OPTIMIZATION OF VEGETABLE OIL DETACHMENT FROM OILSEED BY MINIMIZING INTERFACIAL TENSION

Mr. Nattapong Tuntiwiwattanapun

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Environmental Management
(Interdisciplinary Program)
Graduate School
Chulalongkorn University
Academic Year 2012

การเพิ่มประสิทธิภาพการแยกน้ำมันออกจากเมล็ดของพืชน้ำมันโดยการลดค่าแรงตึงผิว

นายณัฐพงศ์ ตันติวิวัฒนพันธ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2555

Thesis Title	OPTIMIZATION OF VEGETABLE OIL DETACHMENT FROM OILSEED BY MINIMIZING INTERFACIAL TENSION
By	Mr. Nattapong Tuntiwiwattanapun
Field of Study	Environmental Management
Thesis Advisor	Assistant Professor Chantra Tongcumpou, Ph.D.
Thesis Co-advisor	Professor Dennis P. Wiesenborn, Ph.D.

Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

……………………………………………Dean of the Graduate School

(Associate Professor Amorn Petsom, Ph.D.)

THESIS COMMITTEE

……………………………………………….. Chairman
(Assistant Professor Ekawan Luepromchai,Ph.D.)

……………………………………….……. Thesis Advisor
(Assistant Professor Chantra Tongcumpou,Ph.D.)

……………………………………………….. Thesis Co-advisor
(Professor Dennis P. Wiesenborn,Ph.D.)

……………………………………………….. Examiner
(Assistant Professor Pisut Painmanakul,Ph.D.)

……………………………………………….. External Examiner
(Punjaporn Weschayanwiwat,Ph.D.)

ณัฐพงศ์ ตันติวิวัฒนพันธ์ : การเพิ่มประสิทธิภาพการแยกน้ำมันออกจากเมล็ดของพืชน้ำมันโดยการลดค่าแรงตึงผิว. (OPTIMIZATION OF VEGETABLE OIL DETACHMENT FROM OILSEED BY MINIMIZING INTERFACIAL TENSION) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ.ดร.จันทรา ทองคำเภา, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม : ศ.ดร.เดนนิส พี เวสเซ็นบอน, 83 หน้า.

ในอุตสาหกรรมสกัดน้ำมันพืชมีการใช้สารละลายเฮกเซนอย่างแพร่หลาย เนื่องด้วยวิธีนี้มีประสิทธิภาพสูงในการสกัดน้ำมัน แต่เนื่องจากสารละลายเฮกเซนเป็นสารที่ระบุอยู่ในรายการสารเคมีอันตรายเนื่องจากคุณสมบัติของเฮกเซนเป็นสารไวไฟและเป็นสารก่ออันตรายต่อสุขภาพของคนและสภาพแวดล้อม ด้วยเหตุนี้การพัฒนาการสกัดน้ำมันพืชโดยปราศจากสารละลายเฮกเซน จึงเป็นแนวทางเลือกของกระบวนการสกัดน้ำมันที่มีความน่า สนใจและมีความสำคัญเป็นอย่างยิ่ง ในงานวิจัยฉบับนี้สารผสมของสารลดแรงตึงผิวในน้ำเกลือได้ถูกนำเสนอเพื่อการสกัดน้ำมันพืช โดยเรียกว่า การสกัดโดยสารละลายลดแรงตึงผิว (Aqueous Surfactant-assisted Extraction) การสกัดด้วยวิธีนี้มีประสิทธิภาพการแยกน้ำมันของสบู่ดำ (Jatropha) และคาโนล่า (Canola) สูงกว่า 70 เปอร์เซ็นต์ เพื่อเพิ่มประสิทธิภาพการสกัดน้ำมันคาโนล่า วิธีการสกัดโดยสารละลายลดแรงตึงผิวนี้ได้พัฒนาโดยเน้นการปรับปรุงสภาวะและเงื่อนไขต่างๆในกระบวนการสกัด ผลการทดลองแสดงให้เห็นว่าความเข้มข้นของสารละลายลดแรงตึงผิว เวลาในการสกัด สัดส่วนระหว่างเมล็ดน้ำมันพืชกับสารละลายลดแรงตึงผิว มีผลต่อการประสิทธิภาพการสกัดของน้ำมันคาโนล่า ในขณะที่อุณหภูมิการสกัดไม่ส่งผลอย่างมีนัยสำคัญทางสติถิต่อประสิทธิภาพการสกัดน้ำมัน อีกทั้งการใช้การสกัดสามขั้นตอน (Triple Extraction with Three-stages) สามารถลดปริมาณการใช้สารลดแรงตึงผิวในระบบได้ ประสิทธิภาพการแยกน้ำมัน และการสกัดน้ำมันสูงสุดที่ได้ คือ 80 และ 60 เปอร์เซ็นต์ ตามลำดับ จากผลวิเคราะห์เชิงคุณภาพพบว่าน้ำมันคาโนล่าจากการสกัดโดยสารละลายลดแรงตึงผิวมีปริมาณของกรดไขมันอิสระ (Free Fatty Acid) และฟอสโฟลิปิด (Phospholipids) ที่ต่ำกว่าน้ำมันที่สกัดโดยสารละลายเฮกเซน ถือได้ว่าน้ำมันที่สกัดได้จากสารละลายลดแรงตึงผิวนี้มีคุณสมบัติที่เหมาะสมต่อการนำไปผลิตไบโอดีเซล (Biodiesel) ต่อไปในอนาคต

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต

ปีการศึกษา 2555 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

5387523020 : MAJOR ENVIRONMENTAL MANAGEMENT
KEYWORDS : SURFACTANT / JATROPHA / CANOLA / HEXANE-FREE OIL EXTRACTION / AQUEOUS SURFACTANT-ASSISTED EXTRACTION

NATTAPONG TUNTIWIWATTANAPUN : OPTIMIZATION OF VEGETABLE OIL DETACHMENT FROM OILSEED BY MINIMIZING INTERFACIAL TENSION. ADVISOR : ASST.PROF. CHANTRA TONGCUMPOU, CO-ADVISOR : PROF. DENNIS P. WIESENBORN, 83 pp.

N-hexane has been widely used in vegetable oil extraction industry since it yields high extraction efficiency. However, n-hexane is categorized as a hazardous pollutant due to safety, health, and environmental concerns. Thus an alternative approach for oil extraction method that is free from n-hexane would be worthwhile to develop. In this work, mixed commercial anionic and nonionic surfactants in brine solution were purposed to be used for oil extraction. The results showed a good potential to use as extraction medium in aqueous surfactant-assisted extraction method (ASE). The oil detachment efficiency was exceed 70% for both jatropha and canola oil extraction. In case of canola, the ASE conditions were further modified for maximizing the oil yield. The surfactant concentration, stirring and ultrasonication time, and oilseed to extraction medium ratio significantly impacted the oil detachment and oil extraction efficiency. The effect of extraction temperature was not statistically significant. The triple extraction with three-states reduced the use of extraction medium. The highest oil detachment and oil extraction efficiency were 80% and 60%, respectively. In addition the canola oil from ASE method was found to have a superior oil quality to that of Soxhlet extraction in term of lower acid value and phospholipids content which are the important parameters for the quality of biodiesel feedstock.

Field of Study : Environmental Management Student's Signature ....

Academic Year : 2012 Advisor's Signature ....

Co-advisor's Signature ....

ACKNOWLEDGEMENT

I would like to gratefully thank my advisor Dr. Chantra Tongcumpou, Assistant Professor in Environmental and Hazardous Waste Management Program of Chulalongkorn University, and my co-advisor Dr. Dennis P. Wiesenborn, Professor in the Department of Agricultural and Biosystems Engineering of North Dakota State University (NDSU) for their support, guidance and encouragement through the duration of my graduate study. Be an advisee of Dr. Chantra and Dr. Dennis was the most precious experience in my life. It was a great honor to work with them.

I would like to extend my acknowledgement and appreciation to my advisory committees including Dr. Ekawan Luepromchai, Dr. Pisut Painmanukul, and Dr. Punjaporn Weschayanwiwat. Without any of their advice and comments, this work would not be possible. I extend my appreciation to Dr. Eakalak Khan, Professor in the Department of Civil Engineer of NDSU for giving me a great opportunity to do double Master’s degree in Environment and Conservation Sciences Program of NDSU.

Nonetheless, special thanks go to Darrin M. Haagenson, research specialist in the Department of Agricultural and Biosystems Engineering of NDSU, who help me in statistic analysis and analytical methods. I would like to thank the National Research Center for Environmental and Hazardous Waste Management (NRC-EHWM), the International Postgraduate Programs in Environmental and Hazardous Waste Management, and the North Dakota Center of Excellence for Oilseed Development for providing funding.

Thanks to all of my family, friends and staffs in Thailand and United State of America, especially my parents, brother, sister and Manapa Akramas for their endless support and belief in me without any condition.

TABLE OF CONTENTS

Page

CHAPTER

CHAPTER **Page**

CHAPTER **Page**

CHAPTER **Page**

LIST OF TABLES

LIST OF FIGURES

Figure **Page**

Figure **Page**

Figure **Page**

LIST OF ABBREVIATIONS

IFT = Interfacial Tension (mN/m)

CMC = Critical Micelle Concentration

HLB = Hydrophile-Lipophile Balance

S* = Optimum Salinity

OD = Oil Detachment Efficiency

OE = Oil Extraction Efficiency

3E3S = Triple Extraction with Three-stages

CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction

N-hexane has been broadly used as solvent in vegetable oil extraction industry due to low operation cost and high oil extraction efficiency. However, n-hexane is categorized as a hazardous air pollutant and issued strict emission standard (U.S. Environmental Protection Agency (EPA), 2001). In every one ton of oilseed there was n-hexane lost in oil extraction process between 0.7-4.5 L (U.S. Environmental Protection Agency (EPA), 2001). The workers who exposure to n-hexane at 15 ppm/day for 3 months have shown the peripheral nerve damage (Do and Sabatini, 2010). Regardless of safety and health, n-hexane is one of the volatile organic carbons (VOCs) that contribute to the formation of photochemical smog with nitrogen dioxide and ozone, and thus decrease ozone layer (Smith and Chughtai, 1996). Thus, extraction systems must fully contain n-hexane and provide for leak detection (Do and Sabatini, 2010). Future laws may be even more stringent; therefore, hexane-free extraction approaches are needed.

Several extraction mediums have been evaluated to replace n-hexane in vegetable oil extraction process such as: water (Hanmoungjai, Pyle and Niranjan, 2000), ethanol (Kwiatkowski and Cheryan, 2002), acetone (Youngs and Sallans, 1955), iso-hexane with alcohol mixture (Kuk and Hron, 1998), mixed propane with supercritical fluid CO_2 (Pederssetti et al., 2011) and even vegetable oil itself (Strop and Perry, 1989). Recently, aqueous extraction process, which uses water as extraction medium, has been developed by introducing enzyme or surfactant to improve the oil extraction efficiency (Do and Sabatini, 2010; Dominguez, Ndfiez and Lema, 1994; Ghosh, Jayas and Agrawal, 2007; Kadioglu, Phan and Sabatini, 2011; Latif, Diosady and Anwar, 2008; Naksuk, Sabatini and Tongcumpou, 2009).

Aqueous surfactant-assisted extraction (ASE) is one such promising process. The main concept of this method is to use surfactant solution to reduce interfacial tension (IFT) between vegetable oil and extraction media. By definition, IFT is the repulsive energy between two different species of molecules (Rosen, 2004). It is the minimum energy (heat, gravity and shear force) required to make one phase disperse into another phase, increasing the surface area between two different phases. The high IFT implies that these two species of molecules are very different. In the case of water and vegetable oil, the IFT value is between 20 and 30 mN/m (Gunstone, 2004). Surfactants can minimize the IFT of the system and help vegetable oil easily detach from the oilseed surface. Decreased IFT, moreover, results in reduced size of oil droplets, helping them disperse into extraction media (Do and Sabatini, 2010).

The ASE method achieved an oil efficiency of more than 80% without thermal energy in laboratory bench scale (Do and Sabatini, 2010; Kadioglu et al., 2011; Naksuk et al., 2009). The extracted oil also had a lower content of free fatty acids and phospholipids, so the refinery cost of vegetable oil is reduced. Furthermore, ASE eliminates the costs of installing and maintaining a hexane-leak detection system and reduces risk to workers. Absence of toxic *n*-hexane solvent also gives superior co-product meal quality (Rosenthal, Pyle and Niranjan, 1996). Several literature reports suggest that the IFT should be reduced to 0.01 mN/m (ultralow level) for this extraction method (Do and Sabatini, 2010; Kadioglu et al., 2011; Naksuk et al., 2009). A commercial surfactant, alone, cannot reduce IFT to this ultralow level. A co-surfactant such as a short chain alcohol (Sabatini, Acosta and Harwell, 2003) or extended surfactant is required (Do and Sabatini, 2010; Witthayapanyanon et al., 2006). Extended surfactants are a new type of surfactant, in which propoxylate and/or ethoxylate groups are inserted between polar and non-polar parts of the molecule. These groups allow the surfactant molecule to stretch out further into the oil and water phase, resulting in a reduction of IFT of the system to ultralow level (Witthayapanyanon et al., 2006).

However, using a volatile and flammable co-surfactant requires a leak proof system; and the extended surfactant is still not commercialized. Moreover, most of the research on ASE thus far has been conducted at the laboratory bench level (2-5 g oilseed).

1.2 Objectives of the Study

The primary goals of this work were

- select the suitable commercial surfactant system for jatropha and canola oil based on dynamic IFT;
- demonstrate a potential of using mixed commercial surfactant in brine solution as extraction media for jatropha and canola oil extraction in ASE method;
- maximize the canola oil recovery by evaluation the effect of surfactant concentration, stirring and ultrasonication time, extraction temperature, solid-liquid ratio, and triple extraction with three-stages; and
- scale up the ASE process to extract 300 g batch of canola seed for quality analysis.

CHAPTER 2

LITERATURE REVIEW

2.1 Technology and Solvent for Oilseed Extraction

Over five decades, n-hexane has been used as an oilseed extraction solvent in most of the oilseed industries. Due to its economical efficiency and superior solvent characteristics, there have not been any alternative solvents that can replace n-hexane. However, n-hexane still has some disadvantages that make it is not the ideal solvent such as: toxicological and environmental concerns, high investment cost of leaking detection system, and low quality of meal destined for feed or food (Gregory and Horsman, 1997). N-hexane is a volatile organic carbon (VOC) that has been categorized as a hazardous air pollutant and issued strict emission standard (100 mg/Nm^3). In every one ton of oilseed there was n-hexane lost in oil extraction process between 0.7-4.5 L (U.S. Environmental Protection Agency (EPA), 2001). Even the current technology was passed the n-hexane emission standard. The workers who exposure to n-hexane at 15 ppm/day for 3 months have shown the peripheral nerve damage (Do and Sabatini, 2010). Moreover, n-hexane 0.8 mg/kg was typically found in refined vegetable oil (Swanson, 2012). Moreover, in the 1970s, there was growing interest in finding alternative solvents to replace n-hexane, due to economic reasons. At that time, the Organization of Petroleum Exporting Countries (OPEC) increased the price of petroleum and its derivatives, six to eight times greater than the cost of previous several years. Thus, this situation increased the operating cost with n-hexane, as the derivative of petroleum product, in oilseed industrial (Johnson, 1997).

Gregory & Horsman (1997) suggested that the alternative solvent for oilseed extraction should be able to enhance credibility and acceptance through joint involvement between industry and researchers. They provided the criteria to evaluate the efficiency of solvent, shown in Table 1. Finally, they highly recommended that full-scale tests were needed to lend economic credibility to research involving alternative solvents. In this work, we also focused on scale up our alternative extraction media and extraction processes.

2.1.1 Oilseed Extraction Processes

For thousands of years, humans have extracted the oil and fat from the oilseeds, fruits, and fatty animal tissues. The oldest method for extracting the oil is mechanical pressing which usually requires seed pretreatment (Johnson, 1997). In the commercial vegetable oil extraction industry, many processes are involved in order to achieve the highest oil yield and quality (Figure 1). However, different oilseeds require different extraction processes, including pretreatment (Table 2).

Table 1 Numerical weighting factors for attributes and example to evaluate the efficiency of solvent (Gregory and Horsman, 1997).

Weighting Factor	Attribute	n-hexane		Isohexane		Isopropyl alcohol	
		ranking	score	ranking	score	ranking	score
20	Extraction Efficiency	3	60	2	40	1	20
20	Environmental Friendliness	1	20	2	40	3	60
15	Capital Requirements	3	45	2	30	1	15
10	Price Effectiveness	3	30	2	20	1	10
10	Toxicity	1	10	2	20	3	30
10	Flammability	1	10	2	20	3	30
5	Energy Efficiency	3	15	2	10	1	5
5	Meal Quality Enhancement	1	5	2	10	3	15
5	Oil Quality Enhancement	1	5	2	10	3	15
100	**Total**		**200**		**200**		**200**

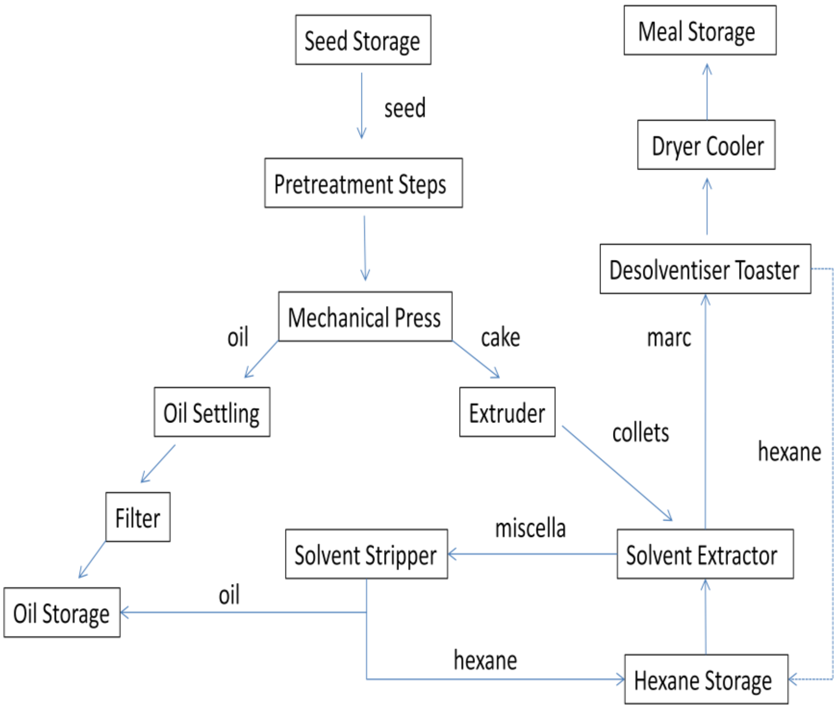


Figure 1 Commercial vegetable oil extraction processes, modified from Booth (2004).

Table 2 Oil content of various oilseeds with the prevalent method of extraction (Johnson, 1997).

Source	Oil Content (%)	Prevalent Method of Recovery
Soybean	19	Direct solvent extraction
Corn (germ)	40	Wet or dry milling and prepress solvent extraction
Tallow (edible)	70-95	Wet or dry rendering
Canola	42	Prepress solvent extraction
Coconut (dried copra)	66	Hard pressing
Cottonseed	19	Hard pressing, or prepress or direct solvent extraction
Lard	70-95	Wet or dry rendering
Palm	47	Hard pressing
Palm Kernel	48	Hard pressing
Sunflower	40	Prepress solvent extraction
Peanut (shelled)	47	Hard pressing or prepress solvent extraction

2.1.1.1 Pretreatment Steps

Pretreatment or conditioning steps are applied to adjust the conditions of oilseeds before extraction processes, presented in Figure 1. These steps are required to increase surface area, reduce moisture content and disrupt the oil cell within the seed (Booth, 2004).Oilseeds are reduced in size by the grinding step. This step breaks down the oilseed's cell structure resulting in increasing surface area and squeezing the oil to the surface of the oilseed. For the most suitable particle size of oilseed extraction, the range of particle size should be between 0.21-0.42 mm (Do and Sabatini, 2010; Kadioglu et al., 2011; Naksuk et al., 2009).

Furthermore, thermal treatment, known as cooking, is used to heat the ground oilseed to 75-85 ^{o}C. It breaks down the remaining oil cells and promotes coalescing of small oil droplet to larger oil droplet. Oil viscosity is also reduced making oil is easier to be extracted by following processes (Booth, 2004). Some paper developed this process to achieve more oil yield. For example, Li et al. (2011) reported that using electric far-infrared oven (60 min with 112^{o}C) was able to increase wheat germ oil enzymatic extraction to 84.82%, compared with regular pressure cooker with 78.37%.

2.1.1.2 Mechanical Extraction

The oilseed, which has oil content more than 30 wt%, should be applied either hard pressing or prepressing before using solvent extraction. According to Khan and Hanna (1983), the mechanical press were classified into three techniques: wedge, hydraulic press, and screw press. Although oilseed is disrupted and extracted most of the oil; some of oil is still adsorbed on the surface of the oilseed and/or inside. In order to extract all of the oil, solvent extraction is applied into the oilseed extraction processes.

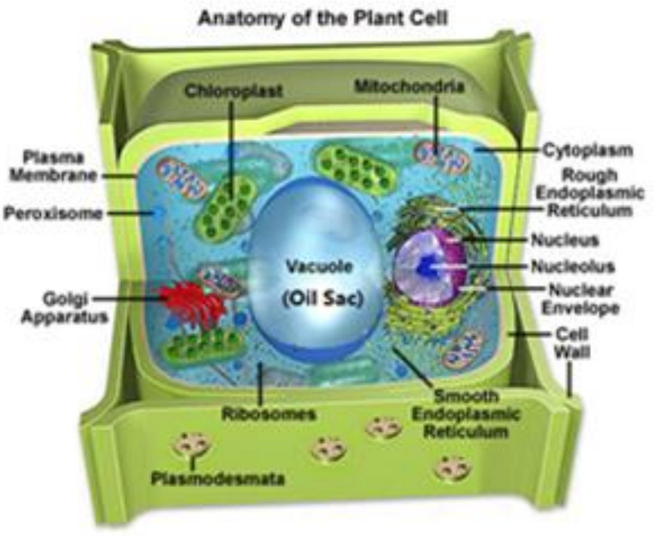


Figure 2 Anatomy of the plant cell: vegetable oil is contained in vacuole (Davidson, 2011).

Moreover, an ultrasonication was used in some oilseed extraction methods. Ultrasonication is the application of using ultrasonic (>20 kHz) waves in liquid media. The effect of ultrasonic wave makes the liquid sample move violently (agitation). The sound wave penetrates through the liquid media generating high pressure (compression) and low pressure (rarefaction) cycles. In rarefaction period, many small vacuum bubbles or voids are created in liquid media by high intensity sonic waves. These voids collapse violently (cavitation) during compression. The implosion of the cavitation bubbles generates hydrodynamic shear-force. This force is very powerful; even the propeller of a warship is eroded by it (David, 2002). Thus, the ultrasonication is applied to reduce the size of oilseed, and breakdown the cell wall. Shah et al. (2004) applied 10 min of ultrasonication on aqueous enzymatic jatropha oil extraction. They found that ultrasonication was able to increase the oil extraction efficiency from 67% to 74% and cut down the process time from 18 h to 6 h.

2.1.1.3 Solvent Extraction

The process of solvent extraction is mass transfer process in which transfers one phase to another phase in order to separate compounds from the mixture. N-hexane has been used in most of commercial vegetable oil extraction plants for the past 50 years (Johnson, 1997). The n-hexane solvent extraction has been developed until it is not necessary to apply the mechanical press process. The good example was the Crow model III from Crow Iron Works Company (Figure 3). Briefly, this extractor applied counter current flow to extract the oilseed by n-hexane. The bed of oil-bearing material should allow solvent percolation. Therefore, seed particles should not be too fine. The fresh oilseed was extracted by miscella coming in from the recycle pumps as the counter current loop extraction. Moreover, compared with a batch extraction method, counter current extraction was able to reduce the solvent in the extraction process (Wisenborn et al., 1993).

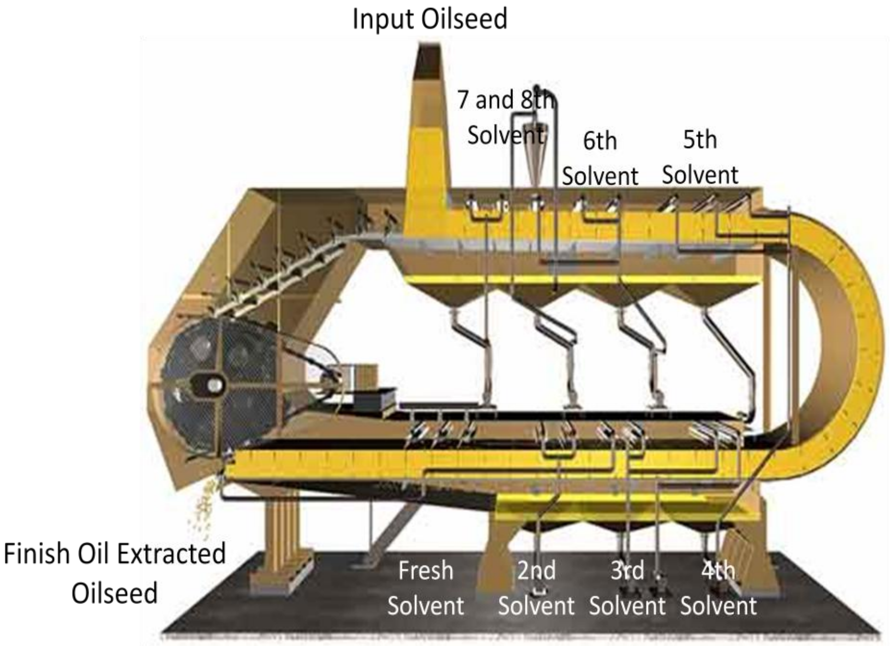


Figure 3 Crown Model III oilseed extractor:
http://www.crowniron.com/technologies/ext_model3.cfm.

However, n-hexane is not the ideal solvent and still has some big disadvantages. Recently many alternative solvents and extraction medium have been developed. One promising extraction media is surfactant solution, used in aqueous surfactant-assisted extraction.

2.2 Aqueous Surfactant-assisted Extraction (ASE)

A surfactant is an amphipathic substance that has both of hydrophobic part (tail group) and hydrophilic part (head group) as shown in Figure 4. Due to having both hydrophobic and hydrophilic part, surfactant has a unique characteristic that is suitable to be used as extraction media. Surfactant can dissolve both non-polar compound and polar compound by reducing interfacial tension (IFT) of the system. By definition, IFT is the repulsive energy between two different species of molecules (Rosen, 2004). In other words, it is the minimum energy (heat, gravity and shear force) that is required to make one phase disperse into another phase, increasing the surface area between two different phases. The high IFT value implies that the two molecules are very different in structure, such as vegetable oil (non-polar compound) and water (polar compound) with IFT value between 20 and 30 mN/m (Gunstone, 2004). Thus, water and oil cannot be homogenously mixed and separate into two immiscible phases. Once surfactant is introduced into this system, the IFT of system is reduced and then the two immiscible phases can be dispersed in each other, called emulsion. Thus, surfactant plays role as a linker between the vegetable oil and water. In conclusion, the main concept of ASE is reducing the IFT of the system for detaching oil from oilseed. Do and Sabatini (2010) suggested that the IFT should be reduced to ultralow level (<0.01 mN/m) to break up the oil droplet, and release oil from the disrupted cell.

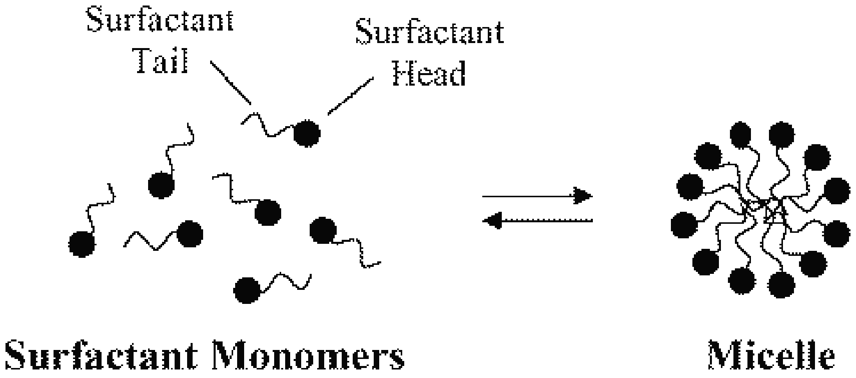


Figure 4 Surfactant structure (Carlota et al., 2005).

2.2.1 How to Reduce Interfacial Tension?

As we mentioned above, IFT is repulsive energy between two different molecules. In Figure5, at the interface of two different pure liquid phases “a” and “b”, there is potential energy between different molecules that is always greater than which of similar molecules in the interior of its bulk phase. The net potential energy of the “a” molecule at the interface over those in the interior of that phase can be presented as ($A_{aa} – A_{ab}$), where A_{aa} and A_{ab} are the molecule interaction energy between molecule “a” and “a”, and “a” and “b”, respectively. Similarly, the net potential energy of “b” molecules at the interface over those in the interior is ($A_{bb} – A_{ab}$), where A_{bb} and A_{ab} are the molecule interaction energy between molecule “b” and “b”, and “a” and “b”, respectively. Thus, the total net potential energy at the interface over those in the interior of the bulk phase is ($A_{aa} – A_{ab}$) + ($A_{bb} – A_{ab}$) or $A_{aa} + A_{bb} – 2A_{ab}$, named interfacial free energy. This is the minimum work required to create the interface, separating into two immiscible phases.

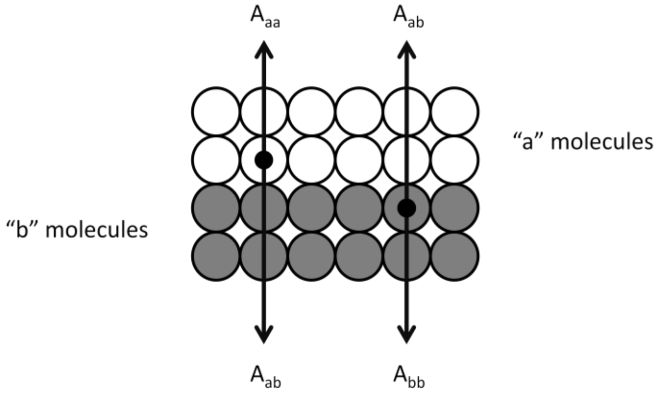


Figure 5 Molecule interaction energy at interface between two pure liquid phase “a” and “b” (Rosen, 2004).

In order to minimize this repulsive energy, the interaction energy between different molecules, A_{ab}, must be large- i.e., molecule “a” and “b” are similar in nature to each other (polar and polar compounds or nonpolar and nonpolar compounds). Once surfactants are introduced into the two immiscible phases, they are absorbed at the interface between two immiscible phases. Surfactants will orient hydrophilic head group toward the polar solvent and the hydrophobic tail group toward the nonpolar solvent, in accordance with the “like dissolves like” concept. This phenomenon produces very large A_{ab} and therefore decreases IFT of the system. There are two rules of thumb of using surfactant to reduce IFT, which are described in more detail below. First, the concentration of surfactant should reach its critical micelle concentration (CMC). Second, the Winsor R ratio, ratio between interaction energy within hydrophobic part and hydrophilic part of the system, should be equal to one and have very high interaction energy in both of hydrophobic part and hydrophilic part.

2.2.1.1 Critical Micelle Concentration

Critical micelle concentration (CMC) is the concentration of surfactant that the first micelle is formed (Figure 6). At this concentration, surfactants are adsorbed on the entire interface area between two immiscible phases. Thus, it provides the largest A_{ab} to the system resulting in the lowest IFT. Moreover, recently, Witthayapanyanon et al. (2006) reported that extended surfactant was able to reduce IFT lower than its CMC level once increase surfactant concentration to critical microemulsion concentration (CμC).

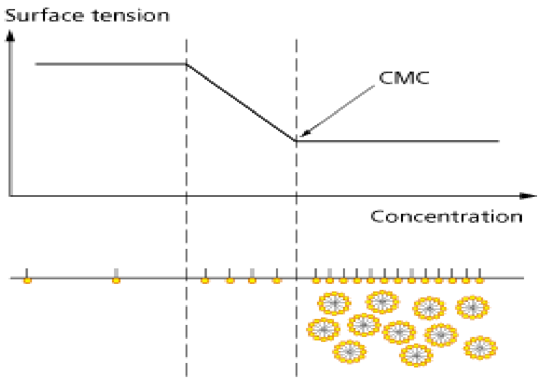


Figure 6 Effect of surfactant concentration on surface tension or interfacial tension (Kunjappu, 2003).

2.2.1.2 Winsor R Ratio

The Winsor R ratio is used to interpret changing in the hydrophilic solvent (W), the lipophilic solvent (O), and the surfactant (S) to the IFT and phase volume in terms of the molecular interaction involved (Rosen, 2004).

$$R = \frac{A_{SO_{NET}}}{A_{SW_{NET}}} = \frac{A_{SO} - A_{OO} - A_{LL}}{A_{SW} - A_{WW} - A_{HH}} \qquad \text{Equation 1}$$

where A_{SO}NET is the net interaction between the surfactant and oil (hydrophobic), A_{SW}NET is the net interaction between the surfactant and water (hydrophilic), A_{SO} is the interaction between the surfactant and oil, A_{SW} is the interaction energy between the surfactant and water, A_{OO} is the interaction energy among oil molecules, A_{LL} is the interaction energy among the tails of the surfactant molecules (hydrophobic part), A_{HH} is the interaction energy among the surfactant heads (hydrophilic part), and A_{WW} is the interaction energy among the water molecules (Witthayapanyanon et al., 2006).

In order to minimize IFT, Winsor R ratio should be equal to one (R=1) and have very high interaction energy in both of hydrophobic part and hydrophilic part. In other word, A_{SO}NET and A_{SW}NET must be high and very close to each other. There are several methods that can modify this ratio.

2.2.1.2.1 Electrolyte concentration and temperature (Turning parameter)

Different type of surfactant has different effect on electrolyte concentration and temperature. Basically, surfactant is divided into four types: anionic surfactant, cationic surfactant, nonionic surfactant and zwitterionic surfactant (have both positive and negative charge), classified by charge on the polar part of the surfactant structure. Introducing electrolyte to the system has an impact on A_{SO}NET and A_{SW}NET of the ionic surfactant by reducing A_{SW} and increasing A_{SO}. Electrolyte, such as NaCl, minimizes the electrical interaction of the ionic head group of the surfactant, causing closer packing. This can cause changing in the micellar structure from normal spherical shape to reverse micelle formation. On the other word, the surfactant is changed from hydrophilic to hydrophobic form. The NaCl concentration that provides the lowest IFT is called optimum salinity (S*). Unlike ionic surfactant, electrolyte concentration marginal affects to nonionic surfactant. In order to modify Winsor R ratio of the nonionic surfactant system, temperature is applied. Increasing temperature can dehydration of the POE chains in the nonionic surfactant structure, the surfactant becomes more hydrophobic (Rosen, 2004). Figure 7 shows effect of molecular environmental conditions on interfacial tension and phase volumes. Introducing electrolyte (NaCl) was the most common method to reduce IFT; and has been applied with other method into many researches (Do and Sabatini, 2010; Naksuk et al., 2009; Tongcumpou et al., 2006; Witthayapanyanon et al., 2006).

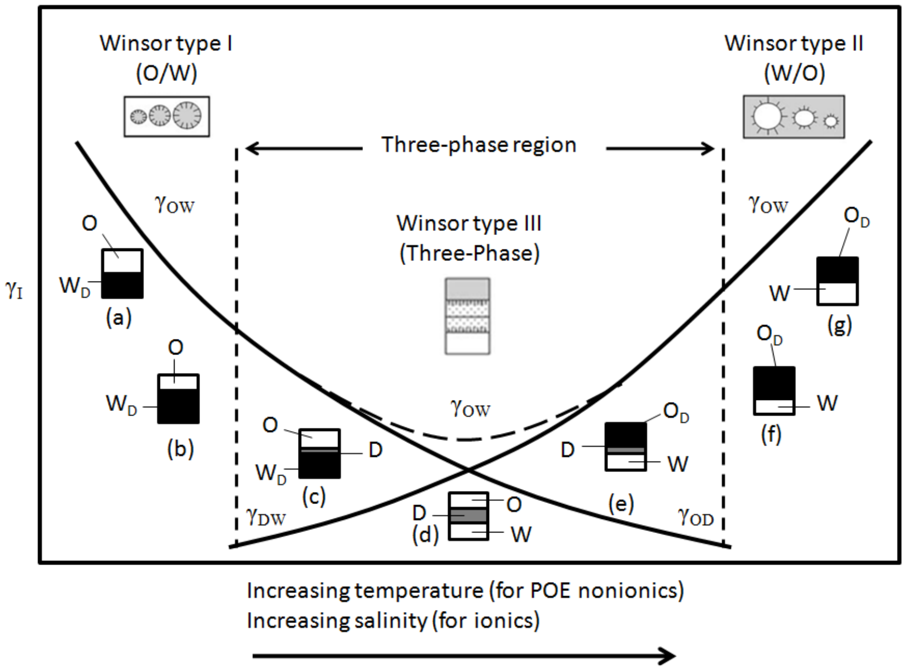


Figure 7 Effect of molecular environmental conditions on interfacial tension and phase volumes. Shaded phases indicate locations of the surfactant. Modified from Rosen (2004).

2.2.1.2.2 Extended surfactant

Extended surfactant is a surfactant in which group of propyleneoxide (PO) and/or ethyleneoxide (EO) are inserted between hydrophobic and hydrophilic part (Figure 8). These groups make surfactant stretch out further into both of oil and water phases, increasing adsorption of surfactant at interfacial region and reducing IFT of the system. Witthayapanyanon et al. (2006) applied extended surfactant, $C_{14\text{-}15}$-$(PO)_8$-SO_4Na (0.2 %wt), to reduce IFT of various of vegetable oil. This extended surfactant reduced IFT into ultralow level (<0.01 mN/m) at optimum salinity. Moreover, Do and Sabatini (2010) used various kinds of extended surfactant, varied number of PO and EO groups, with triolein (representative as a main component of vegetable oil) and achieved ultralow IFT.

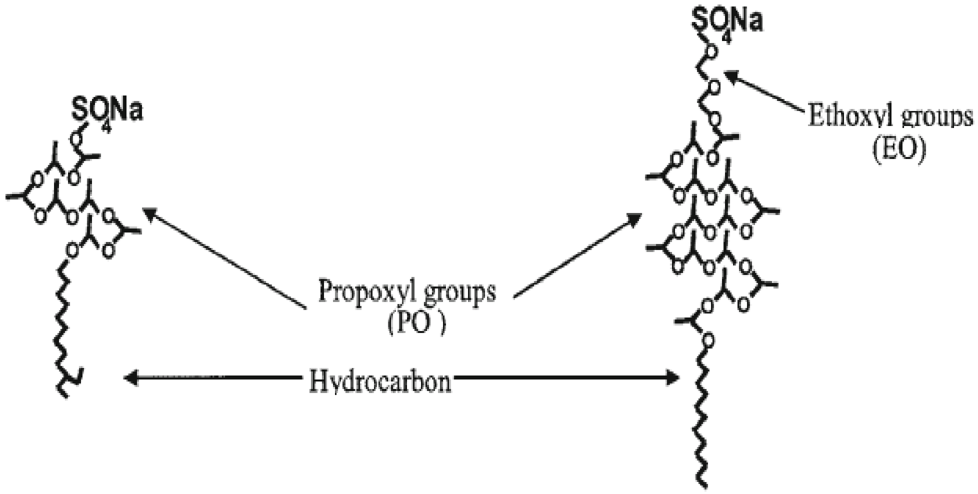


Figure 8 Structure of extended surfactant (Witthayapanyanon et al., 2006).

2.2.1.2.3 Linker (co-surfactant)

Linker, known as co-surfactant or co-solvent, is one kind of amphipathic substance that can reduce IFT of the system, but it cannot form the micellar structure; for example, n-alkyl alcohol (Rosen, 2004). Linker can be classified into two main types, lipophilic linker and hydrophilic linker. Lipophilic linker is the linker of which the molecule is mainly lipophilic such as medium and long chain alcohol. So, it is used as the linker between lipophilic part of the surfactant molecule (tail group) and non-polar phase (vegetable oil). Unlike lipophilic, hydrophilic linker's molecule is mainly hydrophilic such as short chain alcohol. It is used as the linker between hydrophilic part of the surfactant molecule (head group) and polar phase (water). Thus, introducing these linkers into the system increases the similarity among vegetable oil, surfactant, and water leading to reducing IFT of the system. Both Sabatini et al. (2003) and Uchiyama et al. (2000) recommended that the combination of lipophilic and hydrophilic linker gave the higher solubilization between non-polar phase and surfactant solution, resulting in lower IFT value of the system.

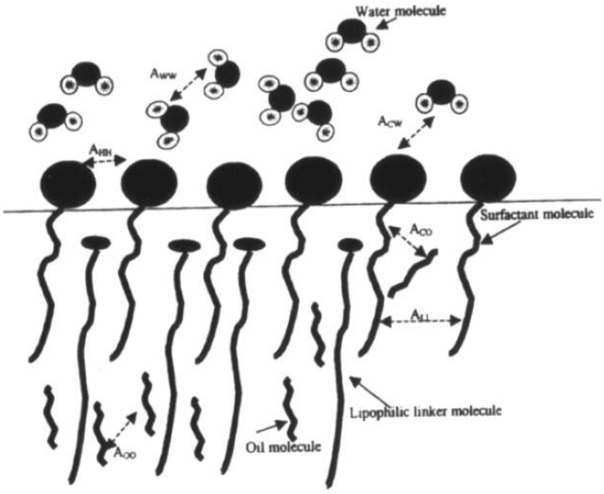


Figure 9 Schematic of the system among oil, surfactant and water with lipophilic linker (Uchiyama et al., 2000).

2.2.1.2.4 Synergism Effect

When two surfactants are mixed and generate better properties (lower CMC level, surface tension (γ) and interfacial tension) than the individual surfactants this effect is called synergism (Figure 10b). This phenomenon occurs due to electrostatic forces that affects the interaction between two surfactants. So, the strength of attractive interaction decreases in the following order: anionic-cationic > anionic-zwitterionic > ionic-nonionic > nonionic-nonionic.

In general, an increase in the electrolyte concentration of the aqueous phase produces a decrease in the attractive interaction. However, in the case of anionic-nonionic mixture, it increases the attractive interaction. It creates the complex formation between the Na^+ and the ether oxygen of the POE chain, resulting in its acquiring a positive charge which increases the strength of its interaction with anionic surfactant (Rosen, 2004). Klongklaew et al. (2005) used mixed surfactant between anionic and nonionic surfactant to reduce IFT of the soybean oil and surfactant solution. Naksuk et al. (2009) also applied this synergism phenomenon, using anionic-nonionic mixed surfactant, to minimize IFT of the palm kernel oil and surfactant system.

Even the mixture of two surfactants can produce the better properties; these two surfactants must be mixed in the suitable ratio. If the ratio between surfactants is not suitable, it creates worse properties (higher CMC, surface tension and interfacial tension). This phenomenon is called negative synergism (Figure 10c).

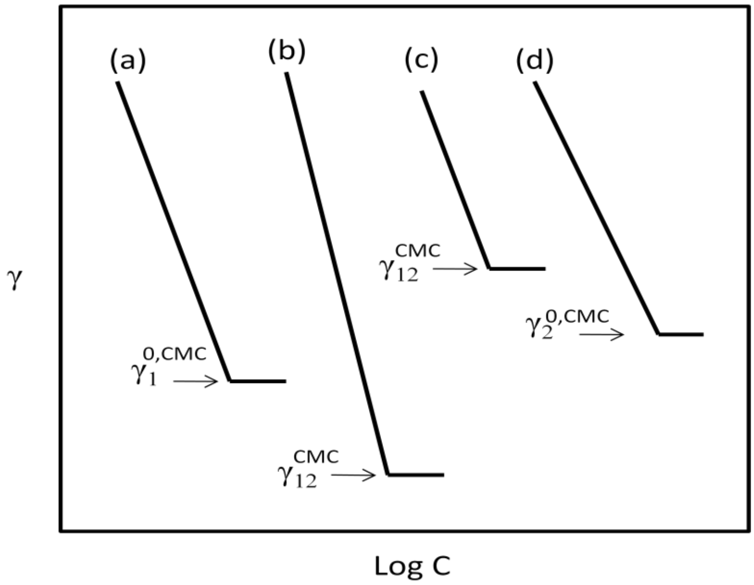


Figure 10 Synergism and negative synergism in surface tension reduction effectiveness: (a) Pure surfactant 1, (b) and (c) mixture of surfactants 1 and 2 in different mole fraction and (d) Pure surfactant 2 (Rosen, 2004).

2.2.2 Extraction Process

Many research studies focused on the possibility of using ASE method to extract vegetable oil and protein. However, most of research still conducted at lab-bench level, extracting 2-5 g of vegetable oil. Table 3 and 4 summarized the extraction process and oil extraction efficiency and extracted oil quality of these researches. Currently, Do and Sabatini (2011) scaled up this process to semi-continuous pilot scale (Figure11 and 12). They applied the same condition as their research in 2010 (Do and Sabatini, 2010), but adding deionized water washing as the second extraction on 150 g of peanut and canola seed. The oil extraction efficiencies were 87.1% and 85.6% of peanut and canola, respectively.

One problem of the ASE method is an emulsion formation. A demulsification process is required to break down the emulsion, resulting in an increase in the oil recovery. Demulsification agent, thermal treatment, enzymatic treatment and centrifugation have been typically used in demulsification process of food industry (Chabrand et al., 2008; Rosenthal et al., 1996). In petroleum industry a high voltage technique was used to demulsify a petroleum emulsion from an oil recovery process (Wang, Lee and Chan, 1994). Microemulsions are very difficult to demulsify since they are thermodynamically stable (Rosen, 2004). Even though using microemulsion technique provides >90% oil extraction efficiency as shown in Table 3; it requires a high performance of demulsification process.

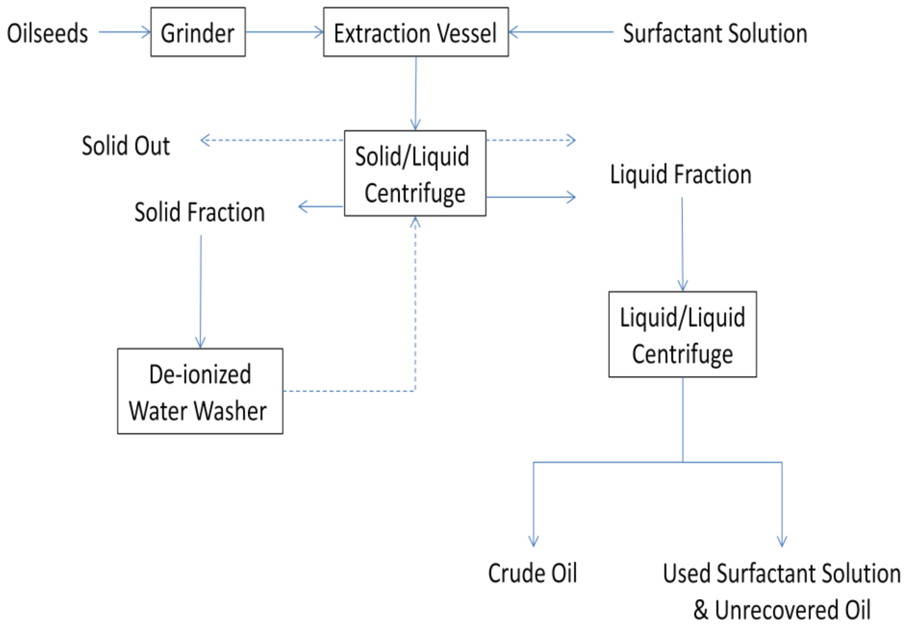


Figure 11 Schematic diagram of laboratory-based pilot scale processing of peanut and canola oil extraction. Solid line (—): surfactant wash step; Dash line (- - -); DI wash step (Do and Sabatini, 2011).

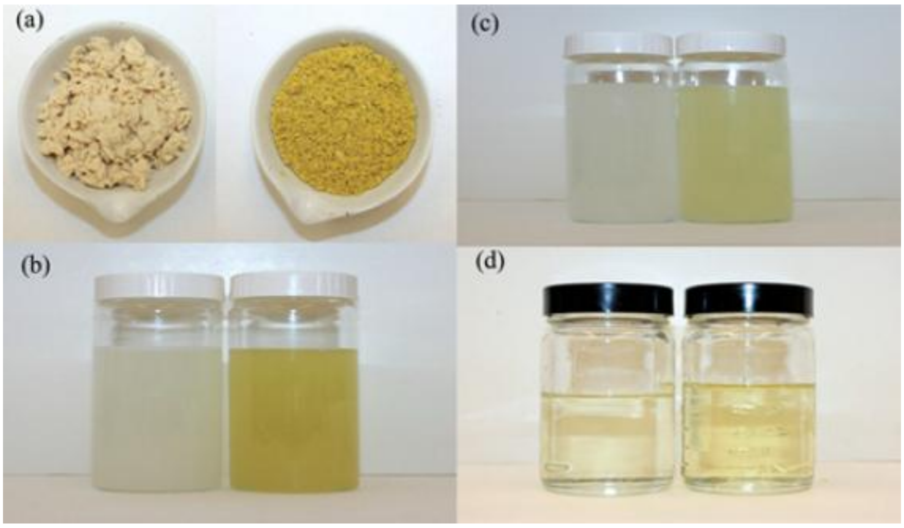


Figure 12 Selected products at different stage of ASE and DI washing at optimum conditions of peanut and canola from left to right, respectively. (a) peanut and canola flours (b) liquid fraction from L=L centrifuge of surfactant wash step (c) liquid fraction from L=L centrifuge of DI washing step (d) free oil crude oil recovered from L=L centrifuge (Do and Sabatini, 2011).

Table 3 Summary of the extraction process and oil extraction efficiency of aqueous surfactant-assisted extraction method.

	Reference	Naksuk et al. (2009)	Do and Sabatini (2010)	Kadioglu et al. (2011)
	Oilseed and sample size	Palm kernel (1g)	Peanut and Canola (2 g)	Corn germ (4 g)
	Surfactant system	Comperland KD (3% wt) Alfoterra 145- 5PO (0.1 %wt) NaCl (10 %wt)	C10-18PO-2EOsulfate (0.15 %wt) NaCl (6 %wt) for peanut NaCl (5 %wt) for canola	C12,14–10PO–2EOsulfate (0.4 %wt) NaCl (1 %wt)
Pretreatment	Grinding	Food processor	Food processor	Coffee mill
	Dehulling	Yes	Yes	Not Reported
	Size Selection	US Sieve size No.40-70 (0.21-0.42 mm)	US Sieve size No.40-70 (0.21-0.42 mm)	US Sieve size No.40-70 (0.21-0.42 mm)
	Thermal Treatment	Not Reported	104 ^{o}C with 35 mins	Yes (dried corn germ)
Extraction	Seed-Liquid ratio	1 to 10 (g/mL)	2 to 10 (g/g)	1 to 10 (g/g)
	Extraction Duration	Not Reported with 30 min	Horizontal shaker 150 cycle/min with 30 min	Horizontal shaker 250 cycle/min with 45 min
	Separation	Not Reported	Centrifuge speed 2,170 g with 30 min	Centrifuge speed 3,500 rpm with 20 min
	Oil Extraction Efficiency	93.99 % (based on soxhlet extraction)	93-95 % (based on soxhlet extraction)	83 % (based on hexane solvent in ASE)

Table 4 Summary of quality analysis of extracted vegetable oil from Table 3.

Reference	Naksuk et.al (2009)		Do and Sabatini (2010)				Kadioglu et.al (2011)		
Oilseed	Palm Kernel		Pea Nut		Canola		Corn Germ		
Extraction method	Hexane	Surfactant	Hexane	Surfactant	Hexane	Surfactant	Hexane	Surfactant	Enzymatic
Color	Clear Yellow	Clear Yellow	-	-	-	-	-	-	-
Water in oil (%wt)	0.385	0.191	-	-	-	-	-	-	-
Triglycerols (%wt)	-	-	-	-	-	-	97.1	92.9	98
Free fatty acid (%wt)	-	-	0.7	0.05	0.6	0.04	-	-	-
12 h cold test	-	-	Pass	Not Pass	Pass	Not Pass	-	-	-
Triglycerol Profile (%wt based on total Triglycerol)									
(C18:3) : (C18:1) : (C18:1)	-	-	-	-	7.7	8.45	-	-	-
(C18:2) : (C18:2) : (C18:1)	-	-	11	14.3	-	-	-	-	-
(C18:2) : (C18:1) : (C18:1)	-	-	14.8	14	24.7	23.9	-	-	-
(C18:2) : (C18:1) : (C16:0)	-	-	10.1	11.8	-	-	-	-	-
(C18:1) : (C18:1) : (C18:1)	-	-	10	14.1	47.8	44.4	-	-	-
Fatty acid (%wt based on total fatty acid)									
C12:0	49.41	49.52	-	-	-	-	-	-	-
C14:0	17.56	17.44	-	-	-	-	-	-	-
C16:0	9.24	9.17	-	-	-	-	-	-	-
C18:0	2.73	2.74	-	-	-	-	-	-	-
C18:1	18.18	18.21	-	-	-	-	-	-	-
C18:2	2.88	2.92	-	-	-	-	-	-	-

2.3 Jatropha *curcas* L.

Due to the impact on food security by using edible oil as the biodiesel feedstock, the non-edible oil deserves special attention. Among of them, Jatropha *curcas* L. (jatropha) or physic nut shows a good potential (Carels, 2009). It provides high yield (2000-4000 kg/ha) (Carels, 2009), and high oil content (60%) (Veronique, Chornick and James, 2002). Moreover, jatropha can grow on wasteland, so it has a smaller impact on land usage (Achten et al., 2008; Kumar and Sharma, 2008).

Figure 13 Jatropha *curcas* L. seed.
http://upload.wikimedia.org/wikipedia/commons/5/54/J_curcas_seed_ies.jpg

The jatropha oil has a superior quality, including better oxidative stability compared to soybean oil, lower viscosity compared to castor oil, and lower pour point compared to palm oil (Augustus, Jayabalan and J, 2002). This is due to the high proportion of unsaturated fatty acid (77.5%), comprising of oleic acid (C18:1) and linoleic acid (C18:2) with 42.02 and 35.38%, respectively (Achten et al., 2008).

Table 5 Fatty acid composition in jatropha and canola oil.

Fatty acid	Composition (%)	
	Jatropha (Achten et al., 2008)	Canola (Gunstone et al., 2000)
Palmitic acid (C16:0)	14.54	3.90
Strearic acid (C18:0)	6.30	1.90
Oleic acid (C18:1)	42.02	64.10
Linoleic acid (C18:2)	35.38	18.70

2.4 Canola (CANadian Oil, Low Acid)

Canola is a trade mark of genetic modified rape seed (Brassica *napus* L.). It has been developed to decrease the proportion of eruric acid, which may be toxic for humans, from 45% in rape seed oil to below than 2% in canola oil (Gunstone et al., 2000). The oil content of canola seed is very economical for extraction with more than 40% oil of seed weight. Even there is a natural range in fatty acid composition; the main composition of canola oil is still oleic acid (C18:1) which is accounted for more than 60% of the total fatty acid. Due to the abundance of monounsaturated fatty acid, canola oil has been applied to many products; for instance, cooking oil, biodiesel, lubricants, surfactant, paints and inks, and polymers (Gunstone, 2004).

Moreover, there is growing interest in biofuel crop due to biofuel support policies. Energy Independence & Security Act in 2007 (EISA) set the target of biofuel production at 12.95 billion gallon in 2010, 20.5 billion gallon in 2015, and 36 billion gallon in 2022 (Cui et al., 2010). Therefore, there will be incentive for developing biodiesel from canola oil in this recent future, especially in North Dakota state where is accounted for approximately 92% of US domestic canola production in 2002 (Berglund, Mckay and Knodel, 2011).

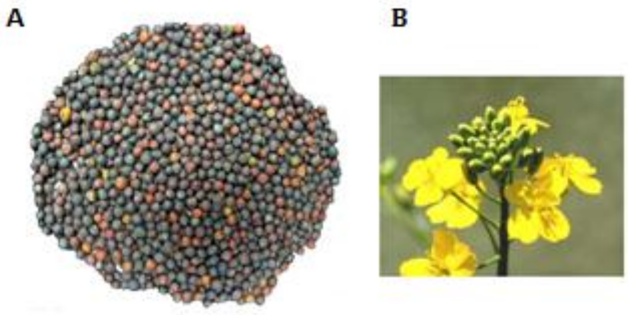


Figure 14 Picture of (a) canola seed and (b) canola tree (NCCRP, 2011).

CHAPTER 3

MATERIALS AND METHODS

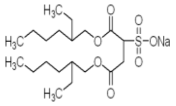
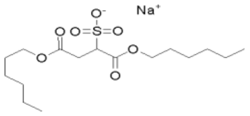
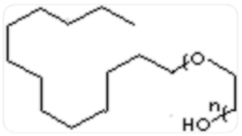
3.1 Materials

Sodium bis(ethylhexyl) sulfosuccinate (AOT) and sodium dihexyl sulfosuccinate (AMA) were purchased from Fisher Scientific Company LLC (Atlanta, GA). Sodium dodecyl sulfate (SDS) and n-hexane were purchased from Sigma-Aldrich Co. LLC (St Louis, MO). Four nonionic surfactants, the fatty alcohol ethylene oxide series (LS-series), were kindly received from PTT Chemical Public Company Limited (Thailand). The properties and structure of surfactant were presented in Table 6. NaCl with 99% purity was purchased from the Fluka Chemical Crop. (Milwaukee, WI). Jatropha oil and seed were purchased from Kasetsart University (Thailand). Wesson® pure canola oil was purchased from ConAgra Food, Inc. (Omaha, NE) and was used to measure dynamic IFT with surfactant system. Flavorite® pure canola oil was purchased from SUPERVALU International (Tacoma, WA) and was used to compare the oil quality. Canola seeds were kindly provided by Dr. Mukhles Rahman of the Plant Sciences Department of North Dakota State University.

3.2 Dynamic Interfacial Tension Measurement

The dynamic interfacial tension (IFT) between surfactant system solution and vegetable oil was measured by a spinning drop tensiometer (model SVT20), purchased from Dataphysic®(Filderstadt, Germany). The analyze procedure was modified from Witthayapanyanon et al. (2006). The surfactant solution served as the dense phase; while vegetable oil was used as a light phase at 25^{o}C with spinning speed at 6000 rpm. In this work, dynamic IFT was defined as the IFT between the fresh surfactant system solution and the vegetable oil after 30 min, which time the IFT value became stable.

Table 6 Surfactant properties and structure.

Surfactant	Type	HLB	MW (g/mol)	Molecular Formula	Molecular Structure
AOT	anionic	10.5	444.56	$C_{20}H_{37}NaO_7S$	
AMA	anionic	14	388	$C_{16}H_{29}NaO_7S$	
SDS	anionic	40	288.38	$NaC_{12}H_{25}SO_4$	
Dehydol LS-1	nonionic	3.6	244	$C_{15}H_{32}O_2$	
Dehydol LS-2	nonionic	6.1	288	$C_{17}H_{36}O_3$	
Dehydol LS-3	nonionic	7.9	332	$C_{19}H_{40}O_4$	
Dehydol LS-9	nonionic	13.4	596	$C_{31}H_{64}O_{10}$	

3.3 Hydrophile-Lipophile Balance Value Calculation

The hydrophile-lipophile balance (HLB) value is the number between 1 and 40 which indicates the emulsification behavior. HLB value also relates to the balance between the hydrophilic and lipophilic portions of the surfactant molecule (Rosen, 2004). In case of mixed surfactant, HLB is calculated based on weight fraction of each surfactant (Equation 2).

$$HLB\ of\ mixture\ surfactant = (HLB_A\ x\ X_A) + (HLB_B\ x\ (1-X_A)) \qquad \text{Equation 2}$$

where HLB_A and HLB_B are HLB value of surfactant “A” and “B”, respectively. X_A is weight fraction of surfactant “A” in the system (Rosen, 2004).

3.4 Oilseed Pretreatment

Prior to pretreatment, jatropha seeds were evaluated for moisture content by dried in a hot air oven 105°C over night; while grain moisture analyzer (model GAC 2100, DICKEY-john®, Auburn, IL) was applied in case of canola seeds. Only jatropha seeds were dehulled before grinding. The oilseeds were ground for 30 s by Protor-Silex coffee grinder (model E160BY, Hamilton Beach Brands, Inc., Southern Pines, NC). Ground oilseed particle size between 0.212 and 0.425 mm were applied in this study as a suggestion size by Do and Sabatini (2010), Kadioglu et al. (2011) and Naksuk et al. (2009).

3.5 Aqueous Surfactant-assisted Extraction (ASE)

Jatropha Ground jatropha (2 g) was suspended in 20 mL of surfactant solution. The suspension was then mixed for 30 min at 5th speed by BECTHAI® multi-magnetic bar stirrer (model RO-10P, Thailand). The slurry was centrifuged 20 min at 2000 x g by Sorvall Stratos Centrifuge (Fisher Scientific Company LLC, Atlanta, GA). After centrifugation two fractions were obtained: liquid fraction (oil, emulsion, and extraction medium) and extracted meal. The extracted meal was dried in a hot air oven 105°C over night for further oil detachment efficiency evaluation.

Canola Ground canola (4 g) was suspended in 40 mL of surfactant solution. The suspension was then mixed for 30 min at 1000 rpm on a PMC Data Plate® digital hot plate/stirrer model 730, and the slurry was then centrifuged 20 min at 2000 X g (model CR412, Jouan, Inc., Winchester, VA). After centrifugation two fractions were obtained: liquid fraction (oil, emulsion, and extraction medium) and extracted meal. The liquid fraction was demulsified by heating to 70°C for 30 min. For quantify the extracted oil only, n-hexane (50 mL) was then added to facilitate recovery of the extracted oil once the temperature was reduced to 30°C. The sample was allowed to stand in a separatory funnel for 10 min to separate the two immiscible phases. The bottom aqueous extraction medium was decanted;

the upper organic phase (oil plus n-hexane) was desolventized at 105°C overnight and weighed.

3.6 Oil Content of Oilseed and Extracted Meal

Crude oil was extracted from ground canola seed and residual oil from extracted canola meal via Soxhlet extractor, using n-hexane as solvent, as described in the AOCS official methods AM2-93 (American Society for Testing and Materials, 2009). The amounts of oil recovered were defined as the total oil (TO) and residual oil (RO) (g oil / g dried oilseed or meal) for ground seed and extracted meal, respectively. The "oil extraction efficiency" was calculated based on the weight of extracted oil (EO) from the extraction process relative to the total oil weight initially present in the ground seed sample (Equation 3a).

$$Oil\ Extraction\ Efficiency\ (\%) = \frac{EO}{TO} \times 100\% \qquad \text{Equation 3a}$$

However, in the case of ASE in this study, some extracted oil was lost to an emulsion, penalizing oil extraction efficiency. Thus, "oil detachment efficiency" (Equation 3b) was defined to better reflect the actual removal of oil from seed during extraction.

$$Oil\ Detachment\ Efficiency\ (\%) = \frac{(TO-RO)}{TO} \times 100\% \qquad \text{Equation 3b}$$

It should be noted that, given a better demulsification process, the value of oil detachment and oil extraction efficiency will be the same.

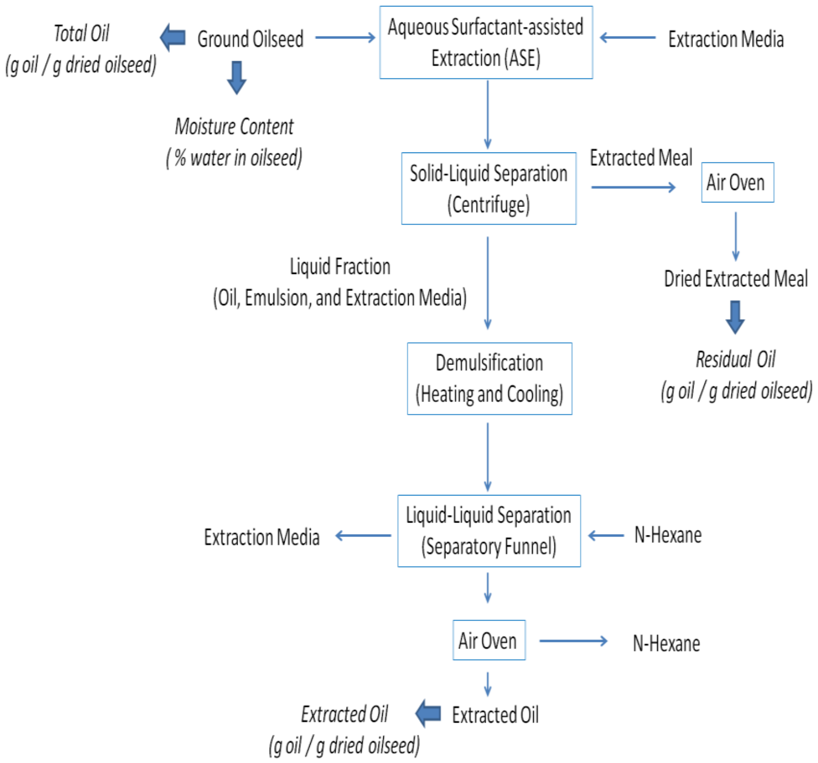


Figure 15 Diagram of aqueous surfactant-assisted extraction

3.7 <u>Experimental Design</u>

The experiments were divided into two main parts. Part 1 (experiment 3.7.1 – 3.7.4) was to formulate the surfactant system which was the most suitable to extract jatropha and canola oil based on dynamic IFT. The selected surfactant system and ASE extraction condition of canola oil in Part 1 were applied into Part 2 (experiment 3.7.5 – 3.7.9). The main objective of this part was to maximize the canola oil extraction efficiency of ASE process by varied extraction conditions. The experimental design was summarized in Table 7 (Part 1) and Table 8 (Part 2).

It should be noted that the dynamic IFT measurement of jatropha and canola and ASE process of jatropha in Part 1 were conducted at Chulalongkorn University (Thailand). The ASE process of canola in Part 1 and Part 2 were conducted at North Dakota State University (USA).

3.7.1 Anionic Surfactant Selection

Three anionic surfactant solution (1 %wt): AOT, AMA and SDS were evaluated the dynamic IFT with jatropha and canola oil. The surfactant solution that provided the lowest dynamic IFT was selected for the subsequent experiments.

3.7.2 Effect of Additional Nonionic Surfactant

The impact of additional 0.01M nonionic surfactant (LS-series) on dynamic IFT between anionic surfactant solution and vegetable oil was investigated. Four nonionic surfactants: LS-1, 2, 3 and 9 were introduced into selected anionic surfactant solution from experiment 1.

3.7.3 Effect of Electrolyte

The impact of electrolyte (NaCl) concentration on a dynamic IFT between the surfactant system from experiment 3.7.2 with jatropha and canola oil was investigated. The NaCl concentration was varied between 0 and 0.5 M in increments of 0.025 M.

3.7.4 Effect of Interfacial Tension on ASE

The correlation between a dynamic IFT and oil detachment efficiency was evaluated. The series of surfactant solution from experiment 3.7.3 was utilized as an extraction medium in the ASE method of each oilseed as described above. It should be noted that the jatropha extraction was conducted at Chulalongkorn University; while canola part was conducted at North Dakota State University with the different magnetic stirrer. Only selected surfactant system and extraction condition of canola were applied into the further experiments (Part 2).

Table 7 Summary of experimental design in Part 1 (3.7.1 – 3.7.4).

Experimental Design	3.7.1	3.7.2	3.7.3	3.7.4	Part 2
Vegetable Oil and Seed	Jatropha and Canola Oil	Jatropha and Canola Oil	Jatropha and Canola Oil	Jatropha and Canola Seed	Canola Seed
Anionic Surfactant (1 %wt)	AOT, AMA, SDS	Selected	Selected	Selected	Shown in Table 8
Nonionic Surfactant (0.01 M)	-	With and Without LS-1, 2, 3, 9	With and Without LS-1, 2, 3, 9	With and Without LS-1, 2, 3, 9	Shown in Table 8
NaCl Concentration (M)	-	-	0 - 0.5	0 - 0.5	Shown in Table 8
Extraction Time (min)	-	-	-	30	Shown in Table 8
Extraction Temperature (^{o}C)	-	-	-	20	Shown in Table 8
ASE Extraction	-	-	-	Single	Shown in Table 8
Solid-Liquid Ratio (g : mL)	-	-	-	1:10	Shown in Table 8
Extraction Method	-	-	-	Stirring	Shown in Table 8

Table 8 ASE extraction conditions for canola seed in Part 2 (3.7.5 – 3.7.9).

Experimental Design	3.7.5	3.7.6	3.7.7	3.7.8	3.7.9
Surfactant Concentration (M)	0.005, 0.01, 0.02, 0.03	Selected	Selected	Selected	Selected
Extraction Time (min)	30	15, 30, 45, 60	Selected	Selected	15
Extraction Temperature (^{o}C)	20	20	20, 50, 70	20	20
ASE Extraction	Single	Single	Single	Single	Triple Extraction with Three-stages
Solid-Liquid Ratio (g : mL)	1:10	1:10	1:10	1:30, 1:20, 1:10, 1:7, 1:5	1:5, 1:7, 1:10
Extraction Method	Stirring	Stirring, Ultrasonication	Stirring	Stirring	Stirring

3.7.5 Effect of Surfactant Concentration

The impact of aqueous surfactant concentration on oil detachment and oil extraction efficiency of canola oil extraction was evaluated at four concentrations: 0.005, 0.01, 0.02 and 0.03 M. The solid-liquid ratio was 1 g : 10 mL. A magnetic stirrer was applied with for 30 min at 20^{o}C. The SDS concentration that yielded the highest oil detachment and oil extraction efficiency was selected for the subsequent experiment.

3.7.6 Effect of Stirring Time and Ultrasonication

The impact of magnetic stirring and ultrasonication time on oil detachment and oil extraction efficiency were investigated at four levels: 15, 30, 45 and 60 min. Ultrasonication was performed using an Aquasonic ultrasonic cleaner (11.4 kW-h/sample, 25 kHz, model 150 HT, VWR Scientific Product, West Chester, PA). Three glass beakers containing ground canola and surfactant solution were placed in the ultrasonic bath with 4 L of distilled water. Selected SDS concentration from experiment 3.7.5 was applied with solid-liquid ratio 1 g : 10 mL at 20^{o}C for both the magnetic stirrer and ultrasonication bath. The extraction time that provided the highest oil detachment and oil extraction efficiency was selected for the subsequent experiment.

In addition, the effect of different ratios of magnetic stirrer and ultrasonication time on oil detachment efficiency was evaluated. The ratio of ultrasonication time : magnetic stirrer time was varied at five levels: 0:60, 15:45, 30:30, 45:15 and 60:0 (min:min). Use of the ultrasonication bath preceded the magnetic stirrer.

3.7.7 Effect of Extraction Medium and Temperature

The impact of extraction medium and extraction temperature on oil detachment efficiency were evaluated. Water and aqueous surfactant solution (utilizing selected concentration from experiment 3.7.5) were used as extraction media. The extraction temperature was varied at three levels: 20, 50 and 70°C. The solid-liquid ratio was 1 g : 10 mL with stirring time selected from experiment 3.7.6. Moreover, n-hexane was used as a reference nonpolar solvent at 20°C, because of its common use for vegetable oil extraction.

3.7.8 Effect of Solid-Liquid Ratio

The impact of solid-liquid ratio on oil detachment and oil extraction efficiency was evaluated at five levels: 1:30, 1:20, 1:10, 1:7 and 1:5 (g : mL). The surfactant concentration and stirring time were selected from the previous experiments at 20°C.

3.7.9 Effect of Triple Extraction with Three-stages

The impact of triple extraction with three-stages (3E3S) on oil detachment and oil extraction efficiency was investigated at three levels of solid-liquid ratio: 1:10, 1:7 and 1:5 (g : mL). The surfactant concentration was selected from the previous experiment. The extraction temperature was 20°C. The stirring time of each extraction stage was 15 min. The three stages (three batches of ground canola), denoted as A, B and C, were operated in six steps (Figure 16). After completion of a step, the liquid fraction (LF) from the previous extraction stage was used as extraction medium for the next stage. For example at solid-liquid ratio 1:10, each fresh surfactant solution (FS), including FS 1, FS 2 and FS 3, was 40 mL with 4 g of ground canola in each stage A, B and C. The liquid fractions from extraction Stage A: LF A1, LF A2 and LF A3, were used as extraction media for Stage B in Step 2, 3 and 4, respectively. The extracted meal from Stage A of Step 1 was re-extracted by using fresh SDS solution, FS 2 and FS 3 in Stage A of Step 2 and 3, respectively. The ground canola in each stage was extracted three times with total extraction time 45 min, exclude the separation time by centrifugation. After the extraction process, approximately 12 g of extracted meal and 120 mL of liquid fraction were obtained in case of solid-liquid ratio 1:10. The total liquid fraction and total extracted meal were analyzed to determine the oil extraction and oil detachment efficiency, respectively, as described above.

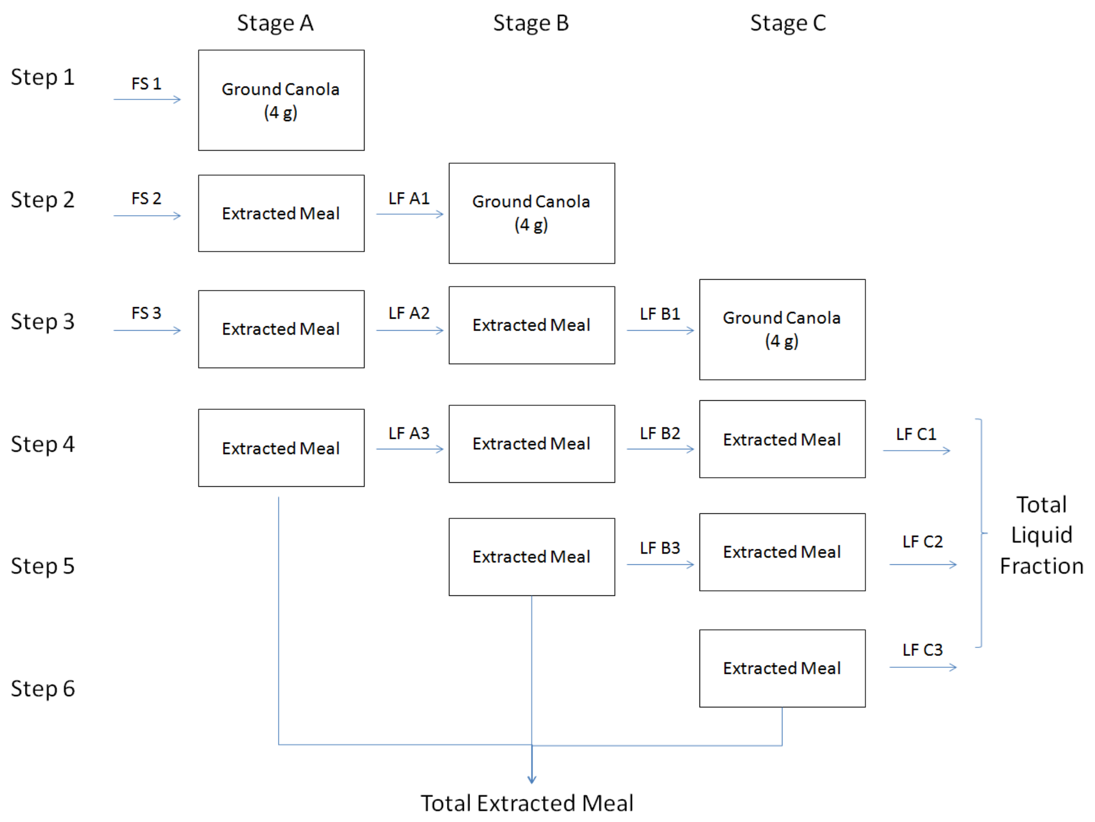


Figure 16 Diagram of triple extraction with three-stage. FS was fresh surfactant solution and LF was liquid fraction.

3.8 Scale up of the ASE Process

The batch size for the ASE process was increased to 300 g of pretreated ground canola using the best combination of extraction conditions from the previous experiments which were surfactant concentration, extraction time, extraction temperature and solid-liquid ratio. An agitator agitator (model VW0708021, Arrow Engineering Co., Inc., Hillside, NJ) with a pitched- three blade impeller was used as a mixer at 1000 rpm. The suspension was heated to 70°C for 30 min; and then allowed to stand for an additional 3 h. The upper layer, approximately 360 mL, was decanted off and centrifuged 45 min at 3750 X g (4000 rpm) to separate the crude oil from extraction medium. This extracted oil was dried in a vacuum oven at 60°C, 80 kPa for 24 h before transferred to a dark amber bottle for further quality analysis.

3.9 Other Extraction Methods

A screw press (Komet Oil Expeller S 87G, IBGMonforts, Germany) was operated following the conditions of Haagenson et al. (2010) with a pre head temperature of 60°C. The screw press oil was transferred to a dark amber bottle without refining.

Soxhlet extraction with n-hexane was performed following the AOCS official methods AM2-93 (American Oil Chemists' Society, 1999) with 30 g of ground canola/batch using an extraction time of 4 h. The extracted oil was transferred to a dark amber bottle without refining.

3.10 Extracted Oil Quality Analysis

The extracted canola oil from the scaled up ASE process, screw press, and Soxhlet extraction were analyzed for biodiesel feedstock quality, specifically water content, acid value, and phosphorus content (Van Gerpen and Knothe, 2004), and compared with commercial canola oil. Water content was determined using a Karl Fischer Coulometer (Model DL 32, Mettler Toledo, Inc., Columbus, OH). Free fatty acid content (acid value) was determined by KOH titration, with phenolphthalein as an indicator (ASTM D 664). Phosphorous content of extracted oils were quantified by inductively couple plasma (ICP) at Archer Daniels Midland (Enderlin, ND).

3.11 Statistical Analysis

All experiments were performed in triplicate. Error bars on charts were represent ± 1 SD. For quality analysis, each sample was analyzed in triplicate except phosphorous content with duplicate analysis. Data were analyzed using the PROC ANOVA (SAS Institute, 2008). An F-protected LSD ($P \leq 0.05$) was calculated for main effect mean comparisons. Significant differences ($P \leq 0.05$) between means of two way and higher order interactions were determined as twice the standard error of the mean (Snedecor and Cochran, 1980).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Anionic Surfactant Selection

Among three anionic surfactants in this study, AOT and SDS provided the lower dynamic IFT with jatropha oil and canola oil, respectively (Figure 17). One explanation of these results was the suitable molecular structure between surfactant and vegetable oil. Comprised of the same sulfosuccinate group, AOT gained the lower dynamic IFT than AMA for both jatropha and canola oil. This might be because the longer carbon chain length of AOT which was more suitable to jatropha and canola oil. However, with the shortest carbon chain length, SDS provided the lower dynamic IFT than AMA for jatropha oil, and the lowest dynamic IFT with canola oil. The sulfate group of SDS might compensate its shorter carbon chain length in reducing dynamic IFT with two vegetable oils.

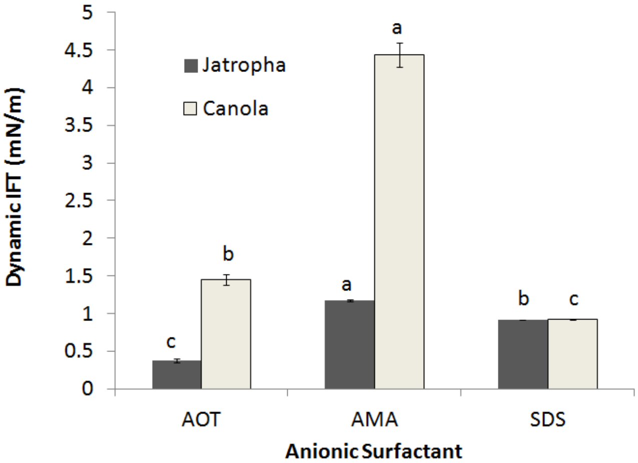


Figure 17 Dynamic IFT between 1 %wt anionic surfactants (AOT, AMA and SDS) with jatropha and canola oil. Means within the bar graph followed by the same color and letter are not significantly different at $P \leq 0.05$.

Changes in carbon chain length and functional groups of surfactants impact on the Winsor R ratio (R) of oil-surfactant-water system. This ratio reflects the proportion between net interaction energy of hydrophobic/hydrophilic parts of the system, consisting of vegetable oil (O), water (W) and surfactant (S) as presented in Equation 4. The lowest IFT is produced when R=1 and the value of Net A_{SO} and Net A_{SW} are high (Rosen, 2004). As the result, AOT and SDS were selected the subsequent experiments of jatropha and canola, respectively.

$$R = \frac{Net\ A_{SO}}{Net\ A_{SW}} = \frac{A_{SO} - A_{OO} - A_{LL}}{A_{SW} - A_{WW} - A_{HH}} \qquad \text{Equation 4}$$

where Net A_{SO} is the net interaction between the surfactant and oil (hydrophobic), Net A_{SW} is the net interaction between the surfactant and water (hydrophilic), A_{SO} is the interaction between the surfactant and oil, A_{SW} is the interaction between the surfactant and water, A_{OO} is the interaction energy among oil molecules, A_{LL} is the interaction among the tails of the surfactant molecules, A_{WW} is the interaction energy among the water molecules, and A_{HH} is the interaction among the surfactant heads (Witthayapanyanon et al., 2006).

4.2 Effect of Introducing Nonionic Surfactant

Introducing nonionic surfactant LS- series into 0.02 M AOT solution and 0.03 M SDS solution reduced the dynamic IFT of the surfactant solution and vegetable oil, except the mixed surfactant solution of LS-9 (Figure18a and 18b). Similar results with mixed surfactant solution on a dynamic IFT are observed in several works (Naksuk et al., 2009; Tongcumpou et al., 2006; Zhu et al., 2009). Changes in these IFT values can be explained via modification of the HLB value of the surfactant system due to the presence of nonionic surfactant, and hence the effect on the Winsor R ratio (Table 9). The Winsor R ratio of anionic surfactant is naturally < 1 due to its high water solubilization (high Net A_{SW}). Introducing a nonionic surfactant (low HLB value surfactant) reduces the HLB value of the surfactant system, resulting in increase Net A_{SO}. Therefore, the Winsor R ratio was closer to 1. However, further decreasing the HLB value tends to increase the Winsor R ratio (R>1), and hence increase the IFT value. The "U" shape correlation between HLB value and IFT was observed (Figure 17). However, dynamic IFT values of these systems were still higher than the suggestion level at < 0.01 mN/m (Do and Sabatini, 2010; Naksuk et al., 2009). Therefore, all surfactant systems were selected for the next experiment.

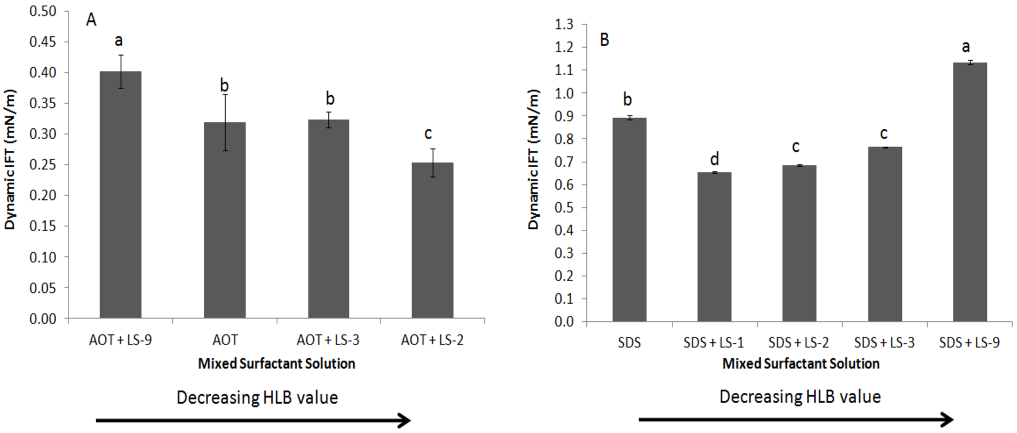


Figure 18 Dynamic IFT of mixed surfactant solution with (a) jatropha oil and (b) canola oil. Means within the bar graph followed by the same letter are not significantly different at $P \leq 0.05$.

Table 9 HLB value of mixed surfactant solution.

Jatropha Part			Canola Part		
Surfactant System	HLB	Mixed HLB	Surfactant System	HLB	Mixed HLB
AOT (0.02 M)	10.5	10.5	SDS (0.03 M)	40	40
AOT (0.02 M)	10.5	9.01	SDS (0.03 M)	40	31.99
LS-1 (0.01 M)	3.6		LS-1 (0.01 M)	3.6	
AOT (0.02 M)	10.5	9.42	SDS (0.03 M)	40	31.53
LS-2 (0.01 M)	6.1		LS-2 (0.01 M)	6.1	
AOT (0.02 M)	10.5	9.79	SDS (0.03 M)	40	31.1
LS-3 (0.01 M)	7.9		LS-3 (0.01 M)	7.9	
AOT (0.02 M)	10.5	11.66	SDS (0.03 M)	40	29.15
LS-9 (0.01 M)	13.4		LS-9 (0.01 M)	13.4	

4.3 Effect of Electrolyte

Increasing electrolyte (NaCl) concentrations affected the IFT value of every surfactant systems from experiment 2. The electrolyte concentration providing the lowest IFT in the surfactant system is named optimum salinity (S*) (Rosen, 2004) as shown in Table 10. Increasing NaCl concentration to S* results in decrease dynamic IFT. However, further increase NaCl concentration tent to increase dynamic IFT value (Figure 20). Salt or electrolyte is commonly used in ionic surfactant solutions to modify the IFT value by changing the Winsor R ratio (Do and Sabatini, 2010; Kadioglu et al., 2011; Naksuk et al., 2009; Salager et al., 1979; Tongcumpou et al., 2006; Witthayapanyanon et al., 2006; Zhu et al., 2009). The electrolyte molecule is inserted between surfactant monomers in micelle molecules, leading to a decrease in electrical interaction between head groups of ionic surfactants. The A_{SW} and Net A_{SW} are reduced, thus an increase in the Winsor R ratio, as shown in Eq.3 (Rosen, 2004; Witthayapanyanon et al., 2006). At S*, the Winsor R ratio is equal to 1 resulting in providing the lowest IFT. After S*, the Winsor R ratio is >1, thus IFT was increased. The surfactant solution AOT with LS-1 and SDS with LS-series were not selected to the next experiment since the high dynamic IFT; and surfactant precipitation was observed in mixed surfactant system at high NaCl concentration (Figure 19).

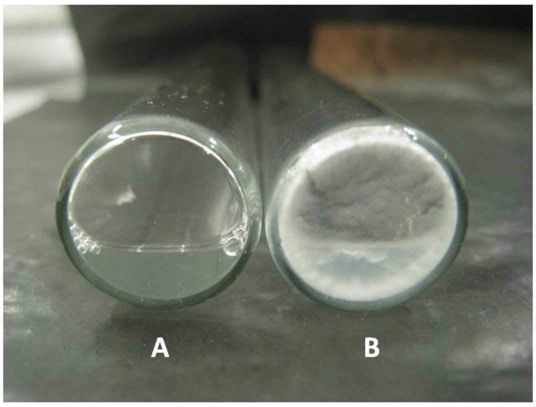


Figure 19 At 0.2M NaCl solution (a) 0.03M SDS solution and (b) 0.03M SDS with 0.01M LS-1 solution.

Table 10 Optimum salinity and dynamic IFT of each surfactant system.

Jatropha Part			Canola Part		
Surfactant System	S* (M)	IFT (mN/m)	Surfactant System	S* (M)	IFT (mN/m)
AOT (0.02 M)	0.06	0.188±0.006	SDS (0.03 M)	0.325	0.148±0.001
AOT (0.02 M) LS-1 (0.01 M)	-	-	SDS (0.03 M) LS-1 (0.01 M)	0.03	0.565±0.004
AOT (0.02 M) LS-2 (0.01 M)	0.05	0.087±0.001	SDS (0.03 M) LS-2 (0.01 M)	0.1	0.571±0.006
AOT (0.02 M) LS-3 (0.01 M)	0.09	0.080±0.003	SDS (0.03 M) LS-3 (0.01 M)	0.35	0.602±0.008
AOT (0.02 M) LS-9 (0.01 M)	0.40	0.078±0.001	SDS (0.03 M) LS-9 (0.01 M)	0	1.136±0.010

Note: LS-1 (0.01M) could not be dissolved in 0.02 M AOT solution.

4.4 Effect of interfacial tension on ASE

The correlation between dynamic IFT and oil detachment efficiency was observed in ASE of jatropha (Figure 21); but there was no such a relationship in case of canola (Figure 20). The low dynamic IFT value implied that the energy requirement (shear force, heat, and gravity) to disperse vegetable oil to extraction media was low. Thus at the same extraction condition (temperature, stirring speed, extraction time) reducing dynamic IFT increased the oil detachment efficiency. This correlation has been observed in many works by using the ultralow IFT (0.01 mN/m) with a horizontal shaker at 150-250 cycle/min (Do and Sabatini, 2010; Kadioglu et al., 2011; Naksuk et al., 2009). Even though the lowest dynamic IFT value in this study was 10 times higher than the suggestion level, desirable oil detachment efficiency was achieved. In case of canola, the oil detachment efficiency at the highest dynamic IFT, 0.869 mN/m, was not significantly different with that of the lowest dynamic IFT ,0.148 mN/m. This might be due to the high shear force from magnetic stirrer at 1,000 rpm might compensate the high dynamic IFT value.

Moreover, the commercial canola oil, used in IFT measurement, is passed several refining processes. Some components in crude oil, such as chlorophyll, phospholipids and proteins, are removed. Phospholipids and proteins are an amphiphilic substance, so presence of them affects an IFT of the system. Therefore, a dynamic IFT value from commercial canola oil is not a good representative for crude oil that is extracted by the ASE method. Crude oil from a screw press extraction should be a better sample for IFT measurement.

The highest oil detachment efficiency of jatropha was 72.5% with a dynamic IFT value of 0.086 mN/m using 0.02M AOT, 0.01M LS-2 and 0.05M NaCl as an extraction medium. The highest oil detachment efficiency of canola was 80.7%, with a dynamic IFT value of 0.869 mN/m using 0.03M SDS solution as an extraction medium. However, an emulsion formation was observed that was a critical problem by using high shear force to compensate the dynamic IFT value at > 0.01 mN/m.

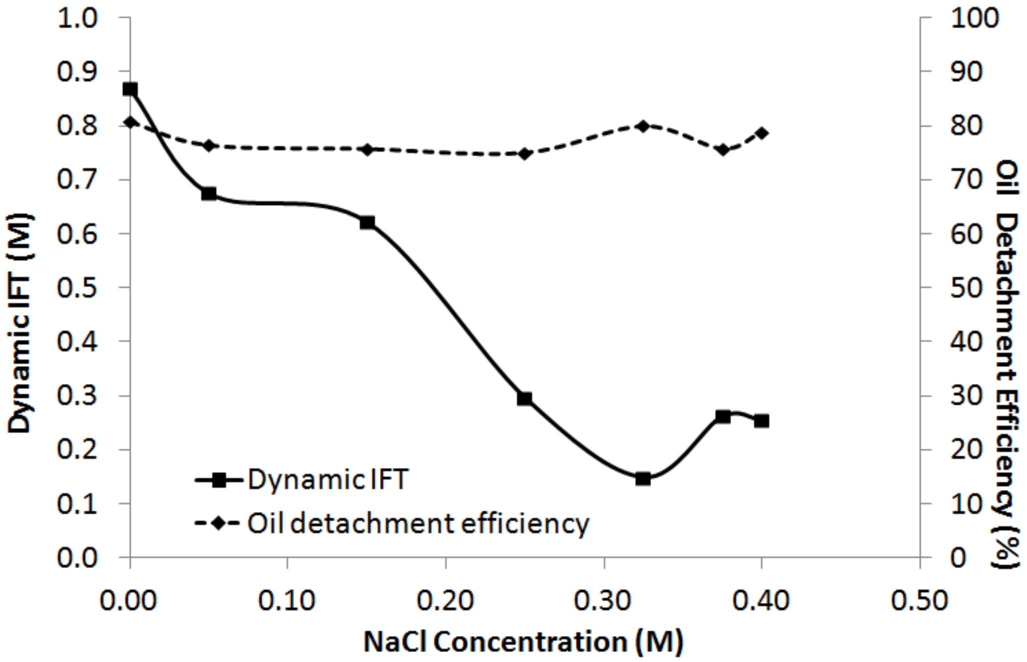


Figure 20 Correlation between dynamic IFT and oil detachment efficiency at various NaCl concentrations of canola oil with 0.03 M SDS

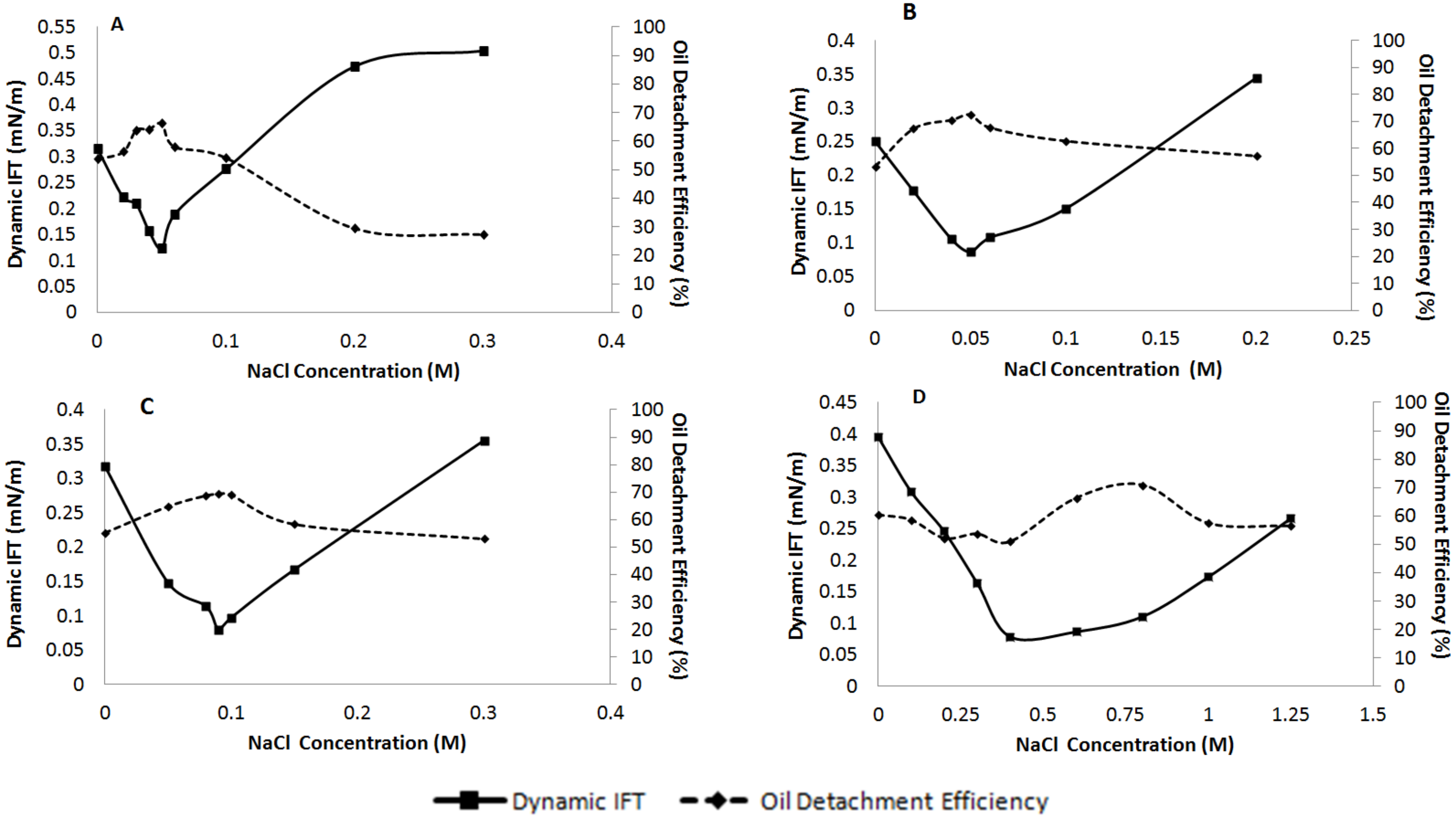


Figure 21 Correlation between dynamic IFT and oil detachment efficiency at various NaCl concentrations of jatropha oil with (a) 0.02M AOT, (b) 0.02M AOT with 0.01M LS-2, (c) 0.02M AOT with 0.01M LS-3 and (d) 0.02M AOT with 0.01M LS-9.

4.5 Effect of Surfactant Concentration

A previous experiments and study (Tuntiwiwattanapun, Wiesenborn and Tongcumpou, 2012) showed that SDS provided a lower IFT (< 1 mN/m) with canola oil than two other commercial anionic surfactants: sodium bis(ethylhexyl) sulfosuccinate (AOT) and sodium dihexyl sulfosuccinate (AMA). Increasing the SDS concentration from 0.005 M to 0.02 M resulted in an increase in both oil detachment and oil extraction efficiency, shown in Figure 21. This observation could be explained by a corresponding reduction in the IFT of the system (Do and Sabatini, 2010; Kadioglu et al., 2011; Naksuk et al., 2009).

At the critical micelle concentration (CMC) of each surfactant system, where the first micelle is formed, the IFT of the system is dramatically reduced (Rosen, 2004). In water, the CMC of SDS was 0.008 M at 25^{o}C (Pierce, 2004). However, in heterogeneous systems (surfactant solution and oilseed particles), the surfactant monomers are adsorbed on the particles surface. This reduces the IFT among solid and two liquid phases (oil and water) leading to detachment of oil into the surfactant solution (Kadioglu et al., 2011; Naksuk et al., 2009). Consequently, in heterogeneous systems, the CMC is generally higher than the system without oilseed particles. So, it can be expected that the CMC of SDS in the extraction process is higher than 0.008 M at 25^{o}C. The oil detachment and oil extraction efficiency achieved with 0.01 M SDS was significantly lower than that with 0.02 M SDS.

However, a further increase in concentration beyond 0.02 M SDS decreased oil extraction efficiency; since some of the detached oil was dissolved into the micelle. As a consequence, the oil detachment efficiency at 0.03 M SDS was slightly higher than that at 0.02 M SDS, but the oil extraction efficiency was lower (Figure 22). Therefore, the results indicated that the CMC was between 0.01 M and 0.02 M SDS, and the 0.02 M SDS solution was selected for subsequent experiments.

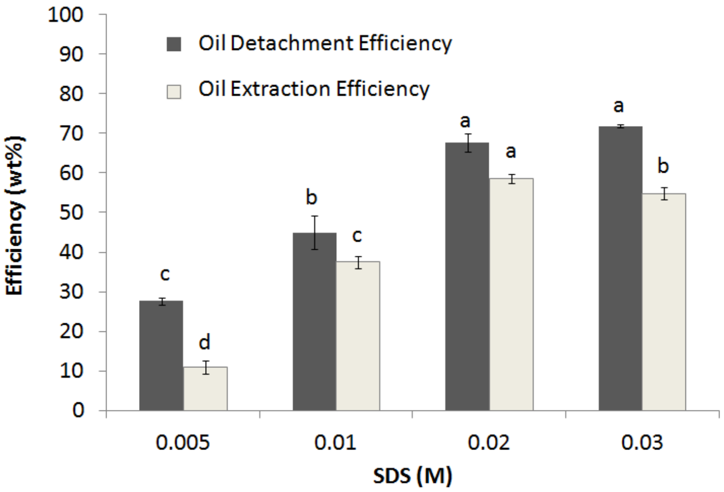


Figure 22 Effect of SDS concentration on oil detachment and oil extraction efficiency at 20°C with solid-liquid ratio 1 g : 10 mL, stirring for 30 min. Means within the bar graph followed by the same color and letter are not significantly different at $P \leq 0.05$.

4.6 Effect of Stirring Time and Ultrasonication

There was no increase in oil extraction or oil detachment efficiency after 45 min extraction time with a magnetic stirrer (Figure 23a). Similar results were observed using an ultrasonication bath (Figure 23b) with a similar power input (kW-h/sample). Increasing extraction time from 30 min to 45 min significantly increased oil detachment and oil extraction efficiency. One explanation may be a reduction of IFT during the extraction time. A preliminary study (data not shown) found the IFT steadily decreased after up to 30 min contact time and then become stable. Thus, that study might imply that the highest oil detachment and oil extraction efficiency should be achieved after 30 min extraction time. Ultrasonication provided a much lower oil extraction efficiency compared to that of magnetic stirrer at all four extraction times. This result might come from the hydrodynamic shear-force which was generated from air bubble cavitation by ultrasonic waves. This high shear force could enhance the emulsion formation, reducing oil extraction efficiency while still achieving high oil detachment efficiency.

The combination of ultrasonication and stirring on oil detachment efficiency was also investigated. However, there was no significant difference in oil detachment efficiency among these ratios, shown in Appendix B (Table 27). As a result of the above mixing study, subsequent extractions were carried out using the magnetic stirrer for 45 min. This resulted in the highest oil detachment efficiency, 80%.

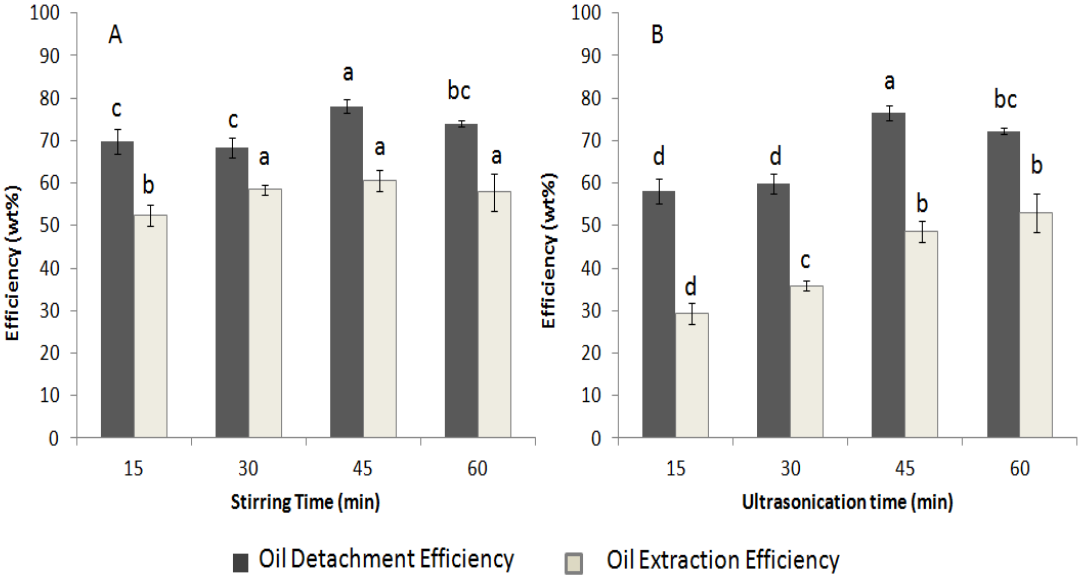


Figure 23 Effect of extraction time on oil detachment and oil extraction efficiency for 0.02 M SDS solution at 20°C with solid-liquid ratio 1 g : 10 mL when mixing with (a) a magnetic stirrer and (b) an ultrasonication bath. Means within the bar graph of both (a) and (b) followed by the same color and letter are not significantly different at $P \leq 0.05$.

4.7 Effect of Extraction Medium and Temperature

Increasing extraction temperature improved the oil detachment efficiency when water without surfactant was used as the extraction medium (Figure 24). In contrast, there was no significant impact of temperature on oil detachment efficiency in the case of surfactant solution. This is due to the fact that anionic surfactants such as SDS are generally insensitive to temperature (Rosen, 2004). Surfactant solution provided much higher oil detachment efficiency than water at every extraction temperature. The oil detachment efficiency achieved by using water was approximately half that of the SDS solution. This result could be explained by the IFT of the system. The IFT between water and vegetable oil is between 20 and 30 mN/m (Do and Sabatini, 2010; Gunstone, 2004), while the IFT between canola oil and SDS solution in this work was < 1 mN/m (Tuntiwiwattanapun et al., 2012). Therefore, surfactant solution reduced the heat energy required to disperse canola oil into the extraction medium. In addition, the oil detachment efficiency for SDS solution at any temperature treatment was not significantly different from that of n-hexane at 20°C (Figure 24). These results suggest the use of 0.02 M SDS solution as an alternative extraction medium to n-hexane for extraction at room temperature. It should be noted that the vegetable oil industry commonly uses n-hexane at 65°C with the oil extraction efficiency exceeding 95% (Beckel, Belter and Smith, 1946).

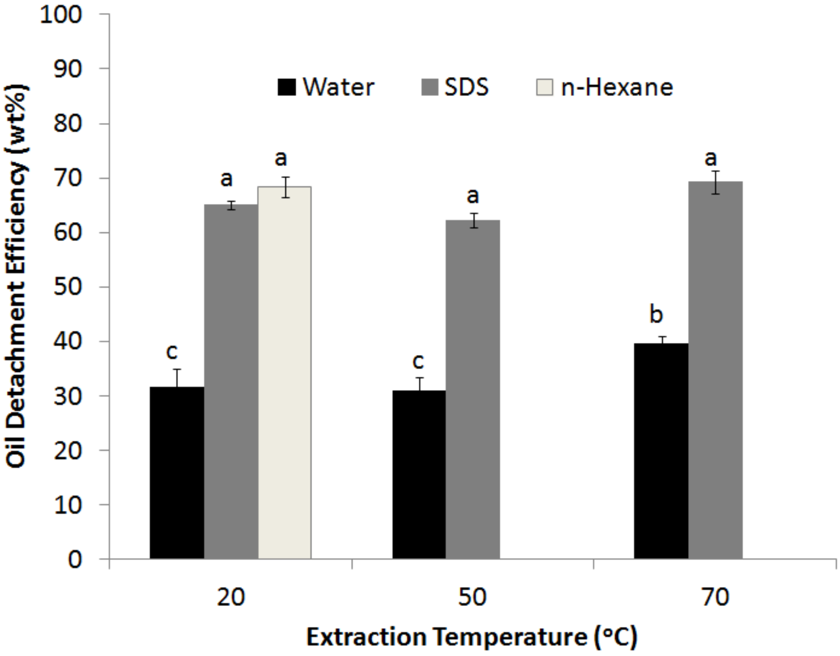


Figure 24 Oil detachment efficiency versus extraction temperature using water, 0.02 M SDS solution and n-hexane as extraction medium with solid-liquid ratio 1 g : 10 mL, stirring for 45 min. Canola particle size was larger than 0.425 mm. Means within the bar graph followed by the same letter are not significantly different at $P \leq 0.05$.

4.8 Effect of Solid-Liquid Ratio

Increasing solid-liquid ratio to higher than 1 g : 10 mL substantially reduced oil detachment and oil extraction efficiency, because there was insufficient surfactant in the system (Figure 25). Reducing the solid to liquid ratio from 1 g : 10 mL to 1 g : 30 mL, there was no impact on oil detachment efficiency, but the oil extraction was decreased. This may be similar to the “effect of surfactant concentration” in which an increase in SDS concentration from 0.02 M to 0.03 M resulted in a larger disparity between oil detachment and oil extraction efficiency. As explained above, increased surfactant mass in the system may increase emulsion formation.

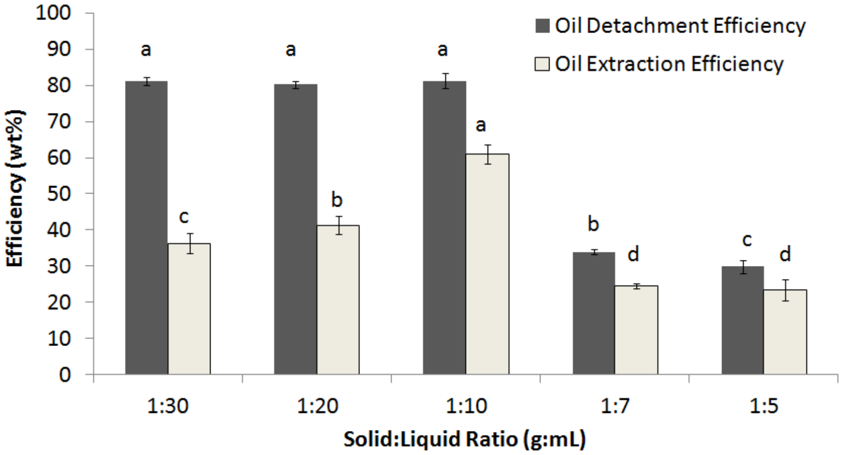


Figure 25 Impact of solid-liquid ratio on oil detachment and oil extraction efficiency for 0.02 M SDS solution at 20^{o}C, stirring for 45 min. Means within the bar graph followed by the same color and letter are not significantly different at $P \leq 0.05$.

4.9 Effect of Triple Extraction with Three-stages (3E3S)

Applying 3E3S improved the oil detachment and oil extraction efficiency at high level of solid -liquid ratio. Increasing the solid-liquid ratio slightly decreased oil detachment efficiency, but the oil extraction efficiency of 3E3S at each solid-liquid ratio was not significantly different (Figure 26 and 27). At solid-liquid ratio higher than 1:10, the 3E3S provided higher oil detachment and oil extraction efficiency than the standard ASE method (single extraction). The solid to liquid ratios applied in this study were higher than those reported for other aqueous extraction processes, which ranged from 1:20 to 1:30 (g : mL) (Rosenthal et al., 1996). Do and Sabatini (2011) also reported that an additional ASE extraction stage increased the oil extraction efficiency of canola and peanut oil, even using DI water alone as the extraction medium in the additional stage.

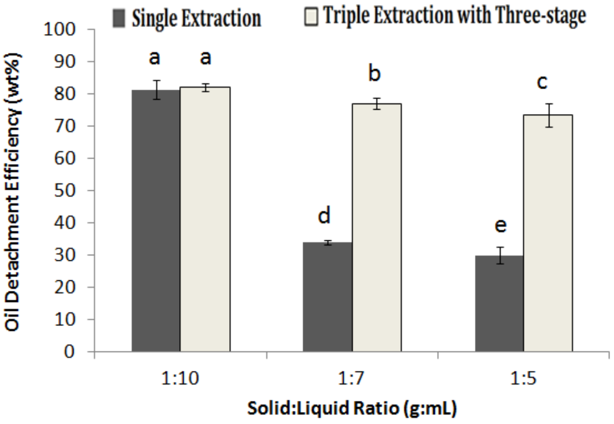


Figure 26 Impact of triple extraction with three-stages on oil detachment efficiency for 0.02 M SDS solution at 20^{o}C, stirring for total contact time 45 min. Means within the bar graph followed by the same letter are not significantly different at P$\leq$0.05.

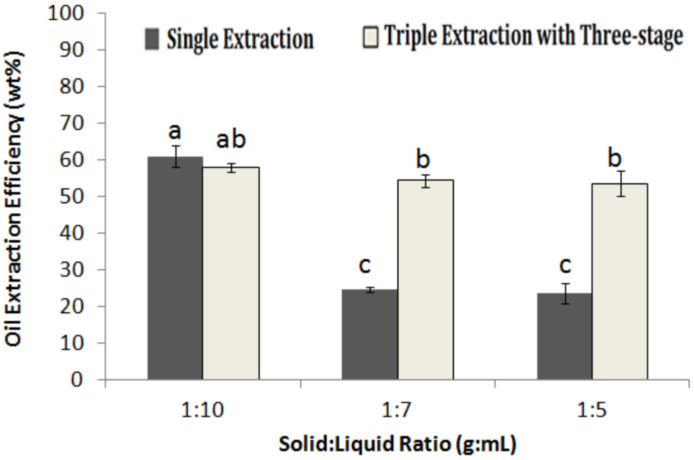


Figure 27 Impact of triple extraction with three-stages on oil extraction efficiency for 0.02 M SDS solution at 20^{o}C, stirring for total contact time 45 min. Means within the bar graph followed by the same letter are not significantly different at P$\leq$0.05.

Table 11 Comparison of extraction conditions and oil efficiency between references and this work.

	Reference	Naksuk et al. (2009)	Do and Sabatini (2010)	Kadioglu et al. (2011)	Results and conditions in this thesis
	Oilseed and sample size	Palm kernel (1g)	Peanut and Canola (2 g)	Corn germ (4 g)	Canola (4 g)
	Surfactant system	Comperland KD (3% wt) Alfoterra 145- 5PO (0.1 %wt) NaCl (10 %wt)	C10-18PO-2EOsulfate (0.15 %wt) NaCl (6 %wt) for peanut NaCl (5 %wt) for canola	C12,14–10PO–2EOsulfate (0.4 %wt) NaCl (1 %wt)	SDS (0.02 M) or SDS (0.58 %wt)
	Dynamic IFT (mN/m)	< 0.01	< 0.01	< 0.01	< 1
Pretreatment	Grinding	Food processor	Food processor	Coffee mill	Coffee mill
	Dehulling	Yes	Yes	Not Reported	No
	Size Selection	US Sieve size No.40-70 (0.21-0.42 mm)	US Sieve size No.40-70 (0.21-0.42 mm)	US Sieve size No.40-70 (0.21-0.42 mm)	US Sieve size No.40-70 (0.21-0.42 mm)
	Thermal Treatment	Not Reported	104 ^{o}C with 35 mins	Yes (dried corn germ)	No
Extraction	Seed-Liquid ratio	1 to 10 (g/mL)	2 to 10 (g/g)	1 to 10 (g/g)	1 to 10 (g/mL)
	Extraction	Not Reported	Horizontal shaker 150 cycle/min	Horizontal shaker 250 cycle/min	Magnetic stirrer 1000 rpm
	Duration	with 30 min	with 30 min	with 45 min	with 45 min
	Separation	Not Reported	Centrifuge speed 2,170 g with 30 min	Centrifuge speed 3,500 rpm with 20 min	Centrifuge speed 2,000 g with 20 min
	Oil Extraction Efficiency	93.99% (based on soxhlet extraction)	93-95 % (based on soxhlet extraction)	83% (based on hexane solvent in ASE)	80 % detachment efficiency 60% extraction efficiency

4.10 Scale up of the ASE Process

Ground canola 300 g were extracted via ASE process using selected extraction conditions form previous experiments which provided 60% oil extraction efficiency: 0.02 M SDS solution, 45 min extraction time, 20°C and solid-liquid ratio 1:10 (g to mL). The oil extraction efficiency was approximately 40% since the low performance of demulsification and liquid-liquid separation processes. In lab-scale (4 g of ground canola), centrifuge was used to separate extracted meal from liquid fraction but it could not be applied in case of 300 g of ground canola. Moreover, extracted oil was adsorbed on the surface of extraction unit. The diagram of scale up ASE process was shown in Fig. 28.

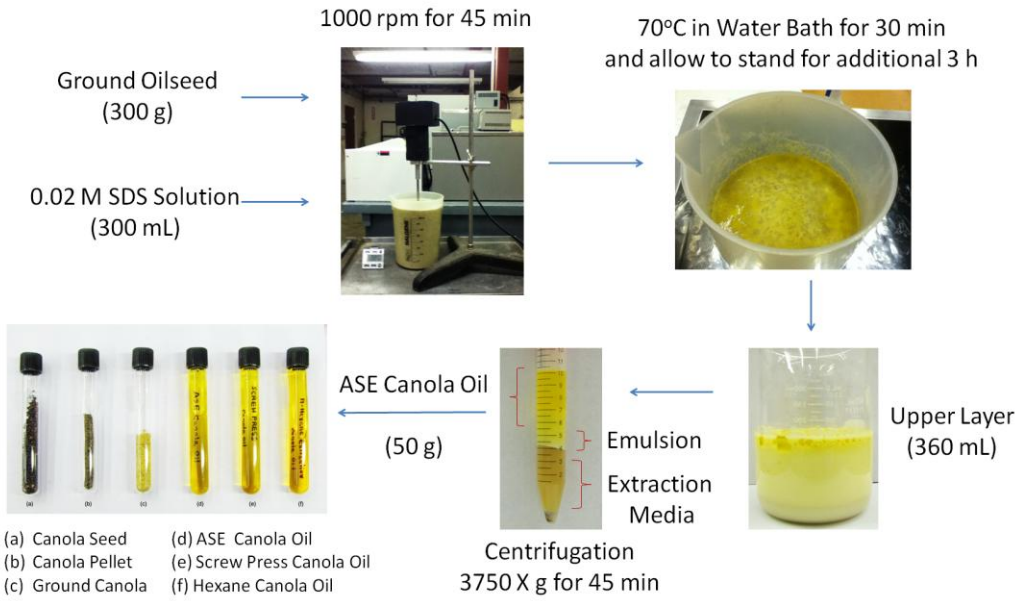


Fig.28 Diagram of scale up ASE process.

4.11 <u>Extracted Oil Quality</u>

The extracted canola oil from the scaled up ASE process, screw press, and Soxhlet extraction were analyzed for biodiesel feedstock quality, specifically water content, acid value, and phosphorus content, and compared with commercial canola oil.

4.11.1 Water Content

The presence of water in vegetable oil leads to poor biodiesel yield and quality by contributing to soap formation (Van Gerpen and Knothe, 2004). All samples passed the recommended limit (Table 12).

4.11.2 Acid Value

The acid value indicates the free fatty acid content in biodiesel feedstock from the hydrolysis of triglyceride. The high content of free fatty acid reduces the biodiesel performance, because it reacts with basic catalysts to form soap. All extracted oils in this study were below the recommended upper limit, despite the absence of a caustic refining process step (Table 12). Therefore, hydrolysis of triglycerides during ASE process was not a problem. Moreover, the extracted oil by ASE had a lower acid value than that of Soxhlet extraction. The higher acid value from Soxhlet extraction may be due to triglyceride hydrolysis under elevated temperature with long extraction time. Similar results were reported by other investigators (Do and Sabatini, 2010; Dunford and Su, 2010; Hanmoungjai et al., 2000; Kadioglu et al., 2011; Latif et al., 2008).

4.11.3 Phosphorus Content

The presence of phospholipids (>300 ppm) has a potential to generate an emulsion during transesterification, resulting in decreased biodiesel yield and quality (Ahn et al., 1995; Van Gerpen and Dvorak, 2002). All samples passed the recommendation for phosphorous content (Table 12). The low phosphorus contents of unrefined extracted oil might be due to the precipitation of phospholipids under long storage time (three weeks) prior to the analysis.

Table 12 Quality of canola oil extracted using ASE and other methods.

Parameter	Extraction Method				Recommended Limit
	Screw Press	ASE	Soxhlet n-Hexane	Commercial Oil	
Water content (vol%)	0.040 a	0.033 c	0.036 b	0.006 d	0.05[A]
Acid value (mg KOH/g)	0.28 c	0.33 b	0.41 a	0.09 d	0.5[A]
Phosphorous Content (ppm)	10	19	49	8	300[B]

Means within each row followed by the same letter are not significantly different at $P \leq 0.05$

[A and B] Recommended upper limit of vegetable oil to be used as biodiesel feedstock by

CHAPTER 5

GENERAL CONCLUSIONS AND RECOMMENDATION FOR FUTURE STUDY

5.1 General Conclusions

The mixture of commercial anionic and nonionic surfactant (LS-series) in brine solution showed a good potential for using as extraction media in ASE method. The mixed surfactant solution and introducing NaCl were found to improve a dynamic IFT of the system resulting in increase oil detachment efficiency. However, surfactant precipitation was a limitation to introducing NaCl into the system in case of SDS and nonionic surfactant solution. Although the ultra low IFT (<0.01 mN/m) was not observed in this study; the desirable oil detachment efficiency of >70% was achieved. Similar to other studies, the ASE method of jatropha showed a correlation between oil detachment efficiency and dynamic IFT. In contrast, the ASE method of canola didn't showed significant difference in oil detachment efficiency between the conditions that provided the lowest dynamic IFT (0.148 mN/m) and the highest dynamic IFT (0.869 mN/m) in this study.

These results may imply that even though dynamic IFT of the system plays an important role on oil detachment efficiency. It does not only one parameter govern the extraction process. Other parameters such as physical conditions are also found to influence the extraction efficiency. However, using high shear force to compensate the dynamic IFT > 0.01 mN/m promoted emulsion formation, and a demulsification process was required. The highest oil detachment efficiency of jatropha was 72.5% with a dynamic IFT value 0.086 mN/m (0.02M AOT, 0.01M LS-2 and 0.05M NaCl). The highest oil detachment efficiency of canola was 80.7% with a dynamic IFT value 0.869 mN/m (0.03M SDS).

Surfactant concentration, extraction time, and solid to liquid ratio had an impact on oil detachment and oil extraction efficiency in ASE method of canola. Meanwhile, there was no effect of extraction temperature on oil detachment and oil extraction efficiency in case of using 0.02 M SDS solution. The highest oil detachment and oil extraction efficiency were 80 and 60%, respectively, using SDS 0.02 M at 20^{o}C with solid-liquid ratio 1 g : 10 mL, stirring 1,000 rpm with contact time 45 min. As the result, the ASE method offered several advantages than n-hexane extraction. It used non-toxic chemicals in the process, thus minimizing pollutant emission and waste generation. Reduce energy consumption since it was able to operate at room temperature. Moreover, the extraction media could be reduced to 5 mL with 1 g of ground canola when triple extraction with three-stage was applied.

The ASE method offered several advantages than n-hexane extraction. It used non-toxic chemicals in the process, thus minimizing pollutant emission and waste generation. It reduced energy consumption since it was able to operate at room temperature. The extracted canola oil from ASE method showed potential to be a good biodiesel feedstock. It provided the superior quality to that of Soxhlet n-hexane extraction in lower free fatty acid and phosphorous content. Thus, it reduced cost of refinery process.

5.2 Recommendation for Future Study

The ASE method is a promising alternative to n-hexane for vegetable oil extraction, since extraction can be accomplished in the absence of any toxic chemicals and operated at room temperature. However, one problem of this method was emulsion formation leading to low oil extraction efficiency, 60%. The performance of demulsification process in this study was not adequate, resulting in the 20% gap between oil detachment and oil extraction efficiency. Optimization of demulsification conditions, including temperature, centrifugation, introducing demulsifying agent, and applying high voltage, would increase the oil extraction efficiency of ASE method. Moreover, surfactant recovery process, such as precipitation by electrolyte and cloud point separation by temperature, should be accounted in the future work.

In addition to vegetable oil extraction, surfactant solution is also applied in protein extraction. Thus, development of simultaneous extraction of vegetable oil and protein may help this process become commercially viable.

Evaluation of surfactants in transesterification would be worthwhile. The surfactant might reduce the amount of methanol and KOH needed as well as the reaction time, due to increased solubilization and surface area (See the Optimize Biodiesel Production and Quality in the *Literature Review* section). Moreover, this knowledge could be applied to *in situ* transesterification. The *in situ* transesterification is the simultaneous extraction and transesterification of the vegetable oil. The surfactant could accelerate the process time for the following reasons. Methanol, alone, has limited ability to extract the oil trapped inside the oilseed matrix. Surfactant can disrupt the trapped oil into droplets, small enough for dispersing into methanol solution. Surfactant may also increase the transesterification rate, since surface area will be increased by reducing IFT.

REFERENCES

Achten, W. M. J., Verchot, L., Franken, Y. J., Mathijs, E., Singh, V. P., Aerts, R. and Muys, B. 2008. Jatropha bio-diesel production and use. Biomass and Bioenergy 32: 1063-1084.

Ahn, E., Koncar, M., Mittelbach, M. and Marr, R. 1995. A low-waste process for the production of biodiesel. Separation Science and Technology 30: 2021-2033.

American Oil Chemists' Society. 1999. "Oil content in oilseeds." AOCS method AM2-93. Champaign, IL: AOCS.

American Society for Testing and Materials. 2009. "Standard specification for biodiesel fuel blend stock (B100) for middle distillate fuels." ASTM D6751-09. West Conshohocken: ASTM.

Augustus, G. D. P. S., Jayabalan, M. and J, S. G. 2002. Evaluation and bioinduction of energy components of *Jatropha curcas*. Biomass and Bioenergy 23: 161-164.

Beckel, A. C., Belter, P. A. and Smith, A. K. 1946. Laboratory study of continuous vegetable oil extraction: countercurrent extractor, rissing-film evaporator, and oil stripper. Industrial and Engineering Chemistry 18(1): 56-58.

Berglund, D. R., Mckay, K. and Knodel, J. Canola Production. [Online]. 2011. Available from: http://www.ag.ndsu.edu/pubs/plantsci/crops/a686w.htm [21 November 2011]

Booth, E. J. Extraction and refining. 2004. In F. D. Gunstone (eds.), Rapeseed and canola oil: production, processing, properties and uses, pp.17-36. Florida: CRC Press.

Carels, N. 2009. *Jatropha curcas*: a review. Advances in Botanical Research 50: 39-86.

Carlota, O., Rangel, Y., Adalberto-Jr, P. and Leoberto, C. T. 2005. Micellar solubilization of drugs. Pharmacy and Pharmaceutical Sciences 8: 147-163.

Chabrand, R. n. M., Kim, H.-J., Zhang, C., Glatz, C. E. and Jung, S. 2008. Destabilization of the emulsion formed during aqueous extraction of soybean oil. Journal of American Oil Chemists Society 85: 383-390.

Cui, J., Lapan, H., Moschini, G. C. and Cooper, J. 2010. "Welfare impacts of alternative biofuel and energy policies." Agricultural & Applied Economics Association's 2011 AAEA, CAES & WAEA Joint Annual Meeting. Denver, Colorado, USA.

David, J. 2002. Fundamentals and applications of ultrasonic waves. Florida: CRC Press.

Davidson, M. W. Plant cell structure. [Online]. 2011. Available from: http://micro.magnet.fsu.edu/cells/plantcell.htm [27 November 2011]

Do, L. D. and Sabatini, D. A. 2010. Aqueous extended-surfactant based method for vegetable oil extraction: proof of concept. Journal of American Oil Chemists Society 87: 1211-1220.

Do, L. D. and Sabatini, D. A. 2011. Pilot scale study of vegetable oil extraction by surfactant-asssisted aqueous extraction process. Separation Science and Technology 46(6): 978-985.

Dominguez, H., Ndfiez, M. J. and Lema, J. M. 1994. Enzymatic pretreatment to enhance oil extraction from fruits and oilseeds: a review. Journal of Food Chemistry 49: 271-286.

Dunford, N. T. and Su, A. 2010. Effect of canola oil quality on biodiesel conversion efficiency and properties. Transaction of the ASABE 53(3): 993-997.

Ghosh, P. K., Jayas, D. S. and Agrawal, Y. C. 2007. "Enzymatic hydrolysis of oilseeds for enhanced oil extraction: current status." Trans. ASABE. ASABE Annual International Meeting. Minneapolis, Minnesota: ASABE. Vol. 076207.

Gregory, S. and Horsman, M. Who needs alternative solvents, and creteria for their selection 1997. In P. J. Wan and P. J. Wakelyn (eds.), Technology and solvents for extraction oilseeds and nonpetroleum oils, pp.1-3. Champaign: AOCS Press.

Gunstone, F. D. 2004. Rapeseed and canola oil: production, processing, properties and uses. Florida: CRS Press.

Gunstone, F. D., Hamiton, R. J., Cast, J., Jee, M. and Hamm, W. 2000. Vegetavle oils in food technology: composition, properties and uses. Florida: CRC Press.

Haagenson, D. M., Brudvik, R. L., Lin, H. and Wiesenborn, D. P. 2010. Implementing an in situ alkaline transesterification method for canola biodiesel quality screening. Journal of American Oil Chemists Society 87: 1351-1358.

Hanmoungjai, P., Pyle, L. and Niranjan, K. 2000. Extraction of rice bran oil using aqueous media. Journal of Chemical Technology and Biotechnology 75: 348-352.

Johnson, L. A. Theoretical, comparative, and historical analyses of alternative technologies for oilseeds extraction. 1997. In P. J. Wan and P. J. Wakelyn (eds.), Technology and solvents for extraction oilseeds and nonpetroleum oils, pp.4-47. Champaign: AOCS Press.

Kadioglu, S. I., Phan, T. T. and Sabatini, D. A. 2011. Surfactant-based oil extraction of corn germ. Journal of American Oil Chemists Society 88: 863-869.

Khan, L. M. and Hanna, M. A. 1983. Expression of oil from oilseeds: a review. Journal of Agricultural and Engineering Research 28: 495-503.

Klongklaew, N., Sabatini, D. A. and Tongcumpou, C. 2005. Hexane replacement for soybean extraction using microemulsion systems. Master's Thesis, Program in Environmental Management interdisciplinary Graduate School, Chulalongkorn University.

Kuk, M. S. and Hron, R. J. 1998. Cottonseed extraction with a new solvent system: isohexane and alcohol mixtures. Journal of American Oil Chemists Society 75: 927-930.

Kumar, A. and Sharma, S. 2008. An evaluation of multipurpose oil seed crop for industrial uses (*Jatropha curcas L.*): A review. Industrial Crops and Products 28: 1-10.

Kunjappu, J. T. Ink chemistry. [Online]. 2003. Available from: http//:www.rsc.org/chemistryworld/issues/2003/march/inkchemistry.asp. [16 April 2011]

Kwiatkowski, J. R. and Cheryan, M. 2002. Extraction of oil from ground corn using ethanol. Journal of American Oil Chemists Society 79: 825-830.

Latif, S., Diosady, L. L. and Anwar, F. 2008. Enzyme-assisted aqueous extraction of oil and protein from canola (*Brassica napus* L.) seeds. European Journal of Lipid Science and Technology 110: 887-892.

Li, H., Song, C., Zhou, H., Wang, N. and Cao, D. 2011. Optimization of the aqueous enzymatic extraction of wheat germ oil using response surface methodology. Journal of American Oil Chemists Society 88: 809-817.

Naksuk, A., Sabatini, D. A. and Tongcumpou, C. 2009. Microemulsion-based palm kernel oil extraction using mixed surfactant solutions. Industrial Crops and Products 30: 194-198.

NCCRP. Canola picture. [Online]. 2011. Available from: http://www.ag.ndsu.edu/nc-canola/ [13 June 2011]

Pederssetti, M. M., Palú, F., Silva, E. A. d., Rohling, J. H., Cardozo-Filho, L. and Dariva, C. 2011. Extraction of canola seed (Brassica napus) oil using compressed propane and supercritical carbon dioxide. Journal of Food Engineering 102: 189-196.

Pierce. Technical resource: Remove detergent from protein samples. [Online]. 2004. Pierce Biotechnology, Inc. Available from: http://wolfson.huji.ac.il/purification/PDF/detergents/PIERCE_DetergentRemoval.pdf [14 May 2012]

Rosen, M. J. 2004. Surfactant and Interfacial Phenomena. 2nd ed. New York: John Wiley & Sons.

Rosenthal, A., Pyle, D. L. and Niranjan, K. 1996. Aqueous and enzymatic process for edible oil extraction. Enzyme and Microbial Technology 19: 402-420.

Sabatini, D. A., Acosta, E. and Harwell, J. H. 2003. Linker molecules in surfactant mixtures. Current Opinion in Colloid and Interface Science 8: 316-326.

Salager, J. L., Morgan, J. C., Schechter, R. S., Wade, W. H., Spe-Aime, M. and E.Vasquez. 1979. Optimum formulation of surfactant/water/oil systems for minimum interfacial tension or phase behavior. Society of Petroleum Engineers 19: 107-115.

SAS Institute. 2008. "Release version 9.2 for window." Cary: SAS Institute.

Shah, S., Shana, A. and Gupta, M. N. 2004. Extraction of oil from Jatropha *curcas* L. seed kernels by combination of ultrasonication and aqueous enxymatic oil extraction. Biosource Technology 96: 121-123.

Smith, D. M. and Chughtai, A. R. 1996. Reaction kinetics of ozone at low concentration with n-hexane soot. Journal of Geophysical Research 101(D14): 19,607-619,620.

Snedecor, G. W. and Cochran, W. G. 1980. Statistical Methods. 7th ed. Ames: Iowa State University Press.

Strop, H. R. and Perry, R. R. 1989. "Vegetable oil extraction process." USA. Vol. 4,808,426.

Swanson, B. G. Hexane extraction in soyfood processing. [Online]. 2012. Available from: http://www.soyfoods.org/wp-content/uploads/Regulatory%20Expert%20Document-Barry%20Swanson%20revised.pdf [20 June 2012]

Tongcumpou, C., Acosta, E. J., Scamehorn, J. F., Sabatini, D. A., Yanumet, N. and Chavadej, S. 2006. Enhanced triolein removal using microemulsions formulated with mixed surfactants. Journal of Surfactants and Detergents 9(2): 181-189.

Tuntiwiwattanapun, N., Wiesenborn, D. and Tongcumpou, C. 2012. "Optimization of vegetable oil detachment efficiency by reducing interfacial tension." <u>2012 ASABE/CSBE North Central Intersectional Conference</u>. Fargo, ND: ASABE, RRV12113.

U.S. Environmental Protection Agency (EPA). 2001. "National emission standards for hazardous air pollutants." <u>Solvent extraction for vegetable oil production</u>. Washington, DC: EPA.

Uchiyama, H., Acosta, E., Tran, S., Sabatini, D. A. and Harwell, J. H. 2000. Supersolubilization in chlorinated hydrocarbon microemulsions: solubilization enhancement by lipophilic and hydrophilic linkers. <u>Industrial Engineering Chemistry Research</u> 39: 2704-2708.

Van Gerpen, J. and Dvorak, B. 2002. "The effect of phosphorus level on the total glycerol and reaction yield of biodiesel." <u>The 10th Biennial Bioenergy Conference</u>. Boise, ID.

Van Gerpen, J. and Knothe, G. Basic of the transesterification reaction. 2004. In G. Knothe, J. Krahl and J. Van Gerpen (eds.), <u>The biodiesel handbook</u>, pp.26-41. Champaign: AOCS Press.

Veronique, J. B., Chornick, T. and James, K. D. 2002. Comparison of methods to measure the oil contents in oilseeds. <u>Journal of Oleo Science</u> 51: 589-597.

Wang, S. S., Lee, C. J. and Chan, C. C. 1994. Demulsification of water-in-oil emulsion by use of a high voltage ac field. <u>Separation Science and Technology</u> 29(2): 159-170.

Wisenborn, D., Glowacki, A., Hettiarachchy, N. and Zander, L. 1993. A batch-scale unit for continuous extraction of red colorant from sunflower hulls. <u>Transaction of the ASAE</u> 36(5): 1441-1416.

Witthayapanyanon, A., Acosta, E. J., Harwell, J. H. and Sabatini, D. A. 2006. Formulation of ultralow interfacial tension systems using extended surfactants. <u>Journal of Surfactants and Detergents</u> 9: 331-339.

Youngs, C. G. and Sallans, H. R. 1955. Acetone as a selective solvent for vegetable oils. Journal of American Oil Chemists Society 32(7): 397-400.

Zhu, Y., Xu, G., Gong, H., Wu, D. and Wang, Y. 2009. Production of ultra-low interfacial tension between crude oil and mixed brine solution of Triton X-100 and its oligomer Tyloxapol with cetyltrimethylammonium bromide induced by hydrolyzed polyacrylamide. Colloids and Surfaces A: Physicochem. Eng. Aspects 332: 90-97.

APPENDICES

APPENDIX A: EXPERIMENTAL DATA OF INTERFACIAL TENSION VALUE

Table 13 Dynamic IFT of three commercial anionic surfactants and jatropha oil.

Replication	Anionic Surfactant (1%wt)	Vegetable Oil	IFT (mN/m)	Mean
1	AOT	Jatropha	0.375	0.363 c
2	AOT	Jatropha	0.355	
3	AOT	Jatropha	0.359	
1	AMA	Jatropha	1.157	1.172 a
2	AMA	Jatropha	1.177	
3	AMA	Jatropha	1.183	
1	SDS	Jatropha	0.921	0.919 b
2	SDS	Jatropha	0.915	
3	SDS	Jatropha	0.92	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 14 Dynamic IFT of three commercial anionic surfactants and canola oil.

Replication	Anionic Surfactant (1%wt)	Vegetable Oil	IFT (mN/m)	Mean
1	AOT	Canola	1.371	1.452 b
2	AOT	Canola	1.462	
3	AOT	Canola	1.522	
1	AMA	Canola	4.586	4.436 a
2	AMA	Canola	4.465	
3	AMA	Canola	4.257	
1	SDS	Canola	0.839	0.836 c
2	SDS	Canola	0.84	
3	SDS	Canola	0.828	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 15 Dynamic IFT of mixed surfactant systems and jatropha oil.

Replication	Anionic Surfactant (0.02 M)	Nonionic Surfactant (0.01 M)	Vegetable Oil	IFT (mN/m)	Mean
1	AOT	-	Jatropha	0.375	0.363 b
2	AOT	-	Jatropha	0.355	
3	AOT	-	Jatropha	0.359	
1	AOT	LS-2	Jatropha	0.245	0.254 d
2	AOT	LS-2	Jatropha	0.257	
3	AOT	LS-2	Jatropha	0.26	
1	AOT	LS-3	Jatropha	0.325	0.324 c
2	AOT	LS-3	Jatropha	0.327	
3	AOT	LS-3	Jatropha	0.319	
1	AOT	LS-9	Jatropha	0.404	0.403 a
2	AOT	LS-9	Jatropha	0.401	
3	AOT	LS-9	Jatropha	0.403	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 16 Dynamic IFT of mixed surfactant systems and canola oil.

Replication	Anionic Surfactant (003M)	Nonionic Surfactant (0.01 M)	Vegetable Oil	IFT (mN/m)	Mean
1	SDS	-	Canola	0.839	0.836 b
2	SDS	-	Canola	0.84	
3	SDS	-	Canola	0.828	
1	SDS	LS-1	Canola	0.618	0.610 d
2	SDS	LS-1	Canola	0.610	
3	SDS	LS-1	Canola	0.601	
1	SDS	LS-2	Canola	0.764	0.771 c
2	SDS	LS-2	Canola	0.769	
3	SDS	LS-2	Canola	0.781	
1	SDS	LS-3	Canola	0.764	0.766 c
2	SDS	LS-3	Canola	0.769	
3	SDS	LS-3	Canola	0.766	
1	SDS	LS-9	Canola	1.128	1.136 a
2	SDS	LS-9	Canola	1.133	
3	SDS	LS-9	Canola	1.147	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 17 Dynamic IFT of AOT solution with jatropha oil at various NaCl concentrations.

Replication	Anionic Surfactant (0.02 M)	Nonionic Surfactant (0.01 M)	NaCl (M)	IFT (mN/m)	Mean
1	AOT	-	0	0.316	0.320 e
2	AOT	-	0	0.323	
3	AOT	-	0	0.32	
1	AOT	-	0.02	0.223	0.222 g
2	AOT	-	0.02	0.212	
3	AOT	-	0.02	0.23	
1	AOT	-	0.03	0.209	0.209 h
2	AOT	-	0.03	0.21	
3	AOT	-	0.03	0.207	
1	AOT	-	0.04	0.158	0.156 j
2	AOT	-	0.04	0.158	
3	AOT	-	0.04	0.152	
1	AOT	-	0.05	0.122	0.121 k
2	AOT	-	0.05	0.12	
3	AOT	-	0.05	0.122	
1	AOT	-	0.06	0.191	0.185 i
2	AOT	-	0.06	0.184	
3	AOT	-	0.06	0.18	
1	AOT	-	0.08	0.187	0.182 i
2	AOT	-	0.08	0.181	
3	AOT	-	0.08	0.177	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Continuous (Table 17)

Replication	Anionic Surfactant (0.02 M)	Nonionic Surfactant (0.01 M)	NaCl (M)	IFT (mN/m)	Mean
1	AOT	-	0.1	0.275	0.266 f
2	AOT	-	0.1	0.258	
3	AOT	-	0.1	0.266	
1	AOT	-	0.125	0.408	0.406 d
2	AOT	-	0.125	0.401	
3	AOT	-	0.125	0.408	
1	AOT	-	0.15	0.416	0.416 cd
2	AOT	-	0.15	0.408	
3	AOT	-	0.15	0.424	
1	AOT	-	0.175	0.443	0.434 ab
2	AOT	-	0.175	0.424	
3	AOT	-	0.175	0.435	
1	AOT	-	0.2	0.433	0.436 a
2	AOT	-	0.2	0.432	
3	AOT	-	0.2	0.442	
1	AOT	-	0.25	0.42	0.424 bc
2	AOT	-	0.25	0.421	
3	AOT	-	0.25	0.431	
1	AOT	-	0.3	0.447	0.443 a
2	AOT	-	0.3	0.425	
3	AOT	-	0.3	0.457	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 18 Dynamic IFT of AOT and LS-2 solution with jatropha oil at various NaCl concentrations.

Replication	Anionic Surfactant (0.02 M)	Nonionic Surfactant (0.01 M)	NaCl (M)	IFT (mN/m)	Mean
1	AOT	LS-2	0	0.245	0.254 c
2	AOT	LS-2	0	0.257	
3	AOT	LS-2	0	0.26	
1	AOT	LS-2	0.02	0.181	0.179 d
2	AOT	LS-2	0.02	0.178	
3	AOT	LS-2	0.02	0.177	
1	AOT	LS-2	0.03	0.13	0.133 f
2	AOT	LS-2	0.03	0.133	
3	AOT	LS-2	0.03	0.135	
1	AOT	LS-2	0.04	0.104	0.106 g
2	AOT	LS-2	0.04	0.105	
3	AOT	LS-2	0.04	0.109	
1	AOT	LS-2	0.05	0.087	0.086 i
2	AOT	LS-2	0.05	0.087	
3	AOT	LS-2	0.05	0.085	
1	AOT	LS-2	0.06	0.104	0.106 g
2	AOT	LS-2	0.06	0.105	
3	AOT	LS-2	0.06	0.11	
1	AOT	LS-2	0.08	0.096	0.096 h
2	AOT	LS-2	0.08	0.095	
3	AOT	LS-2	0.08	0.098	
1	AOT	LS-2	0.1	0.144	0.147 e
2	AOT	LS-2	0.1	0.152	
3	AOT	LS-2	0.1	0.144	
1	AOT	LS-2	0.15	0.313	0.320 a
2	AOT	LS-2	0.15	0.322	
3	AOT	LS-2	0.15	0.325	
1	AOT	LS-2	0.2	0.325	0.317 a
2	AOT	LS-2	0.2	0.319	
3	AOT	LS-2	0.2	0.308	
1	AOT	LS-2	0.3	0.288	0.288 b
2	AOT	LS-2	0.3	0.282	
3	AOT	LS-2	0.3	0.293	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 19 Dynamic IFT of AOT and LS-3 solution with jatropha oil at various NaCl concentrations.

Replication	Anionic Surfactant (0.02 M)	Nonionic Surfactant (0.01 M)	NaCl (M)	IFT (mN/m)	Mean
1	AOT	LS-3	0	0.325	0.324 a
2	AOT	LS-3	0	0.327	
3	AOT	LS-3	0	0.319	
1	AOT	LS-3	0.02	0.265	0.263 c
2	AOT	LS-3	0.02	0.259	
3	AOT	LS-3	0.02	0.266	
1	AOT	LS-3	0.05	0.148	0.147 e
2	AOT	LS-3	0.05	0.14	
3	AOT	LS-3	0.05	0.152	
1	AOT	LS-3	0.08	0.113	0.111 g
2	AOT	LS-3	0.08	0.11	
3	AOT	LS-3	0.08	0.111	
1	AOT	LS-3	0.09	0.08	0.078 i
2	AOT	LS-3	0.09	0.081	
3	AOT	LS-3	0.09	0.074	
1	AOT	LS-3	0.1	0.09	0.094 h
2	AOT	LS-3	0.1	0.093	
3	AOT	LS-3	0.1	0.098	
1	AOT	LS-3	0.125	0.123	0.122 f
2	AOT	LS-3	0.125	0.12	
3	AOT	LS-3	0.125	0.123	
1	AOT	LS-3	0.15	0.15	0.158 d
2	AOT	LS-3	0.15	0.159	
3	AOT	LS-3	0.15	0.165	
1	AOT	LS-3	0.2	0.319	0.322 a
2	AOT	LS-3	0.2	0.321	
3	AOT	LS-3	0.2	0.325	
1	AOT	LS-3	0.3	0.315	0.314 b
2	AOT	LS-3	0.3	0.313	
3	AOT	LS-3	0.3	0.313	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 20 Dynamic IFT of AOT and LS-9 solution with jatropha oil at various NaCl concentrations.

Replication	Anionic Surfactant (0.02 M)	Nonionic Surfactant (0.01 M)	NaCl (M)	IFT (mN/m)	Mean
1	AOT	LS-9	0	0.404	0.403 a
2	AOT	LS-9	0	0.401	
3	AOT	LS-9	0	0.403	
1	AOT	LS-9	0.02	0.364	0.374 b
2	AOT	LS-9	0.02	0.386	
3	AOT	LS-9	0.02	0.372	
1	AOT	LS-9	0.05	0.334	0.346 c
2	AOT	LS-9	0.05	0.368	
3	AOT	LS-9	0.05	0.337	
1	AOT	LS-9	0.1	0.297	0.298 d
2	AOT	LS-9	0.1	0.298	
3	AOT	LS-9	0.1	0.299	
1	AOT	LS-9	0.2	0.228	0.226 e
2	AOT	LS-9	0.2	0.227	
3	AOT	LS-9	0.2	0.223	
1	AOT	LS-9	0.3	0.144	0.144 g
2	AOT	LS-9	0.3	0.141	
3	AOT	LS-9	0.3	0.146	
1	AOT	LS-9	0.325	0.121	0.121 h
2	AOT	LS-9	0.325	0.119	
3	AOT	LS-9	0.325	0.123	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Continuous (Table 20)

Replication	Anionic Surfactant (0.02 M)	Nonionic Surfactant (0.01 M)	NaCl (M)	IFT (mN/m)	Mean
1	AOT	LS-9	0.35	0.151	0.148 g
2	AOT	LS-9	0.35	0.149	
3	AOT	LS-9	0.35	0.143	
1	AOT	LS-9	0.4	0.065	0.066 j
2	AOT	LS-9	0.4	0.067	
3	AOT	LS-9	0.4	0.066	
1	AOT	LS-9	0.5	0.072	0.075 ij
2	AOT	LS-9	0.5	0.078	
3	AOT	LS-9	0.5	0.076	
1	AOT	LS-9	0.6	0.068	0.068 j
2	AOT	LS-9	0.6	0.068	
3	AOT	LS-9	0.6	0.067	
1	AOT	LS-9	0.8	0.082	0.079 i
2	AOT	LS-9	0.8	0.079	
3	AOT	LS-9	0.8	0.077	
1	AOT	LS-9	1	0.114	0.116 h
2	AOT	LS-9	1	0.116	
3	AOT	LS-9	1	0.119	
1	AOT	LS-9	1.25	0.168	0.165 f
2	AOT	LS-9	1.25	0.163	
3	AOT	LS-9	1.25	0.164	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 21 Dynamic IFT of SDS solution with canola oil at various NaCl concentrations.

Replication	Anionic Surfactant (0.03M)	Nonionic Surfactant (0.01 M)	NaCl (M)	IFT (mN/m)	Mean
1	SDS	-	0	0.859	0.869 a
2	SDS	-	0	0.885	
3	SDS	-	0	0.862	
1	SDS	-	0.05	0.688	0.675 b
2	SDS	-	0.05	0.675	
3	SDS	-	0.05	0.663	
1	SDS	-	0.1	0.633	0.637 c
2	SDS	-	0.1	0.636	
3	SDS	-	0.1	0.641	
1	SDS	-	0.15	0.641	0.622 c
2	SDS	-	0.15	0.598	
3	SDS	-	0.15	0.626	
1	SDS	-	0.2	0.618	0.61 c
2	SDS	-	0.2	0.591	
3	SDS	-	0.2	0.622	
1	SDS	-	0.25	0.285	0.296 d
2	SDS	-	0.25	0.297	
3	SDS	-	0.25	0.306	
1	SDS	-	0.3	0.277	0.271 d
2	SDS	-	0.3	0.278	
3	SDS	-	0.3	0.258	
1	SDS	-	0.325	0.148	0.148 g
2	SDS	-	0.325	0.147	
3	SDS	-	0.325	0.149	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Continuous (Table 21)

Replication	Anionic Surfactant (0.03M)	Nonionic Surfactant (0.01 M)	NaCl (M)	IFT (mN/m)	Mean
1	SDS	-	0.35	0.178	0.188 f
2	SDS	-	0.35	0.194	
3	SDS	-	0.35	0.191	
1	SDS	-	0.375	0.248	0.261 e
2	SDS	-	0.375	0.265	
3	SDS	-	0.375	0.271	
1	SDS	-	0.4	0.26	0.254 e
2	SDS	-	0.4	0.244	
3	SDS	-	0.4	0.257	
1	SDS	-	0.45	0.245	0.249 e
2	SDS	-	0.45	0.249	
3	SDS	-	0.45	0.253	
1	SDS	-	0.5	0.245	0.248 e
2	SDS	-	0.5	0.254	
3	SDS	-	0.5	0.246	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 22 Dynamic IFT of SDS and LS-1 solution with canola oil at various NaCl concentrations.

Replication	Anionic Surfactant (0.03 M)	Nonionic Surfactant (0.01 M)	NaCl (M)	IFT (mN/m)	Mean
1	SDS	LS-1	0	0.618	0.610 a
2	SDS	LS-1	0	0.61	
3	SDS	LS-1	0	0.601	
1	SDS	LS-1	0.01	0.587	0.592 b
2	SDS	LS-1	0.01	0.591	
3	SDS	LS-1	0.01	0.598	
1	SDS	LS-1	0.02	0.592	0.587 b
2	SDS	LS-1	0.02	0.589	
3	SDS	LS-1	0.02	0.579	
1	SDS	LS-1	0.03	0.569	0.565 c
2	SDS	LS-1	0.03	0.561	
3	SDS	LS-1	0.03	0.566	
1	SDS	LS-1	0.05	0.574	0.568 c
2	SDS	LS-1	0.05	0.57	
3	SDS	LS-1	0.05	0.559	
1	SDS	LS-1	0.1	Precipitated	
2	SDS	LS-1	0.1	Precipitated	
3	SDS	LS-1	0.1	Precipitated	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 23 Dynamic IFT of SDS and LS-2 solution with canola oil at various NaCl concentrations.

Replication	Anionic Surfactant (0.03M)	Nonionic Surfactant (0.01M)	NaCl (M)	IFT (mN/m)	Mean
1	SDS	LS-2	0	0.764	0.771 a
2	SDS	LS-2	0	0.769	
3	SDS	LS-2	0	0.781	
1	SDS	LS-2	0.05	0.638	0.626 b
2	SDS	LS-2	0.05	0.618	
3	SDS	LS-2	0.05	0.622	
1	SDS	LS-2	0.1	0.578	0.571 c
2	SDS	LS-2	0.1	0.566	
3	SDS	LS-2	0.1	0.57	
1	SDS	LS-2	0.15	0.586	0.574 c
2	SDS	LS-2	0.15	0.571	
3	SDS	LS-2	0.15	0.564	
1	SDS	LS-2	0.2	0.477	0.477 d
2	SDS	LS-2	0.2	0.465	
3	SDS	LS-2	0.2	0.488	
1	SDS	LS-2	0.25	0.465	0.467 d
2	SDS	LS-2	0.25	0.474	
3	SDS	LS-2	0.25	0.463	
1	SDS	LS-2	0.3	0.473	0.473 d
2	SDS	LS-2	0.3	0.48	
3	SDS	LS-2	0.3	0.466	
1	SDS	LS-2	0.325	0.465	0.469 d
2	SDS	LS-2	0.325	0.447	
3	SDS	LS-2	0.325	0.495	
1	SDS	LS-2	0.35	Precipitated	
2	SDS	LS-2	0.35	Precipitated	
3	SDS	LS-2	0.35	Precipitated	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 24 Dynamic IFT of SDS and LS-3 solution with canola oil at various NaCl concentrations.

Replication	Anionic Surfactant (0.03 M)	Nonionic Surfactant (0.01 M)	NaCl (M)	IFT (mN/m)	Mean
1	SDS	LS-3	0	0.764	0.766 a
2	SDS	LS-3	0	0.769	
3	SDS	LS-3	0	0.766	
1	SDS	LS-3	0.025	0.633	0.644 e
2	SDS	LS-3	0.025	0.654	
3	SDS	LS-3	0.025	0.644	
1	SDS	LS-3	0.05	0.674	0.676 d
2	SDS	LS-3	0.05	0.669	
3	SDS	LS-3	0.05	0.684	
1	SDS	LS-3	0.1	0.687	0.692 c
2	SDS	LS-3	0.1	0.69	
3	SDS	LS-3	0.1	0.699	
1	SDS	LS-3	0.15	0.712	0.711 b
2	SDS	LS-3	0.15	0.706	
3	SDS	LS-3	0.15	0.714	
1	SDS	LS-3	0.25	0.683	0.694 c
2	SDS	LS-3	0.25	0.699	
3	SDS	LS-3	0.25	0.701	
1	SDS	LS-3	0.3	0.633	0.644 e
2	SDS	LS-3	0.3	0.654	
3	SDS	LS-3	0.3	0.644	
1	SDS	LS-3	0.325	0.624	0.629 f
2	SDS	LS-3	0.325	0.634	
3	SDS	LS-3	0.325	0.628	
1	SDS	LS-3	0.35	0.599	0.602 g
2	SDS	LS-3	0.35	0.596	
3	SDS	LS-3	0.35	0.611	
1	SDS	LS-3	0.4	0.624	0.629 f
2	SDS	LS-3	0.4	0.634	
3	SDS	LS-3	0.4	0.628	
1	SDS	LS-3	0.45	Precipitated	
2	SDS	LS-3	0.45	Precipitated	
3	SDS	LS-3	0.45	Precipitated	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

APPENDIX B: ASE EXTRACTION CONDITIONS AND EXPERIMENTAL DATA

Table 25 Oil detachment (OD) and oil extraction (OE) efficiency of ASE method with various SDS concentrations (Experimental Design 3.7.5).

	Treatment (4)	Raw Data		Mean	
Replication	SDS Conc. (M)	OD (%)	OE (%)	OD (%)	OE (%)
1	0.005	27.62	9.94	27.99 c	10.96 d
2	0.005	27.27	10.18		
3	0.005	29.09	12.76		
1	0.01	38.15	39.02	43.02 b	37.45 c
2	0.01	45.92	37.43		
3	0.01	44.98	35.89		
1	0.02	70.93	58.91	68.33 a	58.48 a
2	0.02	67.55	57.20		
3	0.02	66.52	59.34		
1	0.03	71.97	53.12	71.74 a	54.84 b
2	0.03	71.42	56.22		
3	0.03	71.84	55.19		

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 26 Oil detachment (OD) and oil extraction (OE) efficiency of ASE method using magnetic stirrer and ultrasonication bath with various extraction times (Experimental Design 3.7.6).

Treatment (2X4)			Raw Data		Mean	
Replication	Mixing method	Extraction Time (min)	OD (%)	OE (%)	OD (%)	OE (%)
1	Stirring	15	69.49	51.58	69.76 c	52.38 b
2	Stirring	15	66.97	50.36		
3	Stirring	15	72.82	55.18		
1	Stirring	30	70.93	58.91	68.34 c	58.48 a
2	Stirring	30	67.56	57.20		
3	Stirring	30	66.53	59.33		
1	Stirring	45	80.01	63.55	78.13 a	60.65 a
2	Stirring	45	76.80	59.81		
3	Stirring	45	77.59	58.60		
1	Stirring	60	73.67	55.18	74.00 ab	57.84 a
2	Stirring	60	73.56	55.32		
3	Stirring	60	74.78	63.03		
1	Ultrasonication	15	55.54	30.57	58.21 d	29.26 d
2	Ultrasonication	15	61.19	30.91		
3	Ultrasonication	15	57.90	26.31		
1	Ultrasonication	30	59.07	33.65	59.79 d	35.88 c
2	Ultrasonication	30	59.16	38.25		
3	Ultrasonication	30	61.14	35.72		
1	Ultrasonication	45	72.30	46.19	76.57 a	48.65 b
2	Ultrasonication	45	79.08	49.96		
3	Ultrasonication	45	78.33	49.81		
1	Ultrasonication	60	71.29	52.59	72.21 bc	52.94 b
2	Ultrasonication	60	74.06	52.96		
3	Ultrasonication	60	71.28	53.28		

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 27 Oil detachment (OD) and oil extraction (OE) efficiency of ASE method using extraction combination between ultrasonication and stirring with various extraction time ratios (Experimental Design 3.7.6).

	Treatment (5)	Raw Data		Mean	
Replication	Extraction time ratio of Ultrasonication to Stirring (min:min)	OD (%)	OE (%)	OD (%)	OE (%)
1	0:60	73.67	55.18	74.00 a	57.84 ab
2	0:60	73.56	55.32		
3	0:60	74.78	63.03		
1	15:45	68.42	52.84	72.23 a	59.27 a
2	15:45	74.26	62.39		
3	15:45	74.02	62.59		
1	30:30	72.79	56.27	73.12 a	55.90 ab
2	30:30	73.72	57.24		
3	30:30	72.85	54.20		
1	45:15	73.10	43.94	73.53 a	45.39 c
2	45:15	74.05	46.81		
3	45:15	73.44	45.41		
1	60:0	71.29	52.59	72.21 a	52.94 b
2	60:0	74.06	52.96		
3	60:0	71.28	53.28		

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 28 Oil detachment (OD) efficiency at 20^{o}C of ASE method oil using water, 0.02M SDS and n-hexane as extraction medium (Experimental Design 3.7.7).

	Treatment (3)	OD (%)	
Replication	Extraction Media	Raw Data	Mean
1	Water	31.10	31.62 b
2	Water	28.58	
3	Water	35.17	
1	SDS	65.70	65.05 a
2	SDS	64.32	
3	SDS	65.14	
1	n-Hexane	66.44	68.32 a
2	n-Hexane	70.24	
3	n-Hexane	68.28	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 29 Oil detachment (OD) efficiency of ASE method using water and 0.02M SDS solution as extraction medium with various extraction temperatures (Experimental Design 3.7.7).

Treatment (2X3)			OD (%)	
Replication	Extraction Media	Extraction Temperature (^{o}C)	Raw Data	Mean
1	Water	20	31.10	31.62 d
2	Water	20	28.58	
3	Water	20	35.17	
1	Water	50	30.83	31.05 d
2	Water	50	28.79	
3	Water	50	33.52	
1	Water	70	41.26	39.63 c
2	Water	70	39.05	
3	Water	70	38.59	
1	SDS	20	65.70	65.05 ab
2	SDS	20	64.32	
3	SDS	20	65.14	
1	SDS	50	63.86	62.34 b
2	SDS	50	61.57	
3	SDS	50	61.61	
1	SDS	70	66.92	69.30 a
2	SDS	70	70.40	
3	SDS	70	70.57	

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 30 Oil detachment (OD) and oil extraction (OE) efficiency of ASE method with various solid-liquid ratios (Experimental Design 3.7.8).

	Treatment (5)	Raw Data		Mean	
Replication	Solid to Liquid (g : mL)	OD (%)	OE (%)	OD (%)	OE (%)
1	1:5	31.90	25.88	29.89 c	23.50 d
2	1:5	28.82	20.15		
3	1:5	28.94	24.46		
1	1:7	33.79	24.88	33.95 b	24.59 d
2	1:7	33.39	23.89		
3	1:7	34.67	25.02		
1	1:10	81.17	60.97	81.30 a	60.88 a
2	1:10	79.30	63.46		
3	1:10	83.43	58.21		
1	1:20	81.00	43.53	80.21 a	41.32 b
2	1:20	79.08	38.58		
3	1:20	80.54	41.85		
1	1:30	80.51	39.34	81.15 a	36.33 c
2	1:30	82.32	33.93		
3	1:30	80.63	35.71		

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

Table 31 Oil detachment (OD) and oil extraction (OE) efficiency of ASE method using triple extraction with three-stages (3E3S) with various solid-liquid ratios (Experimental Design 3.7.9).

	Treatment (2X3)		Raw Data		Mean	
Replication	No of Extraction	Solid to Liquid (g : mL)	OD (%)	OE (%)	OD (%)	OE (%)
1	Single	1:5	31.90	25.88	29.89 e	23.50 c
2	Single	1:5	28.82	20.15		
3	Single	1:5	28.94	24.46		
1	Single	1:7	33.79	24.88	33.95 d	24.59 c
2	Single	1:7	33.39	23.89		
3	Single	1:7	34.67	25.02		
1	Single	1:10	81.17	60.97	81.30 a	60.88 a
2	Single	1:10	79.30	63.46		
3	Single	1:10	83.43	58.21		
1	3E3S	1:5	74.44	52.49	73.36 c	53.53 b
2	3E3S	1:5	72.43	54.99		
3	3E3S	1:5	73.21	53.10		
1	3E3S	1:7	78.32	52.47	76.91 b	54.33 b
2	3E3S	1:7	75.86	55.72		
3	3E3S	1:7	76.55	54.80		
1	3E3S	1:10	83.53	57.86	82.06 a	57.80 ab
2	3E3S	1:10	80.02	54.29		
3	3E3S	1:10	82.62	61.24		

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

APPENDIX C: EXPERIMENTAL DATA OF EXTRACTED CANOLA OIL QUALITY

Table 32 Fatty acid profile of three extracted canola oils and commercial canola oil.

Canola Oil	Fatty Acid (%wt)				
	Palmitic (16:0)	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)
Screw Press Extraction	4.6	1.8	64.0	19.4	8.7
ASE	4.8	1.8	65.2	19.6	8.6
Soxhlet n-Hexane Extraction	4.9	1.8	65.0	19.8	8.6
Commercial Oil	4.6	1.9	64.6	19.9	9.0

Table 33 Water content and acid value of extracted canola oil and commercial canola oil.

Replication	Canola Oil	Raw Data		Mean	
		Water Content (vol%)	Acid Value (mg KOH/g)	Water Content (vol%)	Acid Value (mg KOH/g)
1	Screw Press	0.41	0.26	0.40 a	0.28 c
2	Screw Press	0.40	0.29		
3	Screw Press	0.39	0.28		
1	ASE	0.33	0.33	0.33 c	0.33 b
2	ASE	0.32	0.36		
3	ASE	0.33	0.30		
1	Soxhlet n-Hexane	0.35	0.39	0.36 b	0.41 a
2	Soxhlet n-Hexane	0.35	0.43		
3	Soxhlet n-Hexane	0.36	0.41		
1	Commercial Oil	0.06	0.08	0.06 d	0.10 d
2	Commercial Oil	0.06	0.09		
3	Commercial Oil	0.06	0.12		

Means within each column followed by the same letter are not significantly different at $P \leq 0.05$

BIOGRAPHY

Mr. Nattapong Tuntiwiwattanapun was born on March 15, 1985 in Bangkok, Thailand. He graduated his Bachelor's degree in Food Technology from faculty of Science, Chulalongkorn University in 2006. At Chulalongkorn University, his senior project was "An Application of Turmeric for the Development of Frozen Barbeque-like Product from Chicken Trimmings" which regarded to using natural antioxidant in turmeric to preserve the quality of chicken product during the cold storage. After that, he went to China for studying "Chinese Language for Foreigner" at Qingdao University for one year. Then he worked at United Thai Distiller Co.,Ltd. as a project manager of one product line.

In 2010, he pursued his Master Degree studies in the International Postgraduate Program in Environmental Management (Hazardous Waste Management), Inter-Department of Environmental Management Chulalongkorn University. Moreover, during his graduate study, he got a scholarship to do another Master Degree in Environmental and Conservation Sciences Program of North Dakota State University, United States of America.

His work was to develop aqueous surfactant-assisted extraction to extract vegetable oil for replacing n-hexane solvent extraction. He gave an oral presentation on "Optimization of Vegetable Oil Detachment Efficiency by Reducing Interfacial Tension" at ASABE/CSBE North Central Intersectional Conference in Fargo, ND, March 30, 2012. He extended his work by using the extracted oil from the previous work as the biodiesel feedstock. He presented this work "Develop and Scale up Aqueous Surfactant-assisted Extraction of Canola Oil for Use as a Biodiesel Feedstock" at ASABE International Meeting in Dallas, TX, July 31, 2012. This work also submitted to JAOCS as a manuscript on Aug 10, 2012.