MICROEMULSION BASED RESIDUAL OIL RECOVERY FOR SPENT BLEACHING EARTH FROM BIODIESEL PRODUCTION

Ratiprach Aiamthongkham

. 7

A Thesis Submitted in Partial Fulfillment 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

2015

0

-

I28368836

Microemulsion based Residual Oil Recovery for Spent
Bleaching Earth from Biodiesel Production
Ratiprach Aiamthongkham
Petrochemical Technology
Dr. Ampira Charoensaeng

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

..... College Dean (Asst. Prof. Pomthong Malakul)

Thesis Committee:

σ

.

(Dr. Ampira Charoensaeng)

(Asst. Prof. Apanee Luengnaruemitchai)

(Dr. Chaowalit Senanurakworakul)

ABSTRACT

5671029063: Petrochemical Technology

σ

Ratiprach Aiamthongkham: Microemulsion based Residual Oil Recovery for Spent Bleaching Earth from Biodiesel Production. Thesis Advisor: Dr. Ampira Charoensaeng 101 pp.

Keywords: Spent bleaching earth/ Residual oil/ Extraction/ Microemulsion

Spent bleaching earth (SBE), an industrial solid waste generated at bleaching process of vegetable oil refinery, usually recovers oil retained in SBE through solvent extraction which can lead to environmental impact and high cost of disposal. Consequently, this work investigated the use of microemulsion extraction technique to extract residual oil adsorbed on SBE. The most important criterion of this method is the ability of lowering interfacial tension (IFT) between oil and aqueous surfactant solution in order to liberate oil from SBE. The surfactant systems with different structure (anionic extended and nonionic ethoxylated surfactant) were selected to formulate middle phase microemulsion (Winsor type III) with crude palm oil. In the oil extraction, the predetermined optimum formulations were selected to study the effect of extraction parameters based on total oil extraction efficiency. In addition, the extracted oil qualities were evaluated. The result showed that $C_{12,13}$ -(PO)₄-SO₄Na and C_{12,13}-(PO)₈-SO₄Na produced an ultralow IFT (<0.1 mN/m) with crude palm oil whereas C_{12,14}-(EO)₃-OH and C_{12,14}-(EO)₉-OH were not observed due to limited temperature. The C_{12,13}-(PO)₈-SO₄Na system provided the highest of total oil extraction efficiency (25%) at the optimum surfactant concentration of 1wt.% with 2.5 wt.% NaCl at stirring 1000 rpm, using solid to liquid ratio (g/ml) of 2/15 and contact time 20 min. Microemulsion technology could not replaced a solvent technique due to the interactions between surfactant and waxy solid in vegetable oil is limited compared to that of vegetable oil in liquid form. However, the extracted oil obtained aqueous microemulsion based extraction had superior oil quality in terms of low free fatty acid.

บทค**ัดย่**อ

รติปรัชญ์ เอี่ยมทองคำ : การสกัดน้ำมันที่เหลืออยู่บนดินฟอกสีใช้แล้วจากกระบวนการ ผลิตน้ำมันดีเซลด้วยวิธี ใมโครอิมัลชัน (Microemulsion based Residual Oil Recovery for Spent Bleaching Earth from Biodiesel Production) อ. ที่ปรึกษา : ดร. อัมพิรา เจริญแสง 101 หน้า

ดินฟอกสีที่ผ่านกระบวนการฟอกสีในอุตสาหกรรมการกลั่นน้ำมันพืชกลายเป็นของเสีย ที่ส่งผลต่อสิ่งแวคล้อมและค่าใช้ง่ายในการกำงัค โคยทั่วไปน้ำมันที่เหลืออยู่บนผิวของคินฟอกสี ใช้แล้วจะถูกสกัคด้วยตัวทำละลาย ซึ่งเป็นสารระเหยง่ายมีความอันตรายต่อร่างกายและ สิ่งแวคล้อม ดังนั้นงานวิจัยนี้จึงพิจารณาการสกัคด้วยวิธีไมโครอิมัลชัน หลักการสำคัญของวิธีการ นี้คือการถคแรงตึงผิวระหว่างวัฏภาคน้ำและวัฏภาคน้ำมัน เป็นผลให้อนุภาคน้ำมันหลุดออกจากผิว ของคินฟอกสีใช้แล้ว สารลคแรงตึงผิวที่ใช้ในการศึกษานี้ประกอบด้วยสารลคแรงตึงผิวที่มี โครงสร้างแตกต่างกัน (สารลดแรงตึงผิวที่มีประจุลบและไม่มีประจุ) เพื่อศึกษาการเกิคสภาวะ ใมโครอิมัลชันประเภทที่สาม (Winsor type III) กับน้ำมันปาล์มคิบ หลังจากนั้นสูตรสารลดแรง ์ ตึงผิวที่เหมาะสมจะนำไปศึกษาตัวแปรที่มีผลต่อประสิทธิภาพในการสกัดน้ำมัน นอกจากนี้มีการ เปรียบเทียบคุณภาพของน้ำมันที่สกัดได้จากวิธีไมโครอิมัลชันและสกัดด้วยตัวทำละลาย ผลการศึกษาพบว่าสารลดแรงตึงผิว C12,13H25,27-(PO)4-SO4Na และ C12,13H25,27-(PO)8-SO4 Na สามารถลดแรงตึงผิวระหว่างสารละลายลดแรงตึงผิวและน้ำมันปาล์มดิบได้ต่ำกว่า 0.1 มิลลิ-นิวตันต่อเมตร ในขณะที่ C_{12,14}H_{25,29}-(EO)3-OH และ C_{12,14}H_{25,29}-(EO)9-OH ไม่สามารถลด แรงดึงผิวได้ด่ำ เนื่องจากข้อจำกัดของอุณหภูมิระบบ สารลดแรงดึงผิว C_{12,13}H_{25,27}-(PO)₈-SO₄Na มีประสิทธิภาพในการสกัดสูงที่สุด (ร้อยละ 25) โดยใช้ความเข้มข้นของสารลดแรงตึงผิว และเกลือ ร้อยละ 1 และ 2.5 โดยน้ำหนัก ตามลำดับ ด้วยแรงหมุน 1,000 รอบต่อนาที ใช้อัตรา ้ส่วนของน้ำหนักดินฟอกสีใช้แล้วต่อปริมาตรของสารลดแรงตึงผิว (2 ต่อ 15) และเวลาในการสกัด 20 นาที นอกจากนี้การสกัดด้วยวิธีไมโครอิมัลชันไม่สามารถทดแทนการสกัดด้วยตัวทำละลายได้ แต่อย่างไรก็ตามคุณภาพของน้ำมันที่สกัดได้จากวิธีไมโครอิมัลชันดีกว่าน้ำมันที่สกัดได้จากด้วทำ ละลายในแง่ของกรดใขมันอิสระมีปริมาณต่ำกว่า

D

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my appreciation for those who have been significantly influential and responsible for my achievement in order to complete this thesis.

This research work could not be completed without the assistance and supports of following individuals and organizations.

Firstly, I would like to express my gratitude to my advisor, Dr. Ampira Charoensaeng who had always cared and paid attention to my research work since the beginning, giving valuable suggestions, attentive encouragement, beneficial recommendations and all the helpful supports in my research work.

Secondly, I also would like to thank to the thesis committees, Asst. Prof. Apanee Luengnaruemitchai and Dr. Chaowalit Senanurakworakul for their important suggestions and recommendations in my research work.

Special appreciation is given to Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University for helpful equipment supports and all useful suggestions.

Unforgettably, appreciation is forward to all staff members at The Petroleum and Petrochemical College who have provided helpful assistance and many useful technical supports.

Finally, I am grateful for the partial scholarship and partial funding of the thesis work provided by The Petroleum and Petrochemical College. This research was partially supported by The Ratchadapisek Sompoch Endowment Fund (2013), Chulalongkorn University (CU-56-900-FC) and Thailand Research Fund (IRG5780012).

TABLE OF CONTENTS

	Title P	age	i
	Abstra	ct (in English)	iii
	Abstra	ct (in Thai)	iv
	Ackno	wledgements	v
	Table	of Contents	vi
	List of	Tables	ix
	List of	Figures	xii
CHA	PTER		
	Ι	INTRODUCTION	1
	II	THEORETICAL BACKGROUND AND	
		LITERATURE REVIEW	3
		2.1 Palm Oil	3
		2.2 Spent Bleaching Earth (SBE)	4
		2.2.1 Structure of Bleaching Earth	4
		2.2.2 Application of Bleaching Earth in Vegetable Oil	
		Refining Process	5
		2.2.3 Regeneration and Utilization of Spent Bleaching	5
		2.2.4 Oil Extraction from SBE	7
		2.3 Surfactant	10
		2.3.1 Types of Surfactants	11
		2.3.2 Extended Surfactant	12
		2.4 Microemulsions	14
		2.4.1 Types of Microemulsions	14
		2.4.2 Transformation of Microemulsions Phase	15
		2.4.3 Application of Microemulsion	17
		2.5 Research Motivation	21

PAGE

Ø

CHAPTER

....

PAGE

σ

III	EXPERIMENTAL	22
	3.1 Materials	22
	3.1.1 Surfactants	22
	3.1.2 Oil	23
	3.1.3 Spent Bleaching Earth (SBE)	23
	3.2 Equipments	23
	3.3 Chemicals and Solvents	23
	3.4 Experimental Procedures	25
	3.4.1 Microemulsion Formation	25
	3.4.2 Oil Extraction	26
	3.4.3 Quality of Extracted Oil and Residual of SBE	29
IV	RESULTS AND DISCUSSION	32
	4.1 Microemulsion Formation with Crude Palm Oil	32
	4.1.1 Correlation between Surfactant Structure and	
	their Properties	32
	4.1.2 Microemulsion Phase Behaviour	38
	4.1.3 Interfacial Tension Measurement	45
	4.2 Oil Extraction	51
	4.2.1 Effect of Surfactant Structure	52
	4.2.2 Effect of Salt Concentration	56
	4.2.3 Effect of Surfactant Concentration	57
	4.2.4 Effect of Contact Time	58
	4.2.5 Effect of Solid to Liquid Ratio	59
	4.3 Scale-up of the Microemulsion Based Extraction	61
	4.4 Oil Quality	63
	4.4.1 Color and β -carotene	64
	4.4.2 Free Fatty Acid (FFA)	65
	4.4.3 Fatty Acid Composition	65

•

CHAPTER		PAGE
	4.5 Residual Spent Bleaching Earth	67
	4.5.1 Residual Spent Bleaching Earth Appearance	67
	4.5.2 Microstructure of Spent Bleaching Earth	68
	4.5.3 Functional Groups Analysis	70
V	CONCLUSIONS AND RECOMMENDATIONS	72
	5.1 Conclusions	72
	5.2 Recommendations	73
	5.2.1 Addition of Co-surfactant	73
	5.2.2 Temperature in Extraction	73
	5.2.3 Analysis of Surfactant Content in Extracted Oil	73
	REFERENCES	74
	APPENDICES	74
	Appendix A Experimental Data for Microemulsion Formation	74
	Appendix B Experimental Data for Oil Extraction	85
	Appendix C Experimental Data for Extracted Oil Quality	91
	CURRICULUM VITAE	97

σ

LIST OF TABLES

TABL	E	PAGE
2.1	Fatty acids composition of various types palm oil	3
3.1	Properties and characterization of selected surfactant	22
4.1	Hydrophilic-lipophilic balance (HLB), critical micelle	
	concentration (CMC), surface excess concentration (Γ),	
	and area per molecule	33
4.2	CMC, area per molecule and minimum IFT at optimum salt	
	for anionic surfactant and without salt for non-ionic	
	surfactant	50
4.3	Comparison of extracted oil characteristics between hexane	
	and microemulsion based extraction	63
4.4	Fatty acids composition of palm oil and its fractions	66
A1	Group contributions and group number	74
A2	Surface tension of C _{12,14} H _{25,29} –(EO) ₃ –OH solution at	
	25 ± 2 °C	75
A3	Surface tension of C _{12,14} H _{25,29} –(EO) ₉ –OH solution at	
	25 ± 2 °C	76
A4	Surface tension of C _{12,13} H _{25,27} –(PO) ₄ –SO ₄ Na solution at	
	25 ± 2 °C	77
A5	Surface tension of C _{12,13} H _{25,27} –(PO) ₄ –SO ₈ Na solution at	
	25 ± 2 °C	78
A6	Surface tension of $C_{12,13}H_{25,27}$ -(PO) ₄ -SO ₄ Na solution with	
	5 wt% NaCl at 25 ± 2 °C	79
A7	Surface tension of $C_{12,13}H_{25,27}$ –(PO) ₈ –SO ₄ Na solution with	
	2.5 wt% NaCl at 25 ± 2 °C	80
A8	Surface excess concentration (Γ) and area per molecule	
	(A _{min})	81

0

•

σ

A9	IFT value of 0.5wt% $C_{12,13}H_{25,27}$ -(PO) ₄ -SO ₄ Na with salinity	
	scan	82
A10	IFT value of 0.5wt% $C_{12,13}H_{25,27}$ -(PO) ₈ -SO ₄ Na with salinity	
	scan	82
A11	IFT value of C _{12,14} H _{25,29} –(EO) ₃ –OH system	83
A12	IFT value of C _{12,14} H _{25,29} –(EO) ₉ –OH system	83
A13	IFT value of C _{12,13} H _{25,27} -(PO) ₄ -SO ₄ Na system	84
A14	IFT value of C _{12,13} H _{25,27} -(PO) ₈ -SO ₄ Na system	84
B1	% oil content using hexane extraction method	85
B2	Extraction efficiency using 0.8% surfactant system, stirring	
	1000 rpm, contact time 20 min and solid to liquid ratio of	
	1/10	86
B3	Extraction efficiency using 0.5% C _{12,13} H _{25,27} -(PO) ₈ -SO ₄ Na,	
	stirring 1000 rpm, contact time 20 min and solid to liquid	
	ratio of 1/10	87
B4	Extraction efficiency using $C_{12,13}H_{25,27}$ -(PO) ₈ -SO ₄ Na with	
	2.5 wt% NaCl, stirring 1000 rpm, contact time 20 min and	
	solid to liquid ratio of 1/10	88
B5	Extraction efficiency using 1 wt% C _{12,13} H _{25,27} -(PO) ₈ -	
	SO ₄ Na with 2.5 wt% NaCl, stirring 1000 rpm and solid to	
	liquid ratio of 1/10	89
B6	Extraction efficiency using 1 wt% C _{12,13} H _{25,27} -(PO) ₈ -	
	SO ₄ Na with 2.5 wt% NaCl, stirring 1000 rpm and contact	
	time 20 min	90
C1	β -carotene in crude palm oil and extracted oil obtained from	
	microemulsion based extraction and hexane extraction	91
C2	%FFA in crude palm oil and extracted oil obtained from	
	microemulsion based extraction and hexane extraction	92

TABL	LE	0	PAGE
C3	Triglyceride calibration curve		93
C4	Total triglyceride in fraction of oil	à.*	94

0

-

....

σ

.

LIST OF FIGURES

FIGU	RE	PAGE
2.1	Montmorillonite with (a) structure view and (b) microscopic	
	view.	5
2.2	Transesterification of triglyceride with alcohol.	7
2.3	Schematic diagram of a surfactant molecule.	10
2.4	Schemetric representation of (a) normal and (b) reverse	
	micelle.	11
2.5	Types of surfactant	12
2.6	Structure of extended surfactant.	13
2.7	Winsor type of phase equilibrium.	15
2.8	Winsor phase diagram, where O is an excess oil phase; W is	
	an excess water phase; M is middle phase.	16
2.9	IFT as a function of surfactant concentration.	17
2.10	Oily soil removal from substrate (a) roll up and (b) snap-off	
	mechanism.	18
3.1	Flow chart of surfactant selection for oil extraction.	24
o 3.2	Flow chart of residual oil extraction in SBE.	25
3.3	Experimental procedure of phase transition.	26
3.4	Diagram of microemulsion based extraction.	28
4.1	Schematic of polyethylene oxide (EO) and polypropylene	
	oxide (PO) structure inserted between hydrophilic and	
	hydrophobic part.	34
4.2	Critical micelle concentration of anionic extended and non-	
	ionic surfactant.	35
4.3	Critical micelle concentration of anionic extended surfactant	
	with and without salt at 25 ± 2 °C.	36
4.4	Schematic representation of equilibriums.	37

FIGURE

~

4.5	Relation between surface tension and C _{12,14} H _{25,29} -(EO) ₃ -	
	OH concentration (log).	37
4.6	Microemulsion phase behavior of C _{12,13} H _{25,27} –(PO) ₄ –SO ₄ Na	
	systems as a function of salt concentration (wt%) at	
	30 ± 2 °C.	39
4.7	Microemulsion phase behavior of C _{12,13} H _{25,27} -(PO) ₈ -SO ₄ Na	
	systems as a function of salt concentration (wt%) at	
	$30 \pm 2 ^{\circ}\text{C}.$	39
4.8	Laser light through (a) distillated water (b) crude palm oil.	40
4.9	Fish diagram.	41
4.10	Microemulsion phase behavior of C _{12,13} H _{25,27} -(PO) ₄ -SO ₄ Na	
	systems as a function of surfactant concentration (wt%) at	
	$30 \pm 2 ^{\circ}\text{C}.$	42
4.11	Microemulsion phase behavior of C _{12,13} H _{25,27} -(PO) ₈ -SO ₄ Na	
	systems as a function of surfactant concentration (wt%) at	
	30 ± 2 ° C.	42
4.12	Laser light beam through (a) oil phase (b) yellow	
	transparent phase (c) bottom phase of 0.8% of $C_{12,13}H_{25,27}$ -	
	(PO) ₄ -SO ₄ Na system.	43
4.13	Microemulsion phase behavior of C _{12,14} H _{25,29} -(EO) ₃ -OH	
	systems as a function of surfactant concentration (wt%) at	
	$30 \pm 2 ^{\circ}\mathrm{C}.$	44
4.14	Microemulsion phase behavior of C12,14H25,29-(EO)9-OH	
	systems as a function of surfactant concentration (wt%) at	
	$30 \pm 2 \ ^{\circ}C.$	44
4.15	Dynamic IFT versus salt concentration at anionic extended	
	surfactant concentration of 0.5 wt% at 25 ± 2 °C.	46

FIGUI	RE	PAGE
4.16	Dynamic IFT versus surfactant concentration at optimum	
	salinity of 5 and 2.5 wt% for $C_{12,13}H_{25,27}$ -(PO) ₄ -SO ₄ Na and	
	C _{12,13} H _{25,27} -(PO) ₈ -SO ₄ Na systems, respectively at	
	$25 \pm 2 \ ^{\circ}C.$	47
4.17	Dynamic IFT versus surfactant concentration of $C_{12,14}H_{25,29}$	
	-(EO)3-OH and C12,14H25,29-(EO)9-OH systems at	
	$25 \pm 2 \ ^{\circ}C.$	48
4.18	Dynamic IFT versus anionic extended and non-ionic	
	surfactant concentration at 25 ± 2 °C.	49
4.19	Dynamic IFT as a function of time of $C_{12,14}$ -(EO) ₉ -OH	
	system with crude palm oil at 25 ± 2 °C.	51
4.20	Extraction efficiency versus 1 wt% C _{12,13} H _{25,27} -(PO) ₄ -	
	SO ₄ Na (2.5 wt%) and 1 wt% $C_{12,13}H_{25,27}$ -(PO) ₈ -SO ₄ Na	
	(5wt%) with 1000 rpm for 20 min using solid to liquid ratio	
	1/10.	53
4.21	Extraction efficiency versus 1 wt% of C _{12,14} H _{25,29} -(EO) ₃ -	
	OH and $C_{12,14}H_{25,29}$ -(EO) ₉ -OH with 1000 rpm for 20 min	2
	using solid to liquid ratio 1/10.	54
4.22	Total oil extraction efficiency versus 1 wt% of anionic	
	extended and nonionic surfactant with 1000 rpm for 20 min	
	using solid to liquid ratio 1/10.	55
4.23	Extraction efficiency versus 0.5 wt% C _{12,13} H _{25,27} -(PO) ₈ -	
	SO ₄ Na with 1000 rpm for 20 min using solid to liquid ratio	
	1/10.	56
4.24	Total oil extraction efficiency versus 2.5 wt% NaCl for	
	$C_{12,13}H_{25,27}$ -(PO) ₈ -SO ₄ Na system with 1000 rpm for 20 min	
	using solid to liquid ratio 1/1.	57

σ

- -

FIGURE

 \sim

4.25	Total oil extraction efficiency versus 2.5 wt% NaCl for	
*	1 wt% C _{12,13} H _{25,27} -(PO) ₈ -SO ₄ Na*system with 1000 rpm for	
	20 min using solid to liquid ratio 1/10.	58
4.26	Total oil extraction efficiency versus 2.5 wt% NaCl for	
	1 wt% C _{12,13} H _{25,27} -(PO) ₈ -SO ₄ Na system with 1000 rpm for	
	20 min.	59
4.27	Extracted oil obtained from (a) hexane extraction (b)	
	microemulsion based extraction.	60
4.28	Oil mass balance of microemulsion based extraction.	61
4.29	Triglycerides mass balance of microemulsion based	
	extraction.	62
4.30	Appearance of crude palm oil and extracted oil from hexane	
	and microemulsion based extraction.	64
4.31	appearance of SBE (a), residual SBE obtained	
	microemulsion based extraction (b) and residual SBE	
	obtained hexane extraction (c).	68
4.32	SEM images of SBE (a), residual SBE obtained	
	microemulsion based extraction (b) and residual SBE	
	obtained hexane extraction (c).	69
4.33	FTIR spectrum of extracted oil.	70
4.34	FTIR spectrum of SBE and residual SBE from	
	microemulsion based extraction and hexane extraction.	71
A1	CMC value of $C_{12,14}H_{25,29}$ –(EO) ₃ –OH solution at 25 ± 2 °C.	75
A2	CMC value of $C_{12,14}H_{25,29}$ –(EO) ₉ –OH solution at 25 ± 2 °C.	76
A3	CMC value of C _{12,13} H _{25,27} -(PO) ₄ -SO ₄ Na solution at	
	25 ± 2 °C.	77
A4	CMC value of C _{12,13} H _{25,27} -(PO) ₈ -SO ₄ Na solution at	
	$25 \pm 2 ^{\circ}\text{C}.$	78

xv

FIGURE

-

PAGE

.

A5	CMC value of $C_{12,13}H_{25,27}$ -(PO) ₄ -SO ₄ Na solution with	
	5 wt% NaCl at 25 ± 2 °C.	79
A6	CMC value of $C_{12,13}H_{25,27}$ –(PO) ₈ –SO ₄ Na solution with	
	2.5 wt% NaCl at 25 ± 2 °C.	80
Cl	Calibration curve of triglyceride (retention time 8-28) from	
	extracted oil obtained hexane extraction.	91
C2	Fatty acid compositions of extracted oil from hexane	
	extraction.	95
C3	Fatty acid compositions of extracted oil from	
	microemulsion based extraction.	96