionic surfactant mixtures. *J. Surf. Deterg.*, 3 (4): 491–495.
9. Konduru, R. (1992) Operating a foam fractionating column in simple mode. *J. Chem. Eng. JPN*, 25 (5): 548–54.
10. Lemlich, R. (1972) *Adsorptive Bubble Separation Techniques*; Academic Press: New York, 152–157.
11. John, E.M. and Edward, C.R. (1996) Foam separation processes. In *Handbook of Separation Technique for Chemical Engineering*, 3rd Ed.; Schweitzer, P.A., ed.; Mc Graw Hill: New York, 2–173.
12. Christopher, L.E., Kim, S.H., Bummer, P.M., and Jay, M. (1997) Purification of proteins using foam fractionation. *Pharmaceut. Res.*, 14 (11): 1511–1515.

13. Khristov, K., Exerowa, D., and Minkov, G. (2002) Critical capillary pressure for destruction of single foam films and foam: effect of foam film size. *Colloid Surface A*, 210 (2-3): 159-166.

14. Morgan, G. and Weismann, U. (2003) Foam fractionation of rinsing waters containing surfactants. *Eng. Life Sci.*, 3 (1): 16-20.

15. Moussavi, M. (1992) Separation of cyanide ions by foam fractionation. *Separ. Sci. Technol.*, 27 (6): 783-792.

16. Uraizee, F. and Narsimhan, G. (1992) Effect of coalescence on the performance of a continuous foam fractionation column. *Separ. Sci. Technol.*, 27 (7): 937-53.

17. Wangrattanasopon, P., Scamehorn, J.F., Chavedej, S., Saiwan, C., and Harwell, J.H. (1996) Use of foam flotation to remove tert-butylphenol from water. *Separ. Sci. Technol.*, 31 (11): 1523-1540.

18. Morgan, G. and Weismann, U. (2001) Single and multistage foam fractionation of rinse water with alkly ethoxylate surfactants. *Separ. Sci. Technol.*, 36 (10): 2247-2263.

19. Beneventi, D., Carre, B., and Gandini, A. (2001) Role of surfactant structure on surface and foaming properties. *Colloid Surface A*, 189 (1-3): 65-73.

20. Hedreul, C. and Frens, G. (2001) Foam stability. *Colloid Surface A*, 186 (1-2): 73-82.

21. Lauridsen, J., Michael, T., and Michael, D. (2002) Shear-induced stress relaxation in a two-dimensional wet foam. *Phys. Rev. Lett.*, 89 (9): 098303/1-4.

22. Seader, J.D., Siirola, J.J., and Barnicki, S.D. (1999) Distillation. In *Perry's Chemical Engineers' Handbook*, 7th Ed.; Perry, R.H. and Green, D.W., eds.; Mc Graw-Hill Companies: New York, 1327-1334.

23. Aguayo, G. and Lemlich, R. (1974) Countercurrent foam fractionation at high rates of throughput by means of perforated plate columns. *Ind. Eng. Chem., Process Des. Dev.*, 13 (2): 153-9.

24. Wang, C.H., Hossain, M.M., and Davies, C.E. (2001) Performance of a continuous foam separation column as a function of process variables. *Bioproc. Biosyst. Eng.*, 24 (2): 73-81.

25. Wood, R.K. and Tran, T. (1966) Surface adsorption and the effect of column diameter in the continuous foam separation process. *Can. J. Chem. Eng.*, 44 (6): 322-326.

26. Darton, R.C., Supino, S., and Sweeting, K.J. (2004) Development of a multistaged foam fractionation column. *Chem. Eng. Proc.*, 43: 477-482.

27. Hidenori, T., Horikoshi, R., Yamagiwa, K., Takahashi, K., Yoshida, M., and Ohkawa, A. (2003) Effect of perforated plate on concentration of poly(vinyl alcohol) by foam fractionation with external reflux. *J. Chem. Eng. JPN*, 36 (9): 1107-1110.

28. Darton, R.C. and Sun, K.H. (1999) The effect of surfactant on foam and froth properties. *Chem. Eng. Res. Des.*, 77 (A6): 535-542.

29. Weaire, D. and Hutzler, S. (1999) *The Physics of Foams*, 1st Ed.; Clarendon Press: Oxford, 47-55.

30. Janin, L. and Jarru, M. (1986) Separation of a surface active solute by foam fractionation. *Int. Commun. Heat Mass*, 13 (4): 465-473.

31. Cho, Y.S. and Laskowski, J.S. (2002) Bubble coalescence and its effect on dynamic foam stability. *Can. J. Chem. Eng.*, 80 (2): 299-305.

32. Cho, Y.S. and Laskowski, J.S. (2002) Effect of flotation frothers on bubble size and foam stability. *Int. J. Miner. Process*, 64 (2): 69-80.

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Publications:

1. Boonyasuwat, S., Chavadej, S., Malakul, P., and Scamehorn, J. F. (2003) "Anionic and Cationic Surfactant Recovery from Water using Foam Fractionator", Chemical Engineering Journal. 93, 241-252.

2. Boonyasuwat, S., Chavadej, S., Malakul, P., and Scamehorn, J. F. (2005) "Surfactant Recovery from Water using a Multistage Foam Fractionator : Part I Effect of Air Flowrate, Foam Height, Feed Concentration and Number of Stages", Separation Science and Technology. 40, 1835-1853.

3. Boonyasuwat, S., Chavadej, S., Malakul, P., and Scamehorn, J. F. (2008) "Surfactant Recovery from Water using a Multistage Foam Fractionator : Effect of Surfactant Type", Separation and Purification Technology. (In Press)

Proceedings:

1. Boonyasuwat, S., Chavadej, S., Malakul, P., and Scamehorn, J. F. (2002) "Column Design of Surfactant Recovery from Wastewater" *Proceedings of the Chemical Engineering Conference,* Annual Meeting, Christchurch, New Zealand, October 2002.

2. Boonyasuwat, S., Chavadej, S., Malakul, P., and Scamehorn, J. F. (2002) "Wastetreatment by Foam Fractionation using Applied Distillation Apparatus" *Proceedings of Thailand International Chemical Engineer by King Monkut Institute of Technology*, November 2002.