

**RECOVERY OF MIXED SURFACTANTS FROM WATER
USING MULTI-STAGE FOAM FRACTIONATION: EFFECTS OF FEED
POSITION, REFLUX POSITION AND REFLUX RATIO**

Racharith Sripituk

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
Case Western Reserve University and Institut Français du Pétrole

2006

ISBN 974-9937-73-2

Thesis Title: Recovery of Mixed Surfactants from Water
Using Multi-Stage Foam Fractionation: Effects of
Feed Position, Reflux Position and Reflux ratio

By: Racharith Sripituk

Program: Petrochemical Technology

Thesis Advisors: Assoc.Prof. Sumaeth Chavadej
Prof. John F. Scamehorn
Asst. Prof. Pomthong Malakul

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

Nantaya Yanumet
..... College Director
(Assoc. Prof. Nantaya Yanumet)

Thesis Committee:

Sumaeth Chavadej
.....
(Assoc.Prof. Sumaeth Chavadej)

Pomthong Malakul
.....
(Asst. Prof. Pomthong Malakul)

John Scamehorn
.....
(Prof. John F. Scamehorn)

Pramoch Rangsunvigit
.....
(Assoc. Prof. Pramoch Rangsunvigit)

Thirasak Rirksomboon
.....
(Assoc. Prof. Thirasak Rirksomboon)

490386

ABSTRACT

4771020063: Petrochemical Technology Program

Racharith Sripituk: Recovery of Mixed Surfactants from Water Using Multi-Stage Foam Fractionation: Effects of Feed Position, Reflux Position and Reflux Ratio.

Thesis Advisors: Assoc. Prof. Sumaeth Chavadej, Prof. John F. Scamehorn, and Asst. Prof. Pomthong Malakul, 56 pp.

ISBN 974-9937-73-2

Keywords: Multi-stage foam fractionation/ Surfactant recovery/ Feed position/ Reflux position/ Reflux ratio

Surfactants are widely used in many industries, such as healthcare, food processing, and textile, as well as several surfactant-based separation processes, and the effluent streams of these processes usually contain surfactants that need to be removed and recovered for both environmental and economic reasons. In this study, a multi-stage foam fractionation column using bubble-cap trays was used to recover surfactants, and the effects of feed position, reflux position and reflux ratio on surfactant recovery were investigated for two single-surfactant systems and a mixed system of cetylpyridinium chloride (CPC), a cationic surfactant, and polyethylene glycol tert-octylphenyl ether (OPEO₁₀), a nonionic surfactant. For the two single-surfactant systems, both the surfactant recovery and the enrichment ratio were strongly affected by feed position. The surfactant recovery decreased with increasing reflux position and reflux ratio. In contrast, the effects of reflux position and reflux ratio were not significant on the enrichment ratio. The results of the mixed surfactant system showed that the recovery of CPC was lower than that of the pure CPC system. Interestingly, for the case of OPEO₁₀, it was higher than that of the pure OPEO₁₀ system due to the synergism effect.

บทคัดย่อ

ราชฤทธิ์ ศรีพิทักษ์: การนำสารลดแรงตึงผิวกลับมาใช้ใหม่โดยใช้ Multi-Stage Foam Fractionation Column โดยศึกษาอิทธิพลของตำแหน่งการป้อนสารละลาย ตำแหน่งการป้อนกลับ และอัตราส่วนการป้อนกลับ (Recovery of Mixed Surfactants from Water Using Multi-Stage Foam Fractionation: Effects of Feed Position, Reflux Position and Reflux Ratio) อ.ที่ปรึกษา: รศ.ดร. สุเมธ ชวเดช, ศ. จอห์น เอฟ สกemasอร์น และผศ. ดร. ปมทอง มาลากุล ณ อยุธยา 56 หน้า ISBN 974-9937-73-2

ปัจจุบันนี้ สารลดแรงตึงผิวถูกนำมาใช้ในอุตสาหกรรมต่างๆมากมาย เช่น อุตสาหกรรมการดูแลสุขภาพ อุตสาหกรรมอาหาร อุตสาหกรรมสิ่งทอ และโดยเฉพาะอย่างยิ่งกับกระบวนการแยกโดยใช้สารลดแรงตึงผิว ซึ่งทำให้มีการสูญเสียสารลดแรงตึงผิวจำนวนมากไปกับน้ำเสียที่ปล่อยทิ้งจากกระบวนการเหล่านั้น จึงมีความต้องการที่จะแยกสารลดแรงตึงผิวออกเพื่อนำกลับมาใช้ใหม่ด้วยเหตุผลด้านสิ่งแวดล้อมที่เข้มงวดขึ้นและมูลค่าของสารลดแรงตึงผิว ในงานวิจัยนี้ได้นำวิธีการทำให้เกิดฟองแบบลำดับส่วนมาใช้ในการนำสารลดแรงตึงผิวกลับมาใช้ใหม่ โดยศึกษาผลกระทบของตำแหน่งการป้อนสารละลาย ตำแหน่งการป้อนกลับ และอัตราส่วนการป้อนกลับ ต่อประสิทธิภาพของหอลำดับส่วนทั้งในระบบสารลดแรงตึงผิวแบบเดี่ยวและแบบผสม สารลดแรงตึงผิวที่เลือกใช้ในงานวิจัยนี้มี 2 ชนิด คือ ซีดิลฟิริดิเนียมคลอไรด์ (สารลดแรงตึงผิวชนิดประจุบวก) และ โพลีเอทิลีนไกลคอลเทอเทอเรียอ็อกทิลฟีนิลอีเทอร์ (สารลดแรงตึงผิวชนิดไม่มีประจุ) จากผลการทดลองพบว่าการเปลี่ยนแปลงตำแหน่งการป้อนสารละลายมีผลต่อความสามารถในการนำสารลดแรงตึงผิวกลับมาใช้และอัตราส่วนของสารลดแรงตึงผิวในโฟมเป็นอย่างมาก เมื่อเพิ่มตำแหน่งการป้อนกลับและอัตราส่วนการป้อนกลับส่งผลให้ความสามารถในการนำสารลดแรงตึงผิวกลับมาใช้ลดลง แต่ไม่มีผลต่ออัตราส่วนของสารลดแรงตึงผิวในโฟมมากนัก สำหรับระบบสารลดแรงตึงผิวแบบผสมพบว่า ความสามารถในการนำสารลดแรงตึงผิวชนิดประจุบวกกลับมาใช้ลดลงเมื่อเทียบกับระบบสารลดแรงตึงผิวชนิดประจุบวกแบบเดี่ยว ในทางตรงกันข้าม ในระบบสารลดแรงตึงผิวแบบผสมสามารถนำสารลดแรงตึงผิวชนิดไม่มีประจุกลับมาใช้ใหม่ได้ทั้งหมด

ACKNOWLEDGEMENTS

First of all I would like to sincerely thank Assoc. Prof. Sumaeth Chavadej, Asst. Prof. Pomthong Malakul, and Professor John F. Scamehorn served as my thesis advisors, for their patient guidance, understanding and constant encouragement throughout the course of this research. Their positive attitude contributed significantly to inspiring and maintaining my enthusiasm in the field. I will always be proud to have been their student. I would like to thank Assoc. Prof. Pramoch Rangsunvigit and Assoc. Prof. Thirasak Rirksomboon for their kind advice and for being the thesis committee. I also would like to thank all of my teachers at the Petroleum and Petrochemical College for their generous help.

The Research Unit of Applied Surfactants for Separation and Pollution Control supported by Rachadapisek Sompot Fund of Chulalongkorn University is greatly acknowledged for funding a research assistant to this project. This thesis work is partially funded by Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PTT Consortium).

Finally, I would like to take this opportunity to thank all of my graduate friends for their friendly help, creative suggestions and encouragement. I had a very good time working with them all. I am also greatly indebted to my parents and my family for their support, love and understanding.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	viii
List of Figures	x
 CHAPTER	
I INTRODUCTION	1
 II LITERATURE REVIEW	 2
2.1 Surfactants	2
2.1.1 Structure of Surfactants	2
2.1.2 Types of Surfactants	2
2.2 Foam	4
2.2.1 Foam Formation	4
2.2.2 Structure of Foam	5
2.2.3 Foam Stability	6
2.3 Foam Fractionation	9
2.3.1 Principle of Foam Fractionation	9
2.3.2 Applications of Foam Fractionation Process	11
 III EXPERIMENTAL	 14
3.1 Materials	14
3.2 Apparatus	14
3.3 Methodology	17
3.4 Data Analysis	18

CHAPTER	PAGE
IV RESULTS AND DISCUSSION	19
4.1 Steady-State Operation	19
4.2 Operating Limits	19
4.3 Foam characteristic of Single and Mixed-surfactant Systems	20
4.4 Apparent Diffusion Coefficient of Surfactants (D_{ap})	22
4.5 Multi-Stage Foam Fractionator Efficiencies of Single-surfactant Systems	24
4.5.1 Effect of Feed Position	24
4.5.2 Effect of Reflux Position	29
4.5.3 Effect of Reflux Ratio	33
4.6 Multi-Stage Foam Fractionator Efficiencies of Mixed-surfactant Systems	37
4.6.1 Effect of Feed Position	38
4.6.2 Effect of Reflux Position	40
4.6.3 Effect of Reflux Ratio	41
V CONCLUSIONS AND RECOMMENDATIONS	43
5.1 Conclusions	43
5.2 Recommendations	44
REFERENCES	46
APPENDIX	47
CURRICULUM VITAE	56

LIST OF TABLES

TABLE		PAGE
3.1	Chemical properties of the studied surfactants	14
3.2	Dimensions of the multi-stage foam fractionation column	16
3.3	Operating parameters	18
3.4	The apparent diffusion coefficient	24

LIST OF FIGURES

FIGURE	PAGE
2.1 Schematic of a surfactant molecule	4
2.2 Formation of foam	5
2.3 The structure of liquid foam	6
2.4 Schematic of foam	6
2.5 Stretch portion of foam lamella, illustrating mechanism of film elasticity	7
2.6 Marangoni Effect and Gibbs Film Elasticity	8
2.7 Liquid drainage in lamellae by curvature effect	9
2.8 Classification of bubble separation techniques	10
2.9 Principle of foam formation	11
2.10 Experimental configurations for foam separation	11
3.1 Schematic of multistage foam fractionation column	15
3.2 Schematic of tray (Top view)	16
4.1 Concentration profiles with respect to time under operational condition of [CPC] = 0.225 mM; feed tray number 5; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	19
4.2 Operational zone under operational condition [surfactant] = 0.225 mM; foam height = 60 cm and feed tray number 5	20
4.3 Foam ability of various surfactant systems operated at total surfactant concentration = 0.225 mM; air flow rate = 0.1 L/min and surfactant solution = 250 ml	21
4.4 Foam stability of various surfactant systems operated at total surfactant concentration = 0.225 mM; air flow rate = 0.1 L/min and surfactant solution = 250 ml	22
4.5 The dynamic surface tension of surfactants	23
4.6 $(\gamma_0 - \gamma_t)$ versus $t^{(1/2)}$	23

FIGURE	PAGE
4.7 Effect of Feed Position under operational condition of [CPC] = 0.225 mM; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	25
4.8 Effect of Feed Position under operational condition of [OPEO ₁₀] = 0.225 mM; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	26
4.9 Relations between foam production rate and enrichment ratio under operational condition of [CPC] = 0.225 mM; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	26
4.10 Relations between foam production rate and enrichment ratio under operational condition of [OPEO ₁₀] = 0.225 mM; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	27
4.11 The concentration profile of CPC when vary feed position under operational condition of [CPC] = 0.225 mM; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	27
4.12 The concentration profile of OPEO ₁₀ when vary feed position under operational condition of [OPEO ₁₀] = 0.225 mM; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	28
4.13 Comparison of the surfactant recovery between pure CPC and OPEO ₁₀ systems under operational condition of [surfactant] = 0.225 mM; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	28
4.14 Effect of reflux position under operational condition of [CPC] = 0.225 mM; feed position = tray number 3; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	29

FIGURE	PAGE
4.15 Effect of Reflux Position under operational condition of $[\text{OPEO}_{10}] = 0.225 \text{ mM}$; feed position = tray number 5; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	30
4.16 Relations between foam production rate and enrichment ratio under operational condition of $[\text{CPC}] = 0.225 \text{ mM}$; feed position = tray number 3; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	30
4.17 Relations between foam production rate and enrichment ratio under operational condition of $[\text{OPEO}_{10}] = 0.225 \text{ mM}$; feed position = tray number 5; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	31
4.18 The concentration profile of CPC when vary reflux position under operational condition of $[\text{CPC}] = 0.225 \text{ mM}$; feed position = tray number 3; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	31
4.19 The concentration profile of OPEO_{10} when vary reflux position under operational condition of $[\text{OPEO}_{10}] = 0.225 \text{ mM}$; feed position = tray number 5; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	32
4.20 Comparison of the surfactant recovery between pure CPC and OPEO_{10} system under operational condition of $[\text{surfactant}] = 0.225 \text{ mM}$; feed position of CPC = tray number 3; feed position of OPEO_{10} = tray number 5; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	32

FIGURE	PAGE
4.21 Effect of Reflux Ratio under operational condition of [CPC] = 0.225 mM; feed position = tray number 3; reflux position = tray number 1; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	33
4.22 Effect of Reflux Ratio under operational condition of [OPEO ₁₀] = 0.225 mM; feed position = tray number 5; reflux position = tray number 1; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	34
4.23 Relations between foam production rate and enrichment ratio under operational condition of [CPC] = 0.225 mM; Feed position = tray number 3; reflux position = tray number 1; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	34
4.24 Relations between foam production rate and enrichment ratio under operational condition of [OPEO ₁₀] = 0.225 mM; feed position = tray number 5; reflux position = tray number 1; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	35
4.25 The concentration profile of CPC when vary reflux position under operational condition of [CPC] = 0.225 mM; feed position = tray number 3; reflux position = tray number 1; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	35
4.26 The concentration profile of CPC when vary reflux position under operational condition of [OPEO ₁₀] = 0.225 mM; feed position = tray number 5; reflux position = tray number 1; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	36

FIGURE	PAGE
4.27 Comparison of the surfactant recovery between pure CPC and OPEO ₁₀ system under operational condition of [surfactant] = 0.225 mM; feed position of CPC = tray number 3; feed position of OPEO ₁₀ = tray number 5; reflux position = tray number 1; feed flow rate = 50 ml/min; air flow rate = 80 L/min and foam height = 60 cm	36
4.28 Effect of Feed Position on the %surfactant recovery of each surfactant of the mixed-surfactant system under operational condition of [total surfactant] = 0.225 mM; molar ratio of CPC to OPEO ₁₀ = 1:1	39
4.29 Effect of Feed Position on the enrichment ratio of each surfactant of the mixed-surfactant system under operational condition of [total surfactant] = 0.225 mM; molar ratio of CPC to OPEO ₁₀ = 1:1	39
4.29 Effect of Reflux Position on the %surfactant recovery of each surfactant of the mixed-surfactant system under operational condition of [total surfactant] = 0.225 mM; molar ratio of CPC to OPEO ₁₀ = 1:1; feed position = tray number 5	40
4.30 Effect of Reflux Position on the enrichment ratio of each surfactant of the mixed-surfactant system under operational condition of [total surfactant] = 0.225 mM; molar ratio of CPC to OPEO ₁₀ = 1:1; feed position = tray number 5	41
4.32 Effect of Reflux Ratio on the %surfactant recovery of each surfactant of the mixed-surfactant system under operational condition of [total surfactant] = 0.225 mM; molar ratio of CPC to OPEO ₁₀ = 1:1; feed position = tray number 5; reflux position = tray number 1	42

FIGURE

PAGE

- 4.33 Effect of Reflux Ratio on the enrichment ratio of each surfactant of the mixed-surfactant system under operational condition of [total surfactant] = 0.225 mM; molar ratio of CPC to OPEO₁₀ = 1:1; feed position = tray number 5; reflux position = tray number 1

42