# FORMATION OF VEGETABLE OIL BASED MICROEMULSION BIOFUEL WITH ETHANOL/BUTANOL IN PALM OIL/DIESEL BLENDS

Waritta Apichatyothin

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

Thesis Title: Formation of Vegetable Oil based Microemulsion Biofuel

with Ethanol/Butanol in Palm Oil/Diesel Blends

By: Waritta Apichatyothin

Program: Petrochemical Technology

Thesis Advisors: Dr. Ampira Charoensaeng

Prof. David A. Sabatini

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:

(Dr. Ampira Charoensaeng)

(Prof. David A. Sabatini)

(Assoc. Prof. Pramoch Rangsunvigit)

amoil /

(Dr. Chodchanok Attaphong)

#### **ABSTRACT**

5671036063:

Petrochemical Technology

Waritta Apichatyothin: Formation of Vegetable Oil based

Microemulsion Biofuel with Ethanol/Butanol in Palm Oil/Diesel

Blends.

Thesis Advisors: Dr. Ampira Charoensaeng, and Prof. David A.

Sabatini 78 pp.

Keywords:

Microemulsion biofuel/ Viscosity reducer/ Pseudo ternary phase

diagram

Vegetable oil is an option for renewable fuels production to replace the diesel oils. Because vegetable oils have higher viscosity than diesel oils, the usability of neat vegetable oils can lead to engine stability problems such as poor atomization of the fuel. However, vegetable oil viscosity can be reduced by blending with diesel fuel in thermodynamically stable mixtures using microemulsion formulation. This work focused on the formation of microemulsion biofuels consisting of plam oil/diesel and refined bleached deodorized palm oil (RBDPO)/diesel blends as an oil phase with ethanol and butanol blend as a viscosity reducer. Methyl oleate (MO) and palm oil methyl ester (POME) were used as a surfactant and 1-octanol was used as a cosurfactant at 1:8 surfactant:cosurfactant molar ratio. This work studied the effects of surfactant structure, ethanol/butanol blending ratios, palm oil/diesel blending ratios on phase behaviour, kinematic viscosity, microemulsion droplet size and fuel properties for microemulsion fuel formation and compared their fuel properties to regular biodiesel (B100) and diesel (No.2). The result showed that the phase behaviors of different surfactant systems had similar trend of the miscibility curve. The microemulsion biofuels containing butanol in the mixture showed a remarkable result on phase behavior. Based on our findings, the blending ratios of ethanol/butanol is a major parameter for optimizing the viscosity and other fuel properties of microemulsion biofuels.

# บทคัดย่อ

วริษฐา อภิชาติโยธิน : การผลิตเชื้อเพลิงชีวภาพจากน้ำมันพืชด้วยวิธีการไมโครอิมัลชัน โดยใช้เอทานอลและบิวทานอลในของผสมระหว่างน้ำมันปาล์มและน้ำมันดีเซล (Formation of Vegetable Oil Based Microemulsion Biofuel with Ethanol/Butanol in Palm Oil/Diesel Blends) อ. ที่ปรึกษา : ดร. อัมพิรา เจริญแสง และ Prof. David A. Sabatini 78 หน้า

น้ำมันพืชเป็นทางเลือกสำหรับการผลิตพลังงานหมุนเวียนเพื่อทดแทนน้ำมันดีเซล เนื่องจากน้ำมันพืชมีความหนืดสูงกว่าน้ำมันดีเซล การนำน้ำมันพืชมาใช้ทดแทนน้ำมันดีเซลจะ ก่อให้เกิดปัญหาค้านความเสถียรของเครื่องยนต์คีเซล เช่น ประสิทธิภาพของการกลายเป็นอะตอม ของเชื้อเพลิงจะต่ำ ความหนืดของน้ำมันพืชถูกทำให้ลดลงได้โดยการนำไปผสมกับน้ำมันดีเซลให้ เกิดเป็นของผสมที่มีความเสถียรทางอุณหพลศาสตร์ค้วยวิธีการไมโครอิมัลชั้น งานวิจัยนี้มีมุ่ง หมายเพื่อผลิดเชื้อเพลิงชีวภาพด้วยวิธี ไมโครอิมัลชันซึ่งประกอบไปด้วยน้ำมันปาล์มผสมกับน้ำมัน ดีเซล และน้ำมันปาล์มยังไม่แยกไขผสมกับน้ำมันดีเซลในส่วนของวัฏภาคน้ำมัน รวมกับเอทานอล และบิวทานอลที่นำมาใช้ในส่วนของสารลดความหนืด เมทิลโอลิเอตและกรดไขมันของเมทิล-เอสเตอร์นำมาใช้ในส่วนของสารลคแรงตึงผิวและสารลดแรงตึงผิวร่วมออกทานอลในอัตราส่วน 1:8โดยโมล งานวิจัยนี้ศึกษาผลของโครงสร้างของสารลดแรงตึงผิว อัตราส่วนผสมระหว่างเอทา-นอลและบิวทานอล อัตราส่วนระหว่างน้ำมันปาล์มและน้ำมันดีเชล และการใช้น้ำมันปาล์มยังไม่ แยกไขผสม อันส่งผลกระทบต่อพฤติกรรมวัฏภาค ความหนืด ขนาดของอนุภาคไมโครอิมัลชั้น และคุณสมบัติต่างๆของเชื้อเพลิงชีวภาพเปรียบเทียบตามมาตรฐานของเชื้อเพลิงดีเซลและ ไบ โอ-ดีเซล จากการทคลองพบว่าสารลดแรงตึงผิวทั้งสองชนิดให้ผลของพฤติกรรมวัฏภาคที่มีทิศทางไป ในทางเคียวกันโดยเส้นขอบเขตระหว่างการผสมให้เป็นเนื้อเคียวกัน เชื้อเพลิงชีวภาพที่มีการผสม บิวทานอลในองค์ประกอบให้ผลที่น่าสนใจในด้านพฤติกรรมวัฏภาค จากผลการศึกษาพบว่า อัตราส่วนการผสมของเอทานอลและบิวทานอลคือปัจจัยหลักสำหรับความเหมาะสมที่สุดของ กวามหนืดและคุณสมบัติอื่นๆของเชื้อเพลิงชีวภาพ

#### **ACKNOWLEDGEMENTS**

The author is grateful thanks for the scholarship and funding of the thesis work provided by the Petroleum and Petrochemical College; and the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Thailand; and the new researcher from the Thailand Research Fund (TRG 5780163). In addition, I extend my gratitude to thank Werasuwan Co., Ltd., for providing palm oil methyl ester (POME).

I would like to express my sincere appreciation to my advisors, Dr. Ampira Charcensaeng and Prof. David A. Sabatini for their invaluable guidance, help, encouragement and support provided throughout this research. Additionally, I would like to thank members of my committee, Assoc. Prof. Pramoch Rangsunvigit and Dr. Chodchanok Attaphong. I also extend my heartfelt and sincere thanks to Assoc. Prof. Sutha Khaodhiar, Ramnaree Netvichien, and Noulkamol Arpornpong, for suggestion, valuable comment and Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University for additional laboratory testing and equipment supports for this study. I also would like to thank the officers and my friends at The Petroleum and Petrochemical College, especially Mr. Sachart Manaphati. Finally, I thanks my family for their love and encouragement. This thesis would not have been completed without all the supports that I have always received from them.

## TABLE OF CONTENTS

			PAGE
	Title E	Page	i
	Abstr	act (in English)	iii
	Title Page Abstract (in English) Abstract (in Thai) Acknowledgements Table of Contents List of Tables List of Figures  HAPTER I INTRODUCTION  II THEORETICAL BACKGROUND AND LITERATURE REVIEW 2.1 Vegetable Oils 2.1.1 Palm Oil 2.1.2 Refined Bleached Deodorized Palm Oil (RBDPO) 2.2 Technologies of Reducing Vegetable Oil's Viscosity 2.2.1 Vegetable Oil based Microemulsification 2.3 Alcohol Blended 2.4 Surfactants and Cosurfactants 2.4.1 Alcohol Ethoxylates Surfactant 2.4.2 Methyl Oleate with Cosurfactants 2.4.3 Fatty Acid Methyl Ester (FAME) or Biodiesel 2.5 Pseudo-Ternary Phase Diagram 2.6 Fuel Properties 2.6.1 Kinematic Viscosity 2.6.2 Cloud Point	iv	
		v	
	Table	of Contents	vi
	List of	f Tables	ix
	List of	f Figures	x
CH.	APTER		
	I	INTRODUCTION	1
	**	THE OPERAGA A DA GREEN CAND AND A MEDICAL TRANSPORT	
	11		
			4
			4
		·	4
		2.1.2 Refined Bleached Deodorized Palm Oil (RBDPO)	5
		2.2 Technologies of Reducing Vegetable Oil's Viscosity	60
		2.2.1 Vegetable Oil based Microemulsification	8
		2.3 Alcohol Blended	10
		2.4 Surfactants and Cosurfactants	11
		2.4.1 Alcohol Ethoxylates Surfactant	12
		2.4.2 Methyl Oleate with Cosurfactants	14
		2.4.3 Fatty Acid Methyl Ester (FAME) or Biodiesel	15
		2.5 Pseudo-Ternary Phase Diagram	16
		2.6 Fuel Properties	17
		2.6.1 Kinematic Viscosity	18
		2.6.2 Cloud Point	18
		2.6.3 Gross Heat of Combustion or Heating Value	19

CHAPTER		
	2.6.4 Droplet Sizes	19
III	EXPERIMENTAL	20
	3.1 Materials and Equipment	20
	3.1.1 Equipment	20
	3.1.2 Chemicals	20
	3.2 Experimental Procedures	22
	3.2.1 Microemulsion Biofuels Preparation	23
	3.2.2 Phase Behavior Study	23
	3.2.3 Kinematic Viscosity Measurement	24
	3.2.4 Droplet Size Determination	25
	3.2.5 Fuel Properties of the Microemulsion Biofuels	25
IV	RESULTS AND DISCUSSION	26
	4.1 Phase Behavior Study of Microemulsion Biofules	26
	4.1.1 Comparisons of the System with Single and Mixed	
	Alcohol System	27
	4.1.2 Comparisons of the System with Different Types	
	of Surfactant	30
	4.2 Palm Oil/Diesel Ratio Study	31
	4.3 EtOH/BuOH Ratio Study	32
	4.3.1 Comparisons of Minimum Total Surfactant	
	Concentration to Formulate Single Phase Microemul	sion
	over the Effect of EtOH/BuOH Raios of the System	with
	Different Types of Surfactant	32
	4.3.2 Comparisons of Minimum Total Surfactant	
	Concentration to Formulate Single Phase Microemul	sion
	over Effect of EtOH/BuOH Raios of the System with	1
	Different Types of Palm Oil	33
	4.4 Fuel Properties Determination	35

		•	
CHAPTER			PAGE
	4.4.1 Kii	nematic Viscosity Determination	36
*.en	4.4.2 Dr	oplet Size Determination	39
	4.4.3 Clo	oud Point Determination	42
*	4.4.4 De	nsity Determination	44
	4.4.5 He	at of Combustion	44
	4.5 Summari	zed Results	46
V	CONCLUSI	ONS AND RECOMMENDATIONS	50
	5.1 Conclusion	ons	50
	5.2 Recomm	endations	51
	REFERENC	ES	52
	APPENDICI	ES	58
	Appendix A	Supplemental Materials for Phase Behavior	
		Study	58
	Appendix B	Supplemental Materials for Fuel Properties Study	62
o	Appendix C	Supplemental Materials for Viscosity Study	67
	Appendix D	Supplemental Materials for Droplet Size Study	71
	Appendix E	Supplemental Materials for Density Determination	n 74
	Appendix F	HLB Calculation of Nonionic Surfactant	75
	Appendix G	Supplemental Materials for Heat of Combustion	77
	CURRICUL	UM VITAE	78

## LIST OF TABLES

TABL			PAGE	
2.1	Productivity of different plants		5	
2.2	Palm oil productivity and exports of Thailand (kilotons)		5	
2.3	Cost with Different types of oil		6	
2.4	Chemical and physical properties of vegetable oils		7	
3.1	Properties and structures of materials	4	21	
3.2	Parameters and testing methods of the microemulsion			
	biofuel		26	
4.1	Fatty acid composition of palm oil and refined bleach			
	deodorized palm oil (RBDPO)		35	
4.2	Comparison of the droplet size and distribution of			
	microemulsion biofuels with palm oil/diesel blend (1:1			
	v/v) with MO and POME as surfactants at room			
	temperature (25±2 °C)		40	
4.3	Kinematic viscosity and droplet size of palm oil/diesel			
	blends at a ratio of 1:1 with 20 vol.% ethanol and butanol			
	mixture with MO and POME as surfactants mixed with			
	1-octanol as a cosurfactant at a molar ratio of 1:8		42	
4.4	Cloud point of MO and POME microemulsion biofuels		43	
4.5	Density of microemulsion biofuels		44	

## LIST OF FIGURES

FIGURE		PAGE
2.1	Transesterification of biodiesel.	8
2.2	Winsor-type microemulsion phases.	9
2.3	Reverse micelle structure.	9
2.4	Types of surfactant.	11
2.5	Pseudo ternary phase diagram.	17
3.1	Overall procedure of this study.	22
3.2	Pseudo-ternary phase diagram.	24
4.1	Pseudo ternary phase diagram with single phase and separate	
	phase example.	26
4.2	Comparison of microemulsion biofuel systems of methyl	
	oleate (MO) surfactant at room temperature (25±2 °C) with	
	palm oil/diesel oil ratio at 1:1 (v/v) with 1-octanol as a	
	cosurfactant with a single and mixed ethanol-butanol blend	
	system as a polar phase.	28
4.3	Comparison of microemulsion biofuel systems of biodiesel	
	(POME) as a surfactant at room temperature (25±2 °C) with	
	palm oil/diesel oil blend ratio at 1:1 (v/v), 1-octanol as a	
	cosurfactant and a single and mixed ethanol-butanol blend	
	system as a polar phase.	29
4.4	Comparision of the systems with methyl oleate (MO) and	
	biodiesel (POME) at room temperature (25±2 °C) with palm	
	oil/diesel oil ratio at 1:1(v/v) with EtOH/BuOH	30

o

FIGU	FIGURE	
4.5	Minimum total surfactant concentration to formulate single	
	phase microemulsion (%) versus palm oil/diesel ratio (v/v)	
	compared with methyl oleate and FAME (biodiesel) as	
	surfactants and 1-octanol as a cosurfactant at a molar ratio of	
	1:8 by 20 vol.% of EtOH/BuOH at a ratio of 1:1(v/v).	32
4.6	Minimum total surfactant concentration (%) versus	
*	EtOH/BuOH ratio (v/v) of ME with MO and POME as	
	surfactants, 1-octanol as a cosurfactant at a molar ratio of 1:8	
	and palm oil/diesel ratio at 1:1 (v/v) in 20 vol.% of	
	EtOH/BuOH.	33
4.7	Minimum total surfactant concentration (%) versus	
	EtOH/BuOH ratio (v/v) of ME with MO and POME as	
	surfactants with palm oil and RBDPO as oil phase, 1-	
	octanol as a cosurfactant at a molar ratio of 1:8 and palm	
	oil/diesel ratio at 1:1 (v/v) in 20 vol.% of EtOH/BuOH.	34
4.8	Kinematic viscosities (cSt) at 40 °C of the microemulsion	
1	biofuels of MO and POME with 1-octanol at a molar ratio of	
	1:8 with palm oil/diesel ratio at a ratio of 1:1 (v/v) with	
	varying butanol contained in ethanol and butanol blends at	
	20 vo.1% of ethanol and butanol blend in mixture.	37
4.9	Kinematic viscosity (cSt) at 40 °C versus EtOH/BuOH ratio	
	compared with palm oil and RBDPO as different palm oil	
	with palm oil/diesel ratio at 1:1 (v/v) with MO and POME as	
	surfactants with 1-octanol as a cosurfactant at a molar ratio	
	of 1:8 with 20 vol.% of EtOH/BuOH mixture.	38

rigur	FIGURE	
4.10	Kinematic viscosity (cSt) of palm oil/diesel blend at a ratio	
	of 30:70 (v/v) systems at 40 °C versus EtOH/BuOH ratio	
	with MO and POME as surfactants and 1-octanol as a	
	cosurfactant at a molar ratio of 1:8 with 20 vol.% of	
	EtOH/BuOH mixture.	39
4.11	Heat of combustion of microemulsion biofuels versus	
	EtOH/BuOH ratio with POME as surfactant and 1-octanol as	
	a cosurfactant at a molar ratio of 1:8 with palm oil/diesel at	
	ratio of 1:1 (v/v).	45