UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

FORMATION AND CHARACTERIZATION OF VEGETABLE OIL MICROEMULSIONS AND THEIR APPLICATION IN OILSEED EXTRACTION AND BIOFUEL

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

Degree of

DOCTOR OF PHILOSOPHY

By

LINH DIEU DO
Norman, Oklahoma
2010

FORMATION AND CHARACTERIZATION OF VEGETABLE OIL MICROEMULSIONS AND THEIR APPLICATION IN OILSEED EXTRACTION AND BIOFUEL

A DISSERTATION APPROVED FOR THE
SCHOOL OF CHEMICAL, BIOLOGICAL AND MATERIALS ENGINEERING

BY

Dr. Jeffrey H. Harwell, Chair

Dr. David A. Sabatini

Dr. Tohren C. G. Kibbey

Dr. Lance L. Lobban

Dr. John F. Scamehorn

DEDICATION

This dissertation is dedicated to my grandfather Phan Tử Quang, my mother Phan Xuân Minh, my father Đỗ Ngọc Chính, my brother Đỗ Tuấn Linh, my husband Mai Thế Ánh and my daughter Mai Bảo Hân

ACKNOWLEDGMENTS

I would like to express my sincere appreciation to those who have made the publication of this dissertation possible and have made my graduate student life so enjoyable that I will cherish forever.

I owe my deepest gratitude to my advisor Dr. Sabatini for his eternal encouragement, guidance, wisdom and supervision; without whom this dissertation would not have been possible. He has become my mentor both in academic and personal life. I am grateful for his faith in my ability which has lifted up my confidence and become who I am today. I thank him for giving me the opportunities to present this work in a number of conferences. I would like to express my appreciation to his wife Frances Sabatini for her support and hospitality. Their kindness has given me a feel of a second family in the foreign country.

I am very grateful to Dr. Scamehorn for his valuable advice and support. He was the first who introduced me to the world of surfactant science. I am thankful to Dr. Harwell for his encouragement and valuable discussion. His vision on vital issues and industrial applications of surfactants has inspired me in critical thinking.

I would like to thank Dr. Kibbey for serving as my committee member and his kindness in letting me use his lab equipment. I would like to thank Dr. Lobban for his time and energy in reviewing my dissertation and serving as my committee member. I am indebted to Dr. Gollahalli for his guidance and kindness in permitting me to use his equipment in the combustion lab. I am thankful to Dr. Edgar Acosta for his valuable

information and advice. I am grateful to know Dr. Lowell Busenitz for his guidance in the economic feasibility study.

This dissertation would not have been possible without the love and encouragement from my grandfather, my parents, my in-laws, my brother, my husband and daughter. My deepest appreciation goes to my husband Anh Mai who has continuously encouraged and helped me in many ways. The love and patience from my husband and daughter Han have given me the strength to overcome any obstacles in life.

I am indebted to my past and present colleagues for their friendship and technical discussion. These include: Thu, Komesvarakoul (Cheng), Anuradee (Oat), Tri, Attaphong (Mink), Khwan, Prapas, Laura, Chris, Damon, Sezin, Emma and Vinay. I am thankful to my undergraduate research assistants: Odi, Nicole, Brittany, Megan, Ashley and Bridgett.

I am thankful to my host family, late Uncle Larry and Ha Flanagan, my cousin Lan, my friends, Huong, Ha, Tu, Phuong, Dzung, Son and friends at the Society of Vietnamese Students for their hospitality and friendship.

I would like to acknowledge the assistance of the staff from Civil Engineering and Environmental Science Department and Chemical, Biological and Materials Engineering Department for the administrative work.

Finally, I would like to acknowledge the financial supports for this work from Environmental Protection Agency (EPA), Oklahoma Center for Advanced Science and Technology (OCAST), Oklahoma Department of Energy (DOE), Oklahoma Bioenergy Center and the sponsors of the Institute for Applied Surfactant Research (IASR).

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Microemulsions are thermodynamically stable dispersions of oil and water stabilized by a film of surfactants and/or co-surfactants. They have numerous applications in food, oilseed extraction, drug and cosmetic delivery, enhanced oil recovery, biofuels, etc. Microemulsion formation of vegetable oils at ambient conditions (temperature and pressure) and without the addition of co-oil and/or alcohols is challenging at best. Undesirable phases, such as macroemulsions, liquid crystals and sponge phases, are often encountered when formulating these microemulsions. The goal of this dissertation is to formulate vegetable oil microemulsions using a novel class of surfactants, called extended-surfactants combining with hydrophilic/hydrophobic linker system, and to explore their uses in oilseed extraction and bio-renewable fuel applications. Extended-surfactants are a relatively new type of surfactant with propoxylate (PO) and/or ethoxylate (EO) groups inserted between the hydrophilic head and the hydrophobic alkyl chain of the surfactant molecule. This unique structure of extended-surfactants enables them to produce ultralow interfacial tension with vegetable oils at ambient condition. Environmentally friendly vegetable oil microemulsions were successfully formed without the addition of co-oil/alcohol at ambient temperature. These microemulsions are particularly useful in food, drug and cosmetic applications. Owing to the ultralow interfacial tension reduction between the vegetable oil and aqueous extended-surfactant solution at relatively low surfactant concentration, we have demonstrated that the aqueous extended-surfactant-based method is a viable alternative for vegetable oil extraction as in batch study. The oil quality produced from the aqueous extended-surfactant based method was found to be comparable or even superior to that obtained from hexane-based extraction. Next, we have designed and investigated a semi-continuous pilot-scale study of the aqueous extended-surfactant-based method for vegetable oil extraction. The total oil recovery after two extraction stages was approaching the result obtained from the batch study; however, the free oil recovery was lower. We have shown that the aqueous surfactant based method for oilseed extraction is superior to that of aqueous extraction method and enzyme-assisted extraction method. The last part of the dissertation demonstrated the use of reverse micellar microemulsions of vegetable oil/diesel blend as an alternative to diesel fuel. With appropriate surfactant and co-surfactant systems, we were able to formulate canola and algae/diesel blend microemulsion fuels with fuel properties such as viscosities, cloud points and pour points that satisfy the ASTM standards. The global CO pollutant and radiation emissions of all formulated microemulsion fuels were superior to DF and biodiesel. NOx emissions were lower in the blend containing no nitrate additives, but were higher than DF in the presence of nitrate additives. Thus, these results show that microemulsification is a viable technology for producing biofuels without chemical reactions and that fuel properties can be adjusted via formulation variables.

Chapter 1 Introduction

The oilseed industry is rapidly growing with a 900% increase in trading of oilseed products and 1, 800% increase in global market for vegetable oil from 1964 to 2004 [1]. Owing to their bio-renewable and non-toxic properties, research interest in vegetable oil based microemulsions has increased significantly over the past twenty years [2,3,4]. Vegetable oil based microemulsions have numerous applications in food, oilseed extraction, pharmaceuticals, cosmetics, enhanced oil recovery, cleaning technology and biofuels, etc [5,6]. They can be used as an alternative to petroleum oil based or mineral oil based microemulsions.

By definition, microemulsions are thermodynamically stable, isotropic dispersions of oil and water, stabilized by a film of surfactant and/or co-additives [7]. At low to moderate surfactant concentration, three microemulsion types can be produced. As denoted by Winsor, Winsor Type I microemulsions are normal micelles in equilibrium with the excess oil phase, Winsor Type II microemulsions are reverse micelles in equilibrium with the excess water phase, and Winsor Type III microemulsions are a bicontinuous phase containing oil, water and surfactant in equilibrium with the excess water and excess oil phases [7]. The microemulsion Type I-III-II transition can be achieved by increasing the electrolyte concentration for ionic surfactants or increasing temperature for non-ionic surfactant. Increasing electrolyte concentration (for ionic surfactants) or temperature (for non-ionic surfactant) causes the surfactant solution to become more hydrophobic and thus segregate more towards the oil-water interface, thereby reducing the surfactant film curvature and interfacial tension. At net zero curvature, a Winsor Type III system is formed [7]. A Winsor type IV microemulsion is an extension of a Type III system at higher surfactant concentrations, where the middle phase extends and becomes a single phase.

Microemulsion formation of vegetable oils at ambient conditions (temperature and pressure) and without the addition of co-oil and/or alcohols is challenging at best. Undesirable phases, such as macroemulsions, liquid crystals and sponge phases, are often encountered when formulating these microemulsions [8,9,10]. These are due to the distinctive structure of the triglyceride which is the most abundant composition (> 95%) in vegetable oil [11]. Triglycerides are esters of glycerol with fatty acids which contributes to its complicated behavior [11]. The long and bulky alkyl chain lengths make triglycerides highly hydrophobic, while the ester region in the molecule causes high polarity; combined these lead to poor solubilization by conventional surfactants.

The discovery of extended-surfactants by Minana-Perez et al. has significantly advanced our ability to form triglyceride microemulsions [12]. Extended-surfactants are a new type of surfactant with propoxylate (PO) and/or ethoxylate (EO) groups inserted between the hydrophilic head and the hydrophobic alkyl chain of the surfactant molecule. This unique structure of extended-surfactants enables them to produce ultralow interfacial tension (IFT < 0.01 mN/m) with vegetable oils at ambient condition [13,14]. These properties of extended-surfactants with vegetable oils have opened a new research area in vegetable oil based microemulsions and their applications. The goal of this dissertation is to formulate vegetable oil microemulsions without alcohol or co-oil addition, to apply this ultra low interfacial tension technology to extract oil from oilseeds and to formulate temperature insensitive microemulsion fuels. This dissertation also investigates the laboratory pilot scale study of oilseed extraction using aqueous-surfactant-based method and the combustion properties of some microemulsion fuels.

Chapter 2 explores the use of extended-surfactants and combined hydrophilic/hydrophobic linkers in forming alcohol/co-oil free vegetable oil microemulsions at ambient conditions. Linkers are amphiphiles that can enhance the interactions of surfactant-oil and surfactant-water at the oil-water interface. Linker concepts have been extensively studied in the literature [15,16,17,18]. The lipophilic linkers partition into the surfactant tail region whereas the hydrophilic linkers segregate within the surfactant head group region [16,17]. Linkers are used to enhance solubilization since they improve the interaction of the surfactant membrane in either the oil or water side, and to form microemulsions more economically, as they can replace a certain proportion of the main surfactant [16]. These non-toxic vegetable oil based microemulsions are particular attractive in pharmaceuticals, cosmetics, cleaning technology and food applications.

Chapter 3 investigates the ability of the aqueous extended-surfactant solution to extract vegetable oil from oilseeds as an alternative to hexane method. A series of extended-surfactants were evaluated in this study. We are particularly interested in the lowest surfactant concentration capable of producing ultralow interfacial tension (IFT), which is known as the critical microemulsion concentration (CμC). Removal of oil at the CμC point due to IFT reduction is well known as the mobilization mechanism [19]. This work was motivated by increasing environmental and safety concerns related to hexane extraction method for oilseed extraction. The vegetable oil extraction industry has contributed the primary VOC emissions in the food industry [20]. The annual hexane loss in the soybean oil extraction process alone in the US could be as high as 210 – 430 million liters [20]. Worker exposure to hexane at 15 ppm/day for three months has been shown to cause peripheral nerve damage, and hexane is also a potential hazardous explosive material [21]. Research has shown that vegetable oil and protein qualities produced by aqueous based extraction method using hot water and/or in combination with enzymes are consistently superior to those produced by hexane based method [22]. The use of aqueous surfactant for vegetable oil extraction was hindered in the past due to the high interfacial tension value between the vegetable oil and conventional surfactants. Thanks to the ultralow interfacial tension of extended-surfactants with vegetable oils at ambient conditions, this approach is utilized for vegetable oils in Chapter 3.

Having successfully demonstrated the effectiveness of aqueous extended-surfactant solution in extracting vegetable oil from oilseeds with vegetable oil quality comparable or even superior to that obtained from hexane based method, the goal of Chapter 4 is to evaluate semi-continuous laboratory-based surfactant-assisted aqueous extraction process (SAEP) using laboratory-scale processing equipment similar to that used in industrial processes. The objectives of this work are (1) to study the effect of processing parameters on extraction efficiency and (2) to identify potential problems related to the scale-up system of the SAEP. The comparison of SAEP pilot scale results to other AEP and enzyme AEP are also discussed.

Chapter 5 attempted to formulate reverse micelle microemulsions containing a vegetable oil/diesel blend with ethanol which can be used as an alternative fuel to diesel fuels. Due to increasing energy demands and a desire to reduce our dependence on petroleum fuels, research for viable alternative fuels has received significant attention.

The proposed U.S. renewable fuels initiative targets increasing domestic supply of alternative fuels to 36 billion gallons by 2022 [23]. Algae oil was studied among other vegetable oils in this work. Algae oil is favored over vegetable oils since it does not require landfill, grows much faster than oilseed crops, and does not have to compete with the agricultural industry [24, 25]. To date, there is no paper reported on the phase behavior study or combustion properties of algal-based microemulsion fuels. Microemulsions fuel phase behaviors, viscosities and combustion properties are presented in this chapter.

Finally Chapter 6 summarizes the concluding remarks of this dissertation and discussions on potential impact of the findings from this work.

REFERENCES

---

1. Gale Group (2008) Fats and Oils. Encyclopedia of Global Industries. Online Edition. Reproduced in Business and Company Resource Center. Farmington Hills, Mich. (accessed in February 2009).

   <http://galenet.galegroup.com.ezproxy1.lib.ou.edu/servlet/BCRC>

2. Kukieda H (1989) Phase behaviors in water/nonionic surfactant/hydrocarbon and water/nonionic surfactant/amphiphilic oil system. J Colloid Interface Sci 133:237–243

---

3. Lindman B, Shinoda K, Olsson U, Anderson DM, Karlstrom G, Wennerstrom H (1989) On the demonstration of bicontinuous structures in microemulsions. Colloid Surf 38:205–224

4. Gelbart WM, Ben-Shaul A, Roux D (eds) (1994) Micelles, membranes, microemulsions and monolayers. Spinger, New York, pp 395–426

5. Sabatini DA, Knox RC, Harwell JH, Wu B (2000) Integrated design of surfactant enhanced DNAPL remediation: efficient supersolubilization and gradient systems. J Contam Hydrol 45:99–121

6. Childs JD, Acosta E, Knox R, Harwell JH, Sabatini DA (2004) Improving the extraction of tetrachloroethylene from soil columns using surfactant gradient systems. J Contam Hydrol 71:27–45

7. Bourrel M, Schechter RS (1988) Microemulsions and related systems. Marcel Dekker, New York

8. Joubran RF, Cornell DG, Parris N (1993) Microemulsions of triglyceride and non-ionic surfactant: effect of temperature and aqueous phase composition. Colloids Surf A 80:153–160

9. Corswant C, Engstrom S, Soderman O (1997) Microemulsions based on soybean phosphatidylcholine and triglycerides. Phase behavior and microstructure. Langmuir 13:5061–5070

---

10. Tungsubutra T, Miller CA (1994) Effect of secondary alcohol ethoxylates on bahavior of triolein–water–surfactant systems. JAOCS 71(1):65–73

11. Gomes T (1992) Oligopolymer, diglyceride and oxidized triglyceride contents as measures of olive oil quality. JAOCS 69(12): 1219 – 1233.

12. Minana-Perez M, Graciaa A, Lachaise J, Salager JL (1995) Solubilization of polar oils with extended surfactants. Colloids Surf A Physicochem Eng Asp 100:217–224

13. Withayyapayanon A, Acosta EJ, Harwell JH, Sabatini DA (2006) Formulation of ultralow interfacial tension systems using extended – surfactants. J Surfact Deterg 9:331–339

14. Salager JL, Anton RE, Sabatini DA, Harwell JH, Acosta A, Tolosa LI (2005) Enhacing solubilization in microemulsions – state of the art and current trends. J Surfact Dterg 8:3–12

15. Sabatini DA, Acosta E, Harwell JH (2003) Linker molecules in surfactant mixtures. Curr Opin Colloid Interface Sci 8:316–326

16. Acosta E, Uchiyama H, Sabatini DA, Harwell JH (2002) The role of hydrophilic linkers. J Surfactants Deterg 5(2):151–157

17. Graciaa A, Lachaise J, Cucuphat C, Salager JL (1993) Improving solubilization in microemulsions with additives. 1. The lipophilic linker role. Langmuir 9:669–672

18. Graciaa A, Lachaise C, Cucupht C, Salager JL (1993) Improving solubilization in mciroemulsions with additives. 2. Long chain alcohols as lipophilic linkers. Langmuir 9:3371–3374

19. Childs JD, Acosta E, Scamehorn JF, Sabatini DA (2005) Surfactant-Enhanced Treatment of Oil-Based Drill Cuttings. J Energy Resource Technol 207(2): 153 – 162

20. Darling ER , Yelland WEC (1952) Process of Liberating and Recovering Oil from Materials Containing Starch, Proteins, and Oil. U.S. Patent 2, 606,916

21. H-Hexane Substance Technical Guidelines (assessed in May 2008). <http://ehs.ucsc.edu/lab_research_safety/pubs/facts/Hexane.pdf>

22. Carr RA (1997) Oilseed Processing. In: Wan PJ, Wakelyn PJ (Eds.) Technology and Solvents for Extraction Oilseeds and Nonpetroleum Oils. AOCS Press, Champaign, pp 101 – 120

23. Renewable Fuel Standard (RFS) (accessed in Octorber 2010). <http://www.epa.gov/otaq/fuels/renewablefuels/index.htm>

24. Chisti Y (2007) Biodiesel from microalgae beats bioethanol. Tren Biotechnol 26: 126 – 131

25. Washington post online (2008) A Promising Oil Alternative: Algae Energy (accessed in October 2010) <http://www.washingtonpost.com/wp-dyn/content/article/2008/01/03/AR2008010303907.html>

Chapter 2 Formation and Characterization of Vegetable Oil Microemulsions Using Extended-Surfactants and Linkers[1]

ABSTRACT

Microemulsion formation of triglyceride oils at ambient conditions (temperature and pressure) and without the addition of co-oil and/or alcohols is challenging at best. Undesirable phases, such as macroemulsions, liquid crystals and sponge phases, are often encountered when formulating triglyceride microemulsions. The purpose of this study is to investigate the use of extended-surfactants, lipophilic linkers, and hydrophilic linkers in enhancing triglyceride solubilization and interfacial tension reduction. We have studied two classes of extended-surfactants, linear alkyl-polypropoxylated-sulfates (LAPS) surfactants and linear alkly-polypropoxylated-ethoxylated-sulfates (LAPES) surfactants. Linkers evaluated were oleyl alcohol (lipophilic linker), sodium mono- and dimethyl naphthalene sulfonate (SMDNS), and polyglucoside (hydrophilic linkers). Oils studied include olive, peanut, soybean, canola and sunflower oils. The effect of electrolyte concentration on microemulsion phase behavior was studied. The microemulsion "fish" diagram was presented by plotting the total surfactant and linker

---

[1] This chapter or portions thereof has been published previously in *Journal of Surfactants and Detergents* under the title "Environmentally Friendly Vegetable Oil Microemulsions Using Extended-Surfactants and Linkers", Journal of Surfactants and Detergents, 2009, 12, 91 – 99. This current version has been reformatted for this dissertation.

concentrations versus the electrolyte concentration. We were able to form Winsor Type I, II, III and IV microemulsions at ambient conditions and without co-oil or short and medium chain length alcohol addition. The Winsor Type III and Type IV triglyceride microemulsions are particularly useful in numerous applications such as cosmetics, vegetable oil extraction and soil remediation.

Key words: microemulsions, triglyceride oil, extended-surfactant, hydrophilic linker, hydrophobic linker, vegetable oil, and ultralow interfacial tension

2.1 INTRODUCTION

Microemulsions are thermodynamically stable, isotropic solutions of water and oil stabilized by appropriate surfactant and/or linker molecules. Microemulsions exhibit many unique properties, such as being transparent and producing ultralow interfacial tension and ultra high solubilization. These properties make microemulsions desirable in numerous applications including cosmetics, drug delivery systems, cleaning technologies and soil remediation [1,2]. Figure 2.1 shows the microemulsion phase behavior in a "fish" diagram and the changes in curvature with surfactant concentration and the tuning parameter. At low to moderate surfactant concentration, three microemulsion types can be produced. As denoted by Winsor, Winsor Type I microemulsions are normal micelles in equilibrium with the excess oil phase, Winsor Type II microemulsions are reverse micelles in equilibrium with the excess water phase, and Winsor Type III microemulsions are a bicontinuous phase containing oil, water and surfactant in equilibrium with the excess water and excess oil phases [3]. The microemulsion Type I-III-II transition can be achieved by increasing the electrolyte concentration for ionic surfactants or increasing temperature for non-ionic surfactants (Figure 2.1). Increasing electrolyte concentration (for ionic surfactants) or temperature (for non-ionic surfactant) causes the surfactant solution to become more hydrophobic and thus segregate more towards the oil-water interface, thereby reducing the surfactant film curvature and interfacial tension. At net zero curvature, a Winsor Type III system is formed [3] A Winsor type IV microemulsion occurs when the surfactant concentration is increased in a Type III system, thereby increasing the volume of the middle phase until it becomes a single phase (Figure 2.1).

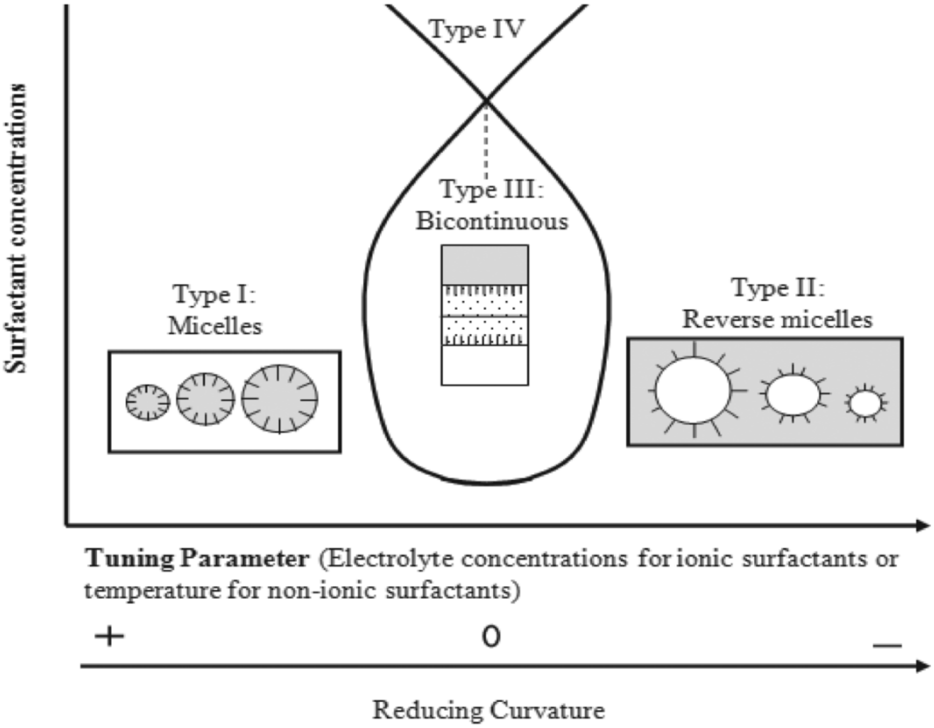


Figure 2.1: Microemulsion phase behaviors presented by a “fish” diagram showing change in curvature with surfactant concentrations and tuning parameters.

Often triglyceride oils do not solubilize well into the middle phase microemulsion, and a “sponge” phase occurs instead, as demonstrated by several researchers over the past twenty years [4,5,6]. Formation of triglyceride/vegetable oil microemulsions at ambient conditions and without the addition of co-oils/alcohols is challenging at best. Vegetable oils are used not only for cooking purposes but are also receiving broader interest because of the toxicological concerns of using petroleum oils; however, they are considerably more difficult to solubilize in microemulsions [7]. Many attempts have been made at forming vegetable oil microemulsions at ambient condition and without addition of co-oil or alcohols but without success [8,9,10]. Co-oils such as isopropyl myristate can easily form microemulsions with conventional surfactants; therefore, they are often mixed with triglyceride oils to enhance the microemulsion formation [11]. The reason that vegetable oil microemulsions are elusive appears to be due to the unique structure of triglyceride molecules. Triglycerides are esters of fatty acid with glycerol which contributes to its complicated behavior. The long and bulky alkyl chain lengths make triglycerides highly hydrophobic, while the ester region in the molecule causes high polarity; combined these lead to poor solubilization by surfactant. Therefore, conventional surfactants are not able to produce low interfacial tension (<0.1 mN/m) with vegetable oils at ambient conditions without alcohol or co-oil addition. In general, microemulsion formation with such systems results in liquid crystal, gel formation or sponge phase formation at ambient conditions. The discovery of extended-surfactants by Minana-Perez et al. has significantly advanced our ability to form triglyceride microemulsions [12]. Minana-Perez et al. group reported Winsor Type III microemulsions with soya oil/soybean oil at 35 Celsius degrees with optimum solubilization parameter (SP*) in the range of 7-15 ml g^{-1} using LAPES surfactants (see below) [12]. However, phase diagrams of Winsor I-III-II-IV systems were not presented [10,11] and the triglyceride microemulsion was reported at 35^o Celsius degrees rather than ambient temperature [12].

In the present study, we will explore the use of extended-surfactants to form Type I-IV triglyceride microemulsions at ambient conditions without short/medium chain alcohol or co-oil addition. We will investigate the performance of two classes of extended surfactants (linear alkyl-polypropoxylated-ethoxylated sulfate, LAPES, and linear alkyl-polypropoxylated sulfate, LAPS). Combined linker and extended-surfactant systems are proposed in this study to form microemulsions with vegetable oils. We have also investigated the detailed phase behavior of microemulsions consisting of extended-surfactants, linkers, vegetable oils (triolein, canola, olive, peanut, and soybean), water and electrolytes. Different from conventional surfactants, the extended-surfactant molecule has an intermediate polar group (i.e. propoxylated group) inserted between the head and the tail of the surfactant molecule. Detailed discussion of the structure, properties and discussion of extended-surfactants can be found in the literature [13 - 16]. Since extended-surfactants studied in this work can not form microemulsions with vegetable oils alone at ambient conditions, we introduce the use of both lipophilic and hydrophilic linkers.

Linkers are amphiphiles that can enhance the interactions of surfactant-oil and surfactant-water at the oil-water interface. Linker concepts have been extensively studied in the literature [17 - 20]. The lipophilic linkers partition into the surfactant tail region whereas the hydrophilic linkers segregate within the surfactant head group region.

Linkers are used to enhance solubilization since they improve the interaction of the surfactant membrane in either the oil or water side, and to form microemulsions more economically, as they can replace a certain proportion of the main surfactant [17]. Linkers also significantly impact coalescence rate of macroemulsions as they equilibrate to microemulsions [21].

Our goal is to form alcohol/co-oil free triglyceride microemulsions at ambient conditions. When we say alcohol free, we mean the absence of short or medium chain length alcohols since these are volatile and thus are of environmental/human exposure concern. By better understanding the triglyceride microemulsion system and finding appropriate surfactant/linker structures that are compatible with triglyceride molecules, we can produce more environmentally friendly triglyceride formulations (i.e., no short/medium chain length alcohol or addition of a second oil to help form microemulsions at ambient temperature).

2.2 EXPERIMENTAL PROCEDURES

2.2.1 Materials

Two classes of anionic extended-surfactants were studied in this work, including linear alkyl-propoxylated-ethoxylated-sulfate (LAPES) surfactants and linear alkyl-propoxylated-sulfate (LAPS) surfactants. The number of PO groups were varied among each class of surfactant. There is no EO group for LAPS surfactants and the number of EO groups was fixed at 2 for LAPES surfactants. The extended-surfactants were kindly provided by Huntsman Chemical Co. (Houston, TX) and used as received. The extended-surfactants studied and their properties are summarized in Table 2.1.

Table 2.1 Properties of extended-surfactants

Surfactant Series	**Name**	**Active%**	**Approx. HLB**[a]
LAPS	C_{16}-2.9PO	22.2	37.7
C_{16}-xPO-SO_4Na	C_{16}-4.5PO	23.2	37.4
	C_{16}-5.5PO	24.7	37.3
	C_{16}-8.2PO	24.1	36.9
	C_{16}-10.7PO	24.2	36.5
LAPES	C_{10}-10PO-2EO	17.4	40.1
$C_{10\ or\ 12}$-xPO-2EO-SO_4Na	C_{10}-14PO-2EO	22.4	39.5
	C_{10}-18PO-2EO	22.5	38.9
	C_{12}-10PO-2EO	24.1	39.2
	C_{12}-12PO-2EO	24.2	38.7
	C_{12}-14PO-2EO	24.1	38.6

[a] Estimated from Equation(2.1)

[a] Group contribution number: Sulfate = 38.7; $-CH_3$, $-CH_2-$ = 0.475; EO = 0.33; PO = 0.15

The hydrophilic-lipophilic balance (HLB) of the surfactants were estimated using Equation (2.1) [22, 23]:

$$HLB = 7 + \sum(\#hydrophilic\,groups) - \sum(\#hydrophobic\,groups)$$
$$HLB = 7 + [(Sulfate) + (\#EO)] - [(\#CH_3) + (\#PO)] \qquad \text{(Equation 2.1)}$$

It is important to note that the HLB equation is not the best approach to the hydrophobic-lipophilic nature of the surfactants. A better approach is to use the hydrophilic-lipophilic deviation (HLD) [24, 25]. However, due to the simplicity of the

HLB equation it is widely used by practitioners and is thus used for comparison purposes (and to illustrate shortcomings of the HLB approach). This is further illustrated in recent work by our group [25].

Sodium dioctyl sulfosuccinate (Aerosol-OT, +99% anhydrous) was purchased from Fisher Scientific and used as received. Triolein 65% practical grade, peanut, soybean and olive oils were purchased from Sigma Chemical Co. (St Louis, MO). Canola, corn and sunflower oils were purchased from the local market. Typical triglyceride compositions of several of these oils are summarized in Table 2.2. Sodium chloride +99% purity was purchased from Fluka Chemical Corp. (Milwaukee, WI). Polyglucoside (Glucopon N425 50 active%) was kindly provided by Cognis – Care Chemicals, sodium mono- and dimethyl naphthalene sulfonate (SMDNS) was received from CKWitco (Houston, TX). Oleyl-alchohol or fatty alcohol at 85% active was purchased from Aldrich (St Louis, MO). Pentane, hexane, n-heptane, n-decane, n-dodecane, n-hexadecane (+99% purity) were purchased from Sigma-Aldrich (St Louis, MO).

Table 2.2: Main fatty acid compositions (%) of some oils

Component	**C16:0** (P, Palmitic)	**C18:0** (S, Stearic)	**C18:1** (O, Oleic)	**C18:2** (L, Linoleic)	**C18:3** (Ln, Linolenic)
Triolein[a]	3.66	N/A	65	N/A	7.36
Peanut[b]	13	3	41	38	N/A
Olive[b]	10	2	78	7	1
Canola[b]	4	2	56	26	10

[a]Triolein, 65% practical grade, data from manufacturer

[b]Data from reference [31]

2.2.2 Methods

Dynamic interfacial tension experiments were performed to evaluate the interaction of extended-surfactant systems with triolein and vegetable oils. These experiments were carried out using a spinning drop tensiometer purchased from the University of Texas (Model 500). All surfactant solutions were diluted to 0.1 wt% for salinity scans. Each sample run was conducted in triplicate and recorded every five minutes for a twenty minute time frame.

Phase behavior experiments were carried out by scanning a single parameter of the formulation (for example, by varying salinity, surfactant concentration, etc) [3]. Five ml of surfactant solution and five ml of oil were added into a 15 ml glass vial tube. The solutions were gently shaken three times a day for three days and left for two weeks to ensure equilibrium. At a constant surfactant and linker concentration, the optimum formulation is obtained at the optimum salinity concentration, as denoted by S* (expressed in wt%). Recalling from the Winsor R ratio definition, the optimum formulations is obtained when R = 1, or surfactant interactions on both the water side and the oil side are equal to each other [22].

2.3 RESULTS AND DISCUSSIONS

2.3.1 Ultralow interfacial tension values (IFTs) with triglyceride oils

Figure 2.2 shows dynamic IFT values of Aerosol-OT(AOT) and C_{12}-14PO-2EO at optimum salinity (S*) with canola oil, and C_{12}-14PO-2EO at S* with triolein, corn, and peanut oils. The optimum salinity (S*) produces the minimum IFT for a given surfactant system. From Figure 2.2, it can be seen that C_{12}-14PO-2EO sulfate produced IFT values two to three orders of magnitude lower than AOT within 10-15 minutes. It is important to note that these results were obtained at ambient condition and with no addition of co-oil or alcohol. To our knowledge, this is the first time such ultralow IFT values have been reported for these vegetable oils at ambient conditions without addition of alcohol or co-oil. Ultralow IFT is defined as the IFT values << 0.1 mN/m. It is very encouraging to see that the extended-surfactant was able to reach equilibrium within a fifteen minute time frame. This result is very important for industrial application as IFT reduction occurs in a reasonable time frame for system scale up.

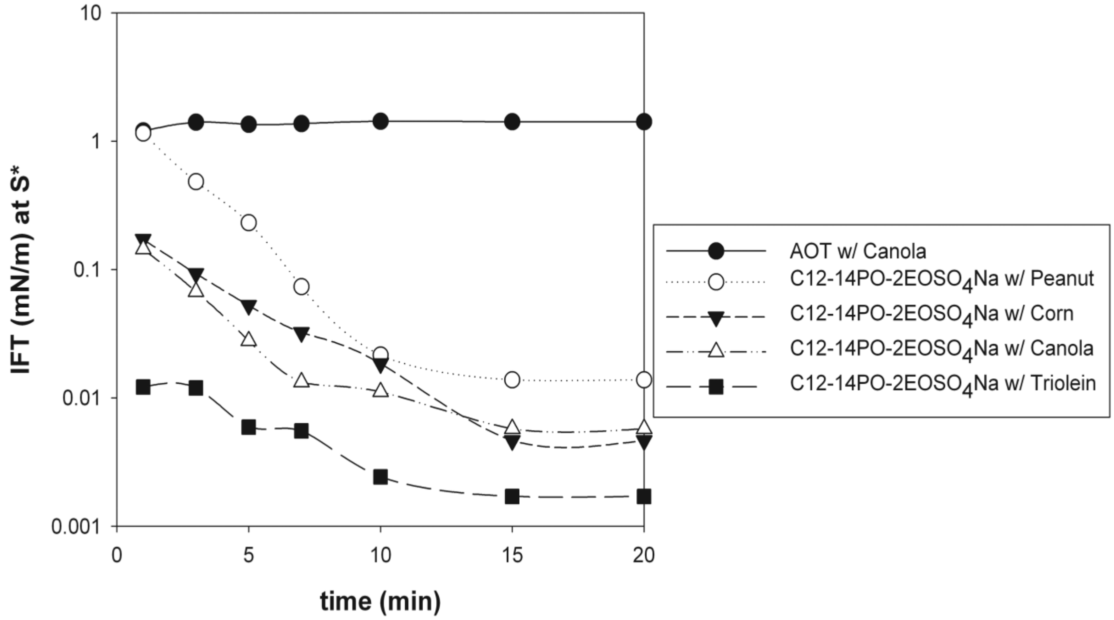


Figure 2.2: Dynamic IFT versus time of C_{12}-14PO-2EOsulfate and Aerosol-OT with various vegetable oils at optimum sodium chloride concentrations. Temperature at 27°C.

Figure 2.3 shows triolein dynamic IFT values using the two classes of extended-surfactants listed in Table 2.1 (LAPS and LAPES). As can be seen from Figure 2.3, all three extended-surfactants produced ultralow IFT values (<0.1 mN/m); recall that the conventional surfactant AOT was unable to do so (>1 mN/m as seen in Figure 2.2). The LAPES surfactants produced IFT values as low as 10^{-3} mN/m. Comparing the two classes of surfactants, both LAPES surfactants (C10 and C12) show lower IFT values than LAPS surfactants. It is important to note that, although ultra low IFT values were observed, middle phase microemulsion systems (or Winsor Type III) were not formed using extended-surfactants alone with triolein and vegetable oils; rather, sponge phases were observed as has been observed by other researchers [9, 26].

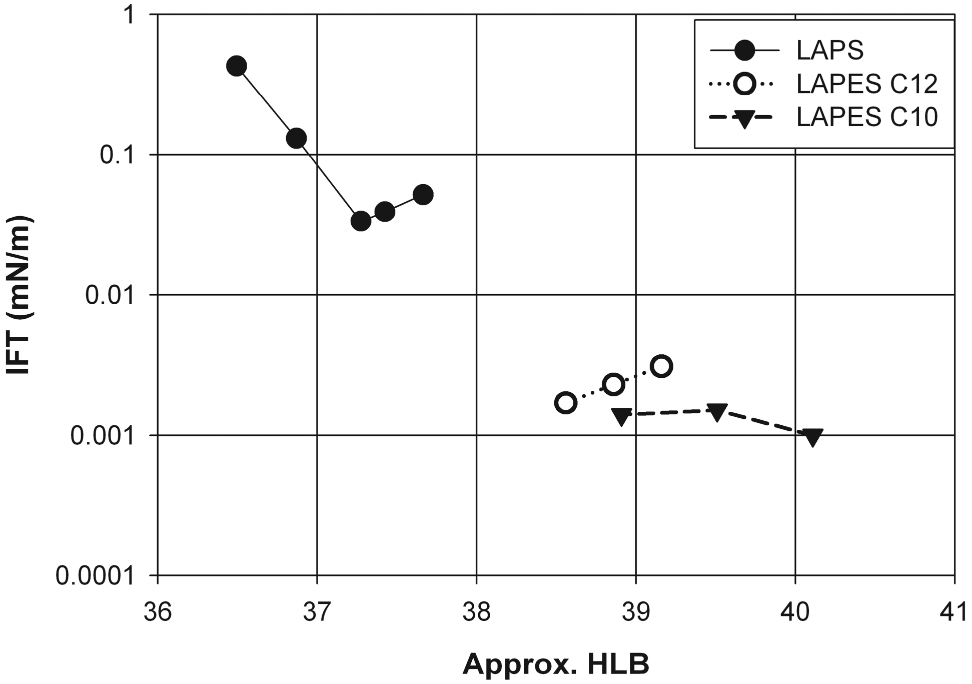


Figure 2.3: Triolein dynamic IFT values using three groups of studied extended-surfactants (temperature at 27^{o}C). Surfactant solutions were at 0.1wt%. LAPS: linear alkyl-propoxylated-sulfate; LAPES C10 and C12: linear-alkyl-propoxylated-ethoxylated-sulfate with alkyl groups of 10 and of 12, respectively.

For comparison purposes, select studies were conducted with hexadecane. Extended-surfactants were able to form a middle phase microemulsion (Winsor Type III) with hexadecane (EACN = 16), while extended-surfactants were unable to form a middle phase microemulsion with vegetable oils with similar EACN values (EACN 16-19 shown in Figure 2.4).

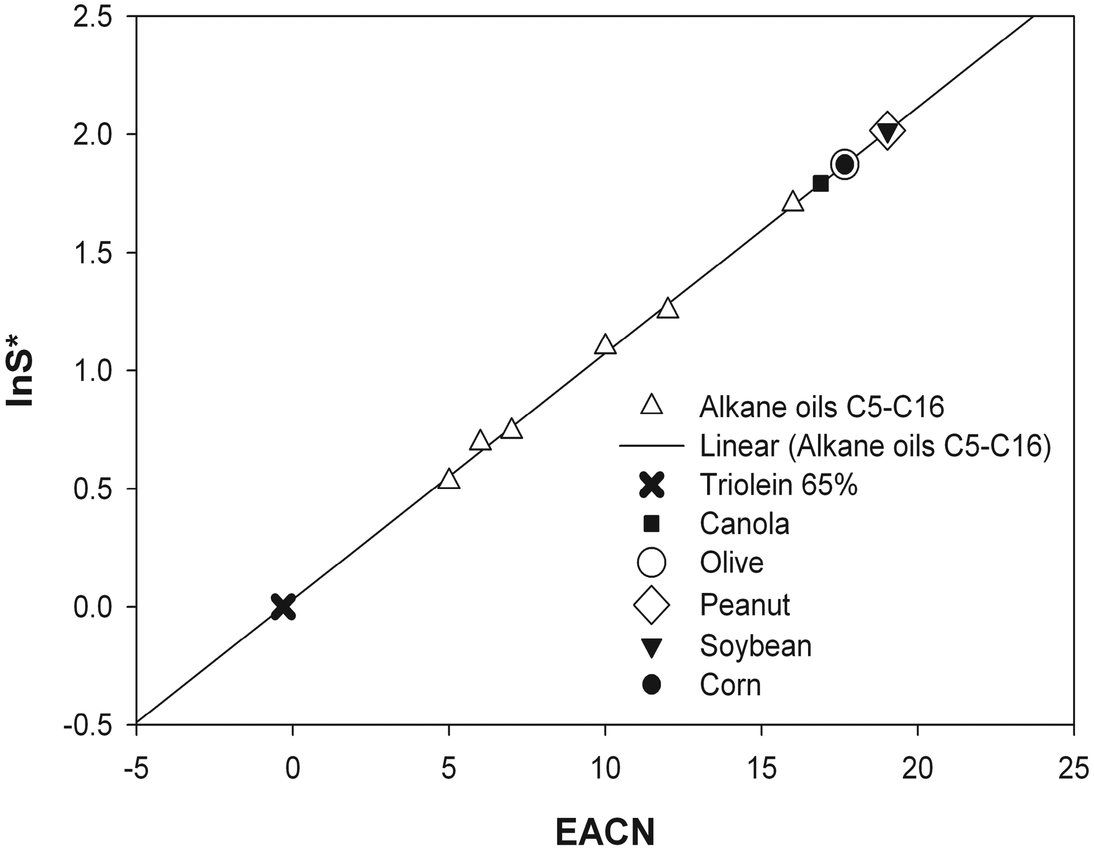


Figure 2.4: lnS* versus EACN of studied oils. Temperature at 25°C.

EACN is defined as the equivalent alkane carbon number, a measurement of the hydrophobicity of the oil [27]. Higher EACN values indicate more hydrophobic oils. Winsor Type I and Type II microemulsions were formed with triolein and vegetable oils with white milky excess oil or water phases, respectively, with negligible solubilization at even high surfactant concentration (i.e. 8 wt%). Even at higher temperature, such as 35°C, no middle phase microemulsion was observed. The low interfacial tension yet failure to form middle phase microemulsions using extended-surfactant alone in this work is likely due to the poor incorporation of the triglyceride oil into the microemulsion phase (poor solubilization). Poor solubilization is desirable in certain applications such as vegetable oil extraction, where high solubilization would require difficult oil-surfactant separation and surfactant recovery processes. Nonetheless, Minana et al. [12] achieved Type III microemulsion formation of soya oil with extended-surfactants, indicating that Type III systems are possible under the right conditions (right surfactant/oil combination).

2.3.2 Determination of equivalent alkane carbon number of vegetable oils

The equivalent alkane carbon number (EACN), which represents the oil's hydrophobicity, is an important parameter in producing an optimal formulation. EACN values of the oils can be found by using the semi-empirical equation proposed by Salager et al.[28]:

$$\ln(S^*) = k(EACN) + f(A) - \sigma + a_T \Delta T \qquad \text{(Equation 2.2)}$$

where S* is the optimum electrolyte concentration; k is a constant reflective of the head group, normally between 0.1 to 0.17; EACN is the equivalent alkane carbon number for unsaturated hydrocarbons (for saturated alkanes, by definition the value equals the number of carbons); σ is a function of the surfactant type; a_T is a constant at the reference temperature; f(A) is a function of short/medium chain alcohol; and ΔT is the temperature difference between the studied temperature and a reference temperature [28]. Since in our study, we did not use alcohol and we kept the temperature constant, Equation (2.2) can be simplified to:

$$\ln(S^*) = k(EACN) - \sigma \qquad \text{(Equation 2.3)}$$

It is important to note that the oleyl alcohol is considered to be a lipophilic linker and does not partition into the interface. Long chain alcohols partition into the oil phase and change the EACN of the oil. In our system, we did not use alcohol; therefore the f(A) term in Equation (2.2) can be neglected. Experimental procedures for determining the EACN values for oils have been described in Acosta et al. where they determined the EACN values of isopropyl myristate and squalene [18]. In our research, we conducted a sodium chloride scan at a fixed 0.1 wt% C_{12}-12PO-2EO-sulfate surfactant concentration for different oils. The IFT values were recorded after equilibrium was reached, i.e. until no change in IFT value was observed (up to 30 minutes). Alkane oils with known EACN values, including pentane (5), hexane (6), n-heptane (7), n-decane (10), n-dodecane (12) and n-hexadecane (16), were used as reference oils. The natural logarithm of S* values were plotted against EACN values of the reference oils to establish the correlation; from Equation (3), the correlation should produce a linear relationship. EACN values of triolein and vegetable oils can be easily found by measuring their S* and establishing their EACN values using the correlation curve established for oils with known EACN values.

Figure 2.4 shows the resulting lnS* versus EACN values of reference oils and interpreted EACN values of triolein (65% practical grade) and vegetable oils on the same plot. A good correlation was obtained for the fit to the alkane data (R^2 value at 0.99). Using C_{12}-12PO-2EO extended-surfactant, the fitting equation for reference oils is:

$$\ln(S^*) = 0.104\,(EACN) + 0.031 \qquad \text{(Equation 2.4)}$$

The k value of 0.104 is within the range reported in the literature (as mentioned above, 0.1 to 0.17). This k value is also similar to that reported by Minana et al.'s [16] group for 12PO extended-surfactants. From Equation (4) the surfactant constant (σ) for C_{12}-12PO-2EO extended-surfactant was found to be at -0.031. Based on their S* with C_{12}-12PO-2EO surfactant and using the correlation in Figure 2.4 and Equation (2.4), the EACN values of triolein 65% practical grade and vegetable oils are shown in Table 2.3; given that these are more than 40 to 50 carbons in these molecules, these EACN values demonstrate that the ester groups in the triglyceride oils greatly increase their hydrophilicity (reduce EACN).

As can be seen from Table 2.3, vegetable oils studied in this work are generally very hydrophobic with EACN values ranging from 17 to 19. Surprisingly, the triolein (65%) shows a negative EACN value of -0.3. From Table 2.2, we observe that triolein (C18:1) is the major triglyceride in the other oils studied, and we thus expected triolein to have a similar EACN to these other oils. However, since we did not use pure triolein, we suspect that impurities in the studied triolein (such as free fatty acid compositions) might contribute to its hydrophilicity due to the segregation of components in the oil [30].

Table 2.3: Measured EACN values of oils:

Oil	S*, wt%	EACN
Triolein (65% grade)	1	-0.3
Canola	6	16.9
Olive	6.5	17.7
Peanut	7.5	19.0
Corn	7.5	19.0
Soybean	6.5	17.7

2.3.3 Microemulsification of Triolein 65% practical grade

Since the studied triolein (65% practical grade) has a very low EACN, a hydrophilic linker was used to improve interaction of the surfactant system with the water side of the interface. A hydrophilic linker sodium mono- and dimethyl naphthalene sulfonate (SMDNS) scan and salinity scan was performed by fixing the surfactant concentration at 3 wt%; this higher surfactant concentration made it easier to visually observe middle phase formation. The optimum surfactant for a given oil should have the lowest salt and hydrophilic linker concentration. When adding the hydrophilic linker up to 1.2 wt%, a normal microemulsion transition behavior from Type I-III-II was observed. At lower linker concentrations, a microemulsion phase was not observed.

Figure 2.5 represents the microemulsion phase diagram of triolein using C_{10}-18PO-2EO, SMDNS as a hydrophilic linker at ratio (3 : 1.2) and sodium chloride. In addition, all the LAPES extended-surfactants studied in this work were able to form middle phase microemulsions at the ratio of surfactant to linker of 3 : 1.2 by weight.

Among LAPES extended-surfactants, the lowest triolein S* value was observed with C_{10}-18PO-2EO surfactant. The "fish" diagram in Figure 2.5 slants to the right with increasing total surfactant and linker concentrations, suggesting a stronger interaction with the water at higher concentration and thus a higher S* required to balance the surfactant at the interface [31].

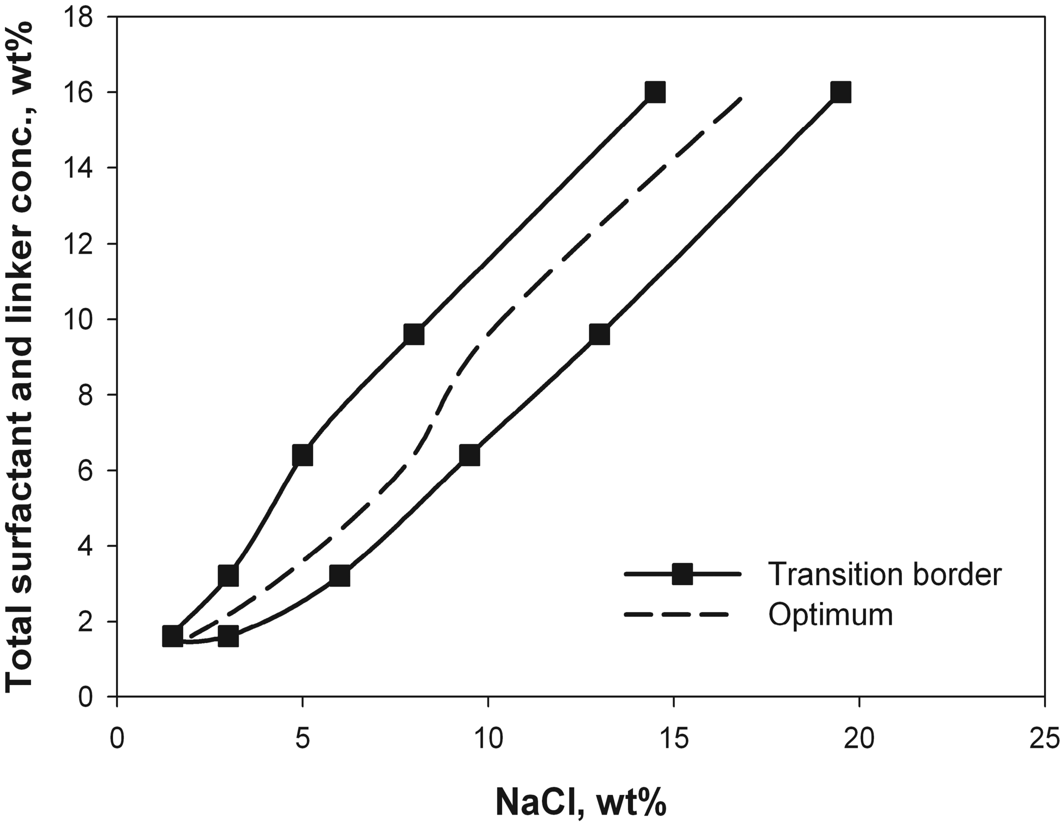


Figure 2.5: Microemulsion "fish" phase diagram of C_{10}-18PO-2EO-$NaSO_4$, a hydrophilic linker sodium mono- and dimethyl naphthalene sulfonate (SMNDS). C_{10}-18PO-2EO-$NaSO_4$/ SMDNS ratio at 3:1.2 by wt% and sodium chloride with triolein 65% practical grade. Temperature at 27°C.

2.3.4 Microemulsification of vegetable oils

As discussed above, vegetable oils are mixture of triglycerides, free fatty acids and other components, with triglycerides making up the greatest fraction. Since triglycerides are esters of fatty acids and a triglycol, many combinations are possible (i.e OOO, LnLnO and POO; see Table 2.4 below for abbreviations) resulting in a mixture of very complicated and different fractions of individual triglycerides.

Table 2.4: Some common triglycerides in vegetable oils and their abbreviations

Triglyceride	Abbreviation
PLL	Palmitoyl-dilinoleoyl-glycerol
POL	Palmitoyl-oleoyl-linoleoyl-glycerol
POO	Palmitoyl-dioleoyl-glycerol
POS	Palmitoyl-oleoyl-stearoyl-glycerol
LnLnLn	Trilinolenin
LnLnL	Dilinolenonyl-linoleoyl-glycerol
LLO	Dilinoleoyl-oleoyl-glycerol
LLL	Trilinolein
OOO	Triolein
SOO	Stearoyl-dioleoyl-glyecerol

An ideal surfactant formulation would be one that can form microemulsions with a range of vegetable oils regardless of the different fraction of triglycerides in vegetable oils. As expected, when applying the C_{10}-18PO-2EO/SMDNS system that formed a middle phase with the low EACN triolein (-0.3) to the vegetable oils with much higher EACN values, no microemulsion phase was formed with the vegetable oils. The EACN values of vegetable oils range from 16 – 19 (see Table 2.3) and are much higher than the triolein studied here; therefore, the formulation optimized for triolein is not compatible with vegetable oils. In addition, when mixing this formulation with vegetable oils, a milky viscous white phase was formed in the oil phase which indicates weak interactions and poor solubilization in the oil phase [31].

To balance the system for the higher EACN vegetable oils, a long chain alcohol was added as a lipophilic linker [19, 20]. In this study, we used oleyl alcohol as the lipophilic linker. A phase study of vegetable oils with extended-surfactants and lipophilic linker was performed, using procedures similar to that used with the hydrophilic linker mentioned above. The phase study using surfactant and lipophilic linker alone showed no microemulsion formation. Instead, white, milky and multiple-phases were observed at any sodium chloride concentration. This is likely due to the fact that the surfactant film at the water-vegetable oil interface had difficulty in penetrating the large triglyceride molecules. This suggests that both lipophilic and hydrophilic linkers may be needed to overcome the poor solubilization [31]. Systems of C_{10}-18PO-2EO and SMDNS at ratio 3 : 1.2 was fixed at 4.2 wt% total concentration and oleyl alcohol and sodium chloride were scanned for peanut oil. A normal microemulsion Type I-III-II transition was observed when the oleyl alcohol (lipophilic linker) concentration reached 2.5 wt%. However, the sodium chloride concentration to obtain the middle phase microemulsion for this system was very high at 15 wt%, which would be impractical in many applications.

In order to reduce the salinity level, we selected a hydrophilic linker which is more hydrophobic than SMDNS. Glucopon, which is a mixture of polyglucosides, was used as a replacement for SMDNS. By using glucopon, S* reduced from 15 wt% to 7.5 wt% at 6.7 wt% total surfactant and linker concentration.

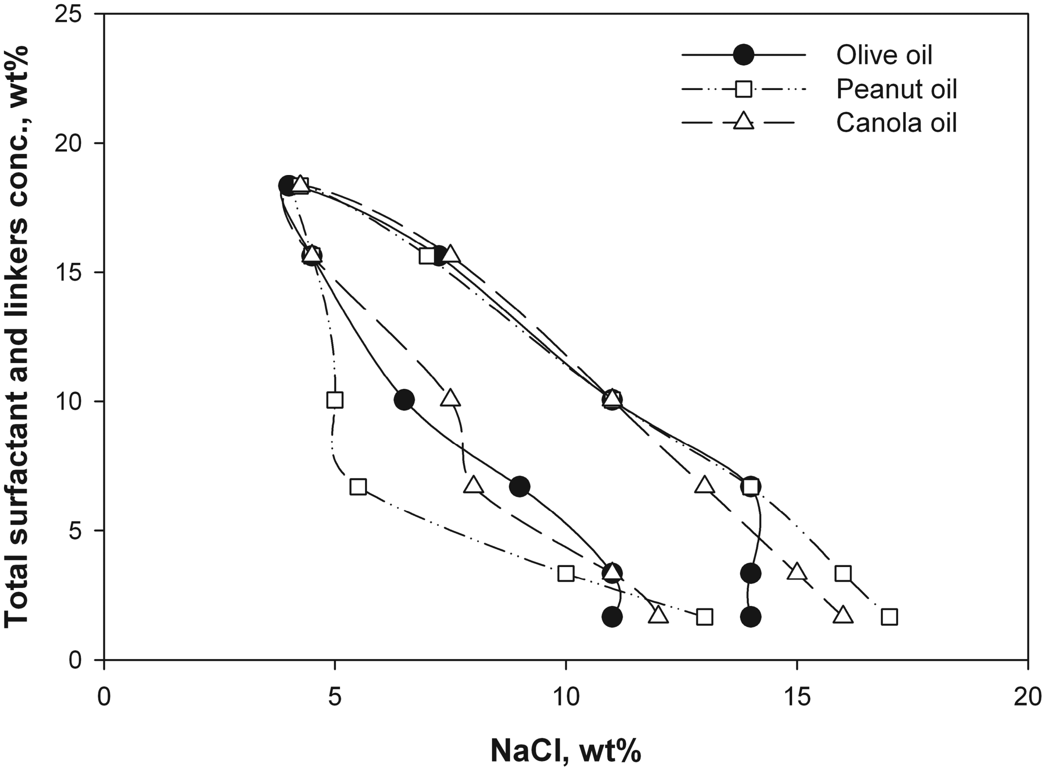


Figure 2.6: Microemulsion "fish" phase diagram of C_{10}-18PO-2EO-$NaSO_4$/Oleyl alcohol/Glucopon/NaCl at ratio of 3/2.5/1.2 by weight and sodium chloride with olive, peanut and canola oils. Temperature at 27°C.

In order to reduce the salinity level, we selected a hydrophilic linker which is more hydrophobic than SMDNS. Glucopon, which is a mixture of polyglucosides, was used as a replacement for SMDNS. By using glucopon, S* reduced from 15 wt% to 7.5 wt% at 6.7 wt% total surfactant and linker concentration. Figure 2.6 illustrates the "fish" diagrams of olive oil, peanut oil and canola oils with this surfactant system. Similar results were observed with other vegetable oils including corn, sunflower, soybean and cottonseed oils (data not shown). At high total surfactant and linker concentration (more than 3 wt%) the formulation reached equilibrium within four hours. At lower concentration (less than 1 wt%), the system required two weeks to reach equilibrium. A Winsor type IV microemulsion was also observed with all studied vegetable oils at total surfactant and linker concentrations of 16.7 wt% at low sodium chloride concentration (4 – 5 wt%) and with solubilization parameters ranging from 6 – 10 ml/g. The microemulsion with canola oil exhibits the lowest solubilization parameter at 6 ml/g, while peanut oil showed the highest solubilization capacity at 10 ml/g. From the fatty acid compositions in Table 2.2, canola oil has the highest fraction of the unsaturated fatty acid, up to 92%, whereas peanut oil has the lowest of 86%. Higher fraction of triglyceride in the oils might contribute to the lower solubilization capacity. This also might be the explanation for the larger fish "body" of peanut oil microemulsion. These results are very interesting as, to our knowledge, this is the first report of Winsor Type I – IV microemulsion formation with vegetable oils at ambient conditions and without the addition of co-oils and/ or low molecular weight alcohols.

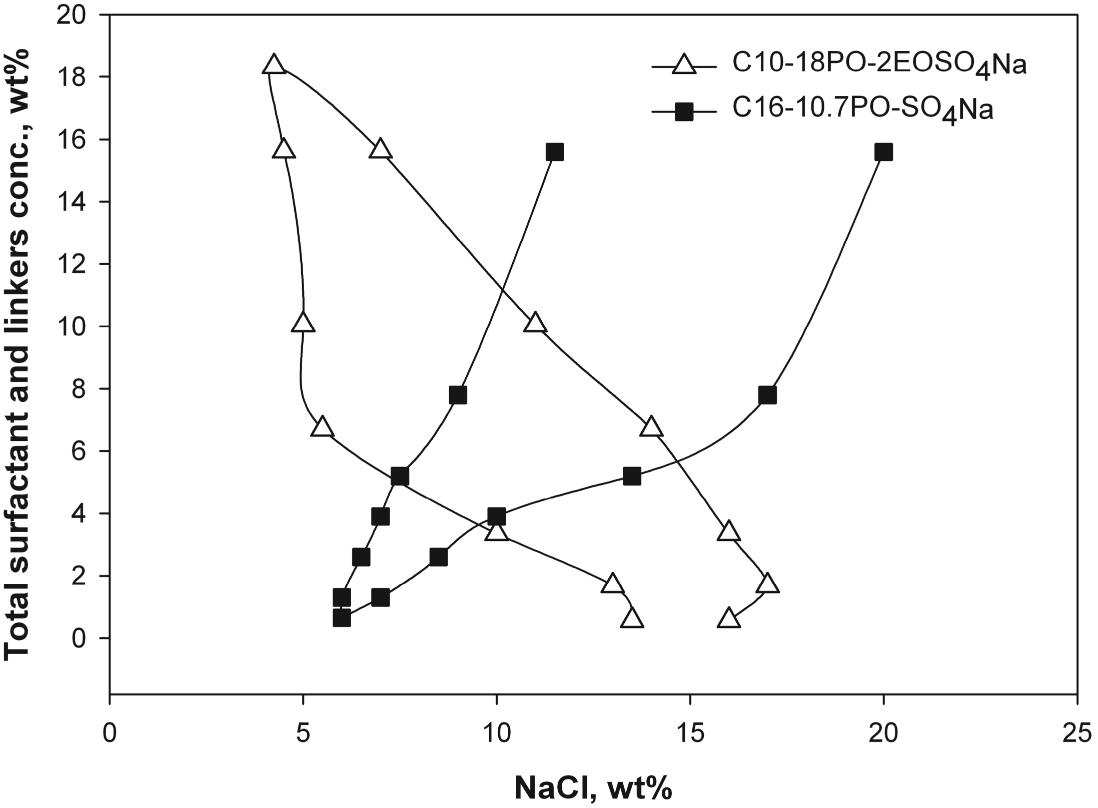


Figure 2.7: Microemulsion phase behavior of C_{16}-10.7PO-Sulfate (LAPS)/ Oleyl alcohol/ Glucopon/ NaCl and C_{10}-18PO-2EO-Sulfate (LAPES)/ Oleyl alcohol/ Glucopon/ NaCl with peanut oil. Temperature at 27°C.

Figure 2.7 shows the fish diagram with peanut oil, using the same linker systems at the same ratio, but using two classes of extended-surfactants, C_{10}-18PO-2EO (LAPES) (as in Figure 2.6) and C_{16}-10.7PO (LAPS). In Figure 2.7, the fish "body" of C_{10}-18PO-2EO sulfate system slants to the left with increasing total surfactant and linker concentrations. In contrast, the fish body of C_{16}-10.7PO sulfate slants to the right with increasing total concentrations. Recall that in Figure 2.3, the LAPS extended-surfactant shows higher IFT values than the LAPES surfactants. Similarly, the formulation using C_{16}-10.7PO sulfate (LAPS) shows much poorer solubilization capacity (4ml/g) than C_{10}-18PO-2EO sulfate (LAPES) (10ml/g) with peanut oil. This is interesting given the longer alkyl chain of the C_{16}-10.7PO sulfate, and suggests that the 18PO-2EO sulfate combination more than offsets the shorter C10 alkyl group of the LAPES surfactant.

HLB values of C_{10}-18PO-2EO sulfate and C_{16}-10.7PO sulfate are 38.5 and 36.5, respectively (see Table 2.1). Such small HLB difference does not predict the difference in the phase behavior reported above. This demonstrates the inadequacy of the HLB method to describe the behavior of extended-surfactants. Rather, the difference might be due to the behavior of the extended-surfactants at the oil – water interface in a way that is not understood. A detailed investigation on the interaction of triglyceride molecules with extended-surfactants and the use of the HLD approach rather than HLB is the subject of ongoing research by our group [25]. From this work, it can be concluded that for different applications, appropriate extended-surfactants should be used. For formulations requiring formation of a Winsor Type IV microemulsion, like many cleaning products, the C_{10}-18PO-2EO sulfate system should be used since it exhibits low optimal salinity, S*, at high concentration, and vice versa.

2.4 CONCLUSIONS

We have demonstrated the use of modified linker and extended-surfactant systems that can form microemulsions with vegetable oils. We were able to form both Winsor Type III and Type IV microemulsions at ambient condition without the addition of co-oil and/or alcohols and at relatively low electrolyte concentrations. Our proposed formulations can form environmentally benign microemulsions with a wide range of oils, regardless of the triglyceride compositions, and can obtain high solubilization parameters, up to 10 ml/g.

2.5 ACKNOWLEDGEMENTS

The authors would like to thank George Smith, Hunstman Petrochemical Corp. (Houston, TX) for providing us the extended-surfactant samples, and Cognis-Care Chemicals for providing us Glucopon N425. Funding for this work has been provided through the United States Environmental Protection Agency's Science to Achieve Results (STAR) program, through grant number Rd-83090301-0. Although the research described in this article has been funded by the United States Environmental Protection Agency, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Partial support was provided by industrial sponsors of the Institute for Applied Surfactant Research at the University of Oklahoma: Akzo Nobel, Clorox, Conoco/Phillips, Church and Dwight, Ecolab, Halliburton, Dow Chemical, Huntsman, Oxiteno, Procter & Gamble, Sasol North America, Shell Chemical, Unilever, and from Dr. Sabatini's Sun Oil Company endowed chair and Dr. Harwell's Conoco/Dupont endowed professorship.

REFERENCES

1. Sabatini DA, Knox RC, Harwell JH, Wu B (2000) Integrated design of surfactant enhanced DNAPL remediation: efficient supersolubilization and gradient systems. J Contam Hydrol 45:99–121

2. Childs JD, Acosta E, Knox R, Harwell JH, Sabatini DA (2004) Improving the extraction of tetrachloroethylene from soil columns using surfactant gradient systems. J Contam Hydrol 71:27–45

3. Bourrel M, Schechter RS (1988) Microemulsions and related systems. Marcel Dekker, New York

4. Kukieda H (1989) Phase behaviors in water/nonionic surfactant/hydrocarbon and water/nonionic surfactant/amphiphilic oil system. J Colloid Interface Sci 133:237–243

5. Lindman B, Shinoda K, Olsson U, Anderson DM, Karlstrom G, Wennerstrom H (1989) On the demonstration of bicontinuous structures in microemulsions. Colloid Surf 38:205–224

6. Gelbart WM, Ben-Shaul A, Roux D (eds) (1994) Micelles, membranes, microemulsions and monolayers. Spinger, New York, pp 395–426

7. Joubran RF, Cornell DG, Parris N (1993) Microemulsions of triglyceride and non-ionic surfactant: effect of temperature and aqueous phase composition. Colloids Surf A 80:153–160

8. Corswant C, Engstrom S, Soderman O (1997) Microemulsions based on soybean phosphatidylcholine and triglycerides. Phase behavior and microstructure. Langmuir 13:5061–5070

9. Tungsubutra T, Miller CA (1994) Effect of secondary alcohol ethoxylates on bahavior of triolein–water–surfactant systems. JAOCS 71(1):65–73

10. Huang L, Lips A (2004) Microemulsification triglyceride sebum and the role of interfacial structure on bicontinuous phase behavior. Langmuir 20:3559–3563

11. Corswant CV, Soderman O (1998) Effect of adding isopropyl myristate to microemulsions based on soybean phosphatidylcholine and triglycerides. Langmuir 14:3506–3511

12. Minana-Perez M, Graciaa A, Lachaise J, Salager JL (1995) Solubilization of polar oils with extended surfactants. Colloids Surf A Physicochem Eng Asp 100:217–224

13. Salager JL, Anton RE, Sabatini DA, Harwell JH, Acosta A, Tolosa LI (2005) Enhacing solubilization in microemulsions – state of the art and current trends. J Surfact Dterg 8:3–12

14. Withayyapayanon A, Acosta EJ, Harwell JH, Sabatini DA (2006) Formulation of ultralow interfacial tension systems using extended – surfactants. J Surfact Deterg 9:331–339

15. Minana-Perez M, Graciaa A, Lachaise J, Salager JL (1996) Systems containing mixtures of extended surfactants and conventional nonionics. Phase behavior and

solubilization in microemulsion. In: Proc 4th World Surfactants Congr, Barcelona, Spain, 3–7 June 1996, 2:226–234

16. Minana-Perez M, Graciaa A, Lachise J, Salager JL (1995) Solubilization of polar oils in microemulsion systems. Progr Colloid Polym Sci 98:177–179

17. Sabatini DA, Acosta E, Harwell JH (2003) Linker molecules in surfactant mixtures. Curr Opin Colloid Interface Sci 8:316–326

18. Acosta E, Uchiyama H, Sabatini DA, Harwell JH (2002) The role of hydrophilic linkers. J Surfactants Deterg 5(2):151–157

19. Graciaa A, Lachaise J, Cucuphat C, Salager JL (1993) Improving solubilization in microemulsions with additives. 1. The lipophilic linker role. Langmuir 9:669 – 672

20. Graciaa A, Lachaise C, Cucupht C, Salager JL (1993) Improving solubilization in mciroemulsions with additives. 2. Long chain alcohols as lipophilic linkers. Langmuir 9:3371–3374

21. Acosta EJ, Le MA, Harwell JH, Sabatini DA (2003) Coalescense and solubilization kinetics in linker-modified microemulsions and related systems. Langmuir 19:566–574

22. Davies JT, Rideal EK (1961) Interfacial phenomena. Academic, New York

23. Davies JT (1957) A quantitative kinetic theory of emulsion type. I. Physical chemistry of the emulsifying agent. In: Schulman JH (ed) Proceedings of the 2nd International Congress of Surface Activity. Butterworths, London, 1:426 – 438

24. Poprawski J, Catte M, Marquez L, Salager JL, Aubry JM (2003) Application of hydrophilic-lipophilic deviation formulation concept to microemulsions containing pine oil and nonionic surfactant. Polym Int 52:629–632

25. Witthayapayanon A, Harwell JH, Sabatini DA (2008) Hydrophilic-lipophilic deviation (HLD) method for characterizing conventional and extended-surfactants. J Colloid Interface Sci 325:259 – 266

26. Mori F, Lim JC, Raney OG, Elsik CM, Miller CA (1989) Phase behavior, dynamic contacting and detergency in systems containing triolein and nonionc surfactants. Colloids Surf 40(3–4):323 – 345

27. Cayias JL, Schechter RS, Wade WH (1976) Modeling crude oils for low interfacial tension. J Soc Pet Engr 16:351 – 357

28. Salager JL, Morgan JC, Schechter RS, Wade WH, Spe-Aime M, Vasquez E (1979) Optimum formulation of surfactant/water/oil systems for minimum interfacial tension or phase behavior. J Soc Petro Engr 19:107 – 115

29. Acosta E, Mai PD, Harwell JH, Sabatini DA (2003) Linkermodified microemulsion for a variety of oils and surfactants. J Surfact Deterg 6:1 – 12

30. Graciaa A, Lachaise J, Cucuphat C, Bourrel M, Salager JL (1993) Interfacial segregation of an ethyl oleate/hexadecane oil mixture in microemulsion systems. Langmuir 9:1473 – 1478

31. Komesvarakul N, Sanders MD, Szekeres E, Acosta EJ, Faller JF, Mentlik T, Fisher LB, Nicoll G, Sabatini DA, Scamehorn JF (2006) Microemulsions of triglyceride-

based oils: the effect of co-oil and salinity on phase diagrams. J Cosmet Sci 55:309 – 325

32. WanPJ, Wakelyn PJ (1997) Technology and solvents for extracting oilseeds and nonpetroleum oils. AOCS Press, Champaign, IL

Chapter 3 Aqueous Extended-Surfactant Based Method for Vegetable Oil Extraction: Proof of Concept[1]

ABSTRACT

The use of hexane to extract vegetable oil from oilseeds is of growing concern due to hexane's environmental impact and because of worker exposure concerns. The goal of our work is to demonstrate that the aqueous extended-surfactant-based method is a viable alternative for vegetable oil extraction. In our method, ground oilseeds were dispersed in the aqueous surfactant solution, allowing the oil to be liberated from the seeds as a separate phase from the aqueous phase. The impact of pH, shaking intensity, shaking time and seed to liquid ratio on oil yield are presented. Extended-surfactants are a new type of surfactant with propoxylate(PO) and/or ethoxylate(EO) groups inserted between the hydrophilic head and the hydrophobic alkyl chain of the surfactant molecule. This unique structure of extended-surfactants enables them to produce ultralow interfacial tension with vegetable oils. We have found that at low aqueous concentrations (less than 0.3 wt%), extended-surfactant solutions are able to produce ultralow interfacial tension between aqueous extraction and vegetable oil phases. At optimum condition (seed to liquid ratio of 1 to 5, 30 minute extraction at 150 shakes/min and 30 minute

---

[1] This chapter or portions thereof has been published previously in *Journal of American Oils and Chemists' Society* under the title "Aqueous Extended-Surfactant Based Method for Vegetable Oil Extraction: Proof of Concept", Journal of American Oils and Chemists' Society, 2010, 87, 1211 – 1220. This current version has been reformatted for this dissertation.

centrifugation at 2170×g) we achieved 93 – 95% extraction efficiency for peanut and canola oils at 25^{o}C. The oil quality produced from the aqueous extended-surfactant based method was found to be comparable or even superior to that obtained from hexane-based extraction, further demonstrating the viability of aqueous extended-surfactant based extraction.

Key words: vegetable oil, oilseed extraction, ultralow interfacial tensions, extended-surfactants

3.1 INTRODUCTION

Vegetable oils are typically produced from oilseeds by either hexane extraction or a combination of mechanical processing and hexane extraction. However, worker exposure to hexane at 15 ppm/day for three months has been shown to cause peripheral nerve damage, and hexane is also a potential hazardous explosive material [1]. Therefore, hexane-based extraction requires airtight, leak-proof equipment and highly-skilled labor in hexane extraction plants. In 2001, the U.S. Environmental Protection Agency (EPA) established regulations on hexane emission due to growing environmental concerns. In addition, oils produced by hexane extraction are high in free fatty acid, wax and unsaponifiable matter, and might also suffer from dark greenish-brown color [2]. Further there is a growing demand for vegetable oil to be used in biodiesel production.

In view of the disadvantages of existing extraction processes, a number of alternative technologies have been evaluated for oilseed extraction, including water-based (aqueous) extraction or use of other volatile organic solvents [3,4,5,6,7]. The aqueous extraction process (AEP) was studied in the 1950s because it was believed that this process was cheaper and safer than hexane. AEP for oilseed extraction eliminates the potential of explosion and emissions of volatile organic solvents when using hexane. Simultaneous recovery of oil and protein by AEP is possible with lower equipment costs and energy consumption than hexane extraction [8,9,10]. AEP is based on the water soluble components of oilseeds dissolving in the water, thereby releasing the oil which was previously bound to the cell structure [11]. AEP has consistently been reported to produce vegetable oil superior in quality to that produced by hexane-based processes [11]. However, AEP with water alone has low oil extraction efficiency (less than 70%) because water cannot effectively release the oil which is trapped in the plant cell structure by high capillary force. In addition, AEP is operated at relatively high temperatures (50-60^{o}C) and high water to solid ratio (20:1 to 30:1), both of which are undesirable in application [12].

Enzyme-assisted aqueous extraction has been introduced in an attempt to improve the oil yield with the AEP process. The enzyme-assisted aqueous extraction process uses an enzyme system to disrupt the cell walls, thereby improving the oil release by mechanical means alone [12]. Greater than 90% oil extraction efficiency has been achieved for various vegetable oils (e.g. canola, peanut and coconut oils) using this approach [6]. The structure of the plant cell wall, made of various strata, is very complex. The strata are composed of many compounds such as cellulose, hemicelluloses and lipids. Since each type of enzyme can only degrade a certain type of compound, an effective extraction system requires a combination of at least three types of enzymes [13]. The oil extraction efficiency of different oilseed types is greatly dependent on the combination of enzymes [13,15]. In addition, since enzyme activity is pH and/or temperature dependent, optimization of reaction conditions for multiple enzymes can be challenging when evaluating an effective enzyme system [15]. These disadvantages make the enzyme-assisted aqueous extraction complicated and thus to date there is no versatile enzyme system that can be applied for all types of oilseeds as is true with hexane [10,12,14]. Another drawback of this method is the enzyme cost [15,16]. Similar to AEP process, enzyme-assisted aqueous extraction process produce vegetable oil with superior quality to hexane. However, this method also requires long incubation time (up to 18 hours) and high temperatures (30-55°C), both of which are undesirable in application [6,10,17].

In this research study, we investigated the use of surfactant-microemulsion-based extraction of vegetable oil extraction from oilseeds. The goal of this work is to develop surfactant-based formulations with simplicity of operation, acceptable energy consumption and desirable extraction performance. Our group is unique in investigating the use of aqueous-surfactant-based method for oil extraction from oilseeds [18]. Past research has evaluated the efficiency of water-in-oil (W/O) microemulsions (surfactant solubilized in an oil phase, in this case) in extracting vegetable oils [19,20,21]. Microemulsions are thermodynamically stable dispersion of water and oil, stabilized by a film of surfactant where the microemulsion droplet size is generally smaller than 100 nm [22]. In W/O microemulsions (also referred to as Winsor II microemulsion systems), the reverse micelles (head groups in the core and the hydrophobic tails outward) solubilize water while they are dispersed in the continuous oil phase [22]. In the studies of W/O microemulsion-based extraction of sodium dioctyl sulfosuccinate (AOT) /isooctane/water or cetyltrimethylammonium bromide (CTAB)/isooctane/n-butanol/water, the W/O microemulsions have the same role as hexane solvent where the vegetable oil in the oilseed is solubilized. This method requires high surfactant concentrations (2 - 4 wt%), an organic solvent (isooctane) and relatively complicated separation processes to isolate the oil from the W/O microemulsions, both of which are undesirable and not necessary for our system [19,20]. An aqueous-surfactant-based method is a different approach.

In the past, the use of aqueous surfactant-based processes for vegetable oil extraction was impractical since conventional surfactants proved unable to produce ultralow interfacial tension with vegetable oils, a critical factor in efficient vegetable oil extraction by this method. By definition, interfacial tension (IFT) is the surface tension caused by intermolecular interactions at the surface separating two immiscible fluids [22]. We define ultralow IFT as IFT values <<0.1 mN/m (preferably < 0.01 mN/m). In the microscopic study of aqueous oil extraction mechanisms, it was found that when employing water alone, the unextracted oil was trapped in an insoluble matrix of denatured proteins. The coalesced oil size was too large to diffuse through the disrupted cellular matrix [23]. The oil release mechanisms when using surfactant is to disrupt the oil/water interface by lowering the interfacial tension between the surfactant solution and the oil, thereby facilitating the oil droplet breakup and making it possible for the oil to diffuse through and be librated from the disrupted cell [23]. Thus, a system that produces ultralow IFT between the extracting solution, an aqueous-based surfactant system in our case, and the vegetable oil in the seeds will release the oil trapped in the disrupted cells. The high IFT that conventional surfactants produce between water and vegetable oils is due to the hydrophobicity of triglycerides, which are the main component in vegetable oils. Vegetable oils are hydrophobic oils with the equivalent alkane carbon number

(EACN) ranging from 16 – 20 [24]. In order to achieve ultralow IFT, the hydropobicity-hydrophilicity between surfactant solution and the oil must be balanced [25]. The surfactant solution can be made more hydrophobic by increasing the alkyl chain of the surfactant molecule [25]. However, increasing the alkyl chain too much will decrease the water solubility of the surfactant. Eventually, the surfactant phase will separate from water. Therefore, aqueous conventional surfactant solution could not achieve ultralow IFT with vegetable oils because the hydrophobic-hydrophilic balance was not achieved within the limiting solubility of the surfactants. A recently developed new class of surfactants known as extended-surfactants is able to achieve ultralow IFT. Distinct from conventional surfactants, the extended-surfactant molecule has an intermediate polar group (e.g. propoxylate group) inserted between the head and the tail of the surfactant molecule. The propoxylate groups in the surfactant molecule make the surfactant become more hydrophobic and also extend the surfactant tail [25]. Therefore, the surfactant tail segregates further into the oil phase without sacrificing the water solubility as often observed when increasing the alkyl chain [25]. Detailed studies on extended-surfactants, the dynamic interfacial tension properties of extended-surfactants with vegetable oils and the role of extended-surfactants in forming microemulsions and ultralow IFT with vegetable oils is reported in the literature [25,26,27,28].

For vegetable oil extraction, we are particularly interested in the lowest surfactant concentration capable of producing ultralow interfacial tension (IFT), which is known as the critical microemulsion concentration (CμC). Removal of oil at the CμC point due to IFT reduction is well known as the mobilization mechanism in enhanced-oil recovery (EOR). In this case, the oil is liberated as a separate phase rather than solubilized into the aqueous surfactant phase [29]. This property is desirable since vegetable oil can be effectively extracted without requiring an additional process to separate the solubilized oil from the surfactant micelles. Use of surfactant systems near the CμC was first tested by our group for extraction of oil from drill cuttings using about 0.1 wt% surfactant [29].

In this work, we evaluated the use of several extended-surfactant based systems for vegetable oil extraction. We also studied the effect of process parameters such as pH, shaking intensity and time, and seed to liquid ratio on the extraction efficiency. Assessment of the oil quality using our method is also discussed in this paper.

3.2 MATERIALS AND METHODS

3.2.1 Materials

Two classes of anionic extended-surfactants were studied in this work: alkyl-propoxylate-ethoxylate-sulfate (APES) surfactants and alkyl-propoxylate-sulfate (APS) surfactants. The number of PO groups varied within each class of surfactant. While there is no EO group in the APS surfactants, the number of EO groups is fixed at two for APES surfactants. These surfactants are all predominantly linear in configuration. The extended-surfactants were kindly provided by Huntsman Chemical Co. (Houston, TX) and used as received. The surfactants studied, the optimum salinity and optimum interfacial tension between the aqueous surfactant solution and triolein oil are summarized in Table 3.1. Sodium dioctyl sulfosuccinate (Aerosol-OT or AOT), +99% anhydrous was purchased from Fisher Scientific (Fair Lawn, NJ) and used as received.

Triolein 65% practical grade and peanut oil were purchased from Sigma Aldrich (St Louis, MO). Triolein was used as a model oil in the surfactant selection study as it is a major component in most vegetable oils. Crisco® pure canola oil (The J.M Smucker Company, Orrville, OH) was used without modification. Sodium chloride +99% purity was purchased from Fluka Chemical Corp. (Milwaukee, WI). Deshelled peanut seeds were purchased from Wal-Mart (Norman, OK). Canola seeds were kindly provided by Prairie Gold Oil Seeds (Okeene, OK).

Table 3.1: List of propoxylate and propoxylate ethoxylate surfactants studied in this work and their optimum salinity (S*) and optimum interfacial tension (IFT*) with triolein oil at 25°C[a].

	Surfactant Series	S* (wt%)	IFT*(mN/m)
1. APS[b]			
	C_{16}-xPOsulfate		
	C16-2.9PO	2.0	0.052 ± 0.0021
	C16-4.5 PO	3.0	0.039 ± 0.0013
	C16-5.5 PO	2.0	0.033 ± 0.0033
	C16-8.2PO	1.3	0.13 ± 0.0026
	C16-10.7PO	0.60	0.043 ± 0.0009
2. APES[c]			
	C_{10}-xPO-2EOsulfate		
	C10-10PO-2EO	2.5	0.0090 ± 0.0004
	C10-14PO-2EO	2.0	0.0037 ± 0.0011
	C10-18PO-2EO	0.50	0.0014 ± 0.0015
	C_{12}-xPO-2EOsulfate		
	C12-10PO-2EO	3.5	0.0031 ± 0.0014
	C12-12PO-2EO	2.5	0.0023 ± 0.0018
	C12-14PO-2EO	0.50	0.0017 ± 0.0006

[a] All surfactant concentrations were at 0.1 wt%. Electrolyte used was NaCl.

[b] Alkyl propoxylate surfactant

[c] Alkyl propoxylate ethoxylate surfactant

3.2.2 Methods

Interfacial tension experiments

Dynamic interfacial tension experiments were performed to evaluate the interaction of extended-surfactant systems with triolein and vegetable oils. These experiments were carried out using a spinning drop tensiometer purchased from the University of Texas (Model 500). Salinity scans were conducted by varying the NaCl concentration in surfactant solutions of 0.1 wt%. Each sample was conducted in triplicate and the IFT data were recorded every five minutes during a twenty minute time frame. We define the dynamic IFT as the IFT between the freshly prepared surfactant solution with the studied oils recorded at different time interval; in contrast, the equilibrium IFT refers to the IFT between the aqueous surfactant phase and oil phase from a phase behavior study that was equilibrated for two weeks.

Oilseed pretreatment

Deshelled peanut seeds were dehulled, whereas canola seeds were not since it is not economically feasible to dehull canola seeds [30]. Peanut and canola seeds were ground using a food processor. The particle size used in this study is in the range of 0.21 to 0.42 mm size by using US Sieve size No. 40 and No.70, which is in the recommended range for oilseed extraction [31] The oilseeds were then oven-dried at 104°C for 35 minutes to inactivate myrosinase enzymes, gossypols and other unfavorable compounds [31,32]. Moisture level in the oilseeds were determined by AOAC standard procedure (Method 925.40) [33]. Moisture level in both peanut and canola seeds were in the range of 4 - 6 wt% which is well in the recommended range [31].

Oil content

For oil content analysis, crude peanut and canola oils were extracted from seeds using hexane and a Soxhlet extraction method following AOAC standard procedure (Method 948.22) [33]. The amount of oil extracted by the Soxhlet extraction method was evaluated as the total oil present in peanut/canola seeds. In this method, the Soxhlet extractor was heated to 60^{o}C on a mantle and 50 mL of hexane was used. The thimble was filled with 5 grams of peanut/canola seeds and extracted for 4 hours. Hexane containing extracted peanut and canola oils was evaporated in a hot air oven at 70^{o}C until no change in mass of the oils was observed to eliminate residual hexane. In the second Soxhlet extraction step, no more oil was collected. The total oil analysis gave 42% peanut and 40% canola oil based on dry weight basis, consistent with values reported in the literature [34]. Oil extraction efficiency was calculated as weight percentage of oil extracted divided by the total oil present in the seeds as determined by this method. It is important to note that, in order to avoid the variation in oil content and removal efficiency in different batches, the total oil content was analyzed in each batch and the oil removal efficiency was calculated based on the corresponding oil content of the same batch.

Oil extraction

Pretreated oilseeds were put into the surfactant solution in a 25 mL glass tube. Then, the tubes were put in the shaker (Ping-Pong^{TM}, model 51504-00) at varying shaking speeds in the horizontal position. The slurry was centrifuged at $2170\times g$ (IEC centrifuge, model HN) for 30 minutes to gravity separate into three different parts: free oil phase, meal and aqueous surfactant phase. The top oil phase was transparent and clear. The meal was dried in an oven at 104°C overnight for oil residual analysis by Soxhlet extraction method, allowing for a complete mass balance for oil. The amount of oil extracted by aqueous extended-surfactant based method and the oil residual were summed and compared to the total oil content analyzed by Soxhlet extraction. Mass balance confirmed that the oil was not solubilized in the aqueous extended-surfactant solution but rather present as the liberated oil phase or remaining as residual oil in the seeds.

Triglyceride composition profile

The triglyceride composition (TGC) profile was obtained by reversed-phase high-performance liquid chromatography (RP-HPLC) with an evaporative light scattering detector (ELSD) SEDEX Model 75. The mobile phases were dichloromethane(A) and acetonitrile(B). The column used was Alltima HP C18 Hi-Load, 5 μm, 250 x 4.6 mm. Elution was performed at a solvent flowrate of 1.2 mL/min for 30 minutes. The mobile phase gradient condition followed the method described in Alltech application book [35] For solvent composition program, the fraction of acetonitrile was set as follows: 0 min 70%B, 10 min 55%B, 18 min 70%B and 30 min 70%B. TGC peaks were determined based on the retention time of standards and the results in Alltech application book [35]. Triglyceride profile was detected by an ELSD with the following settings: evaporation temperature at 35°C, air pressure at 3.2 bars and photomultiplier sensitivity at 6. Peak areas were used to quantify the components based on relative percentages. Internal normalization method was used to quantify the triglyceride compounds, assuming that the detector response is the same for all compounds. Validation of this quantification method for olive oil was reported by Cunha et al. [36]. The interpretation of the triglyceride composition profile from retention data was based on the method described in Peter et al. [37].

Oil quality analysis

Free fatty acid content was determined according to AOAC standard procedures [38]. The oil stability was tested by the AOCS cold test method (Method Cc 11-53) [39].

3.3 RESULTS AND DISCUSSIONS

3.3.1 Surfactant selection

The most important criterion for the surfactant used in vegetable oil extraction is the ability to produce ultralow interfacial tension between the surfactant solution and vegetable oils in order to liberate the oil from the seed. A number of aqueous conventional surfactant systems were evaluated in the absence of co-oils and/or alcohols, but failed to achieve low IFT at ambient temperature (see AOT in Figure 3.1).

However, aqueous extended-surfactant solutions were able to achieve ultralow interfacial tension with vegetable oils at ambient temperature and without the addition of co-oils and/or alcohols (see Figure 3.1 for C_{10}-18PO-2EOsulfate with canola oil and peanut oil as well as previous work with other oils [24]). All the surfactant solutions contained 0.1 wt% surfactants and 6.0 wt% NaCl. As seen from Figure 3.1, while the IFT of AOT and canola oil is always above 1 mN/m (peanut oil was likewise, data not shown), the IFT of extended-surfactant solution with canola and peanut oil are as low as

0.01 mN/m; i.e., two orders of magnitude lower than AOT. Another important criterion for surfactant selection is the time frame for the surfactant solution to reach equilibrium interfacial tension with vegetable oils. It can be seen that the equilibrium IFT values in Figure 3.1 was achieved within 20 minutes, highly desirable for the scale-up of the extraction process [6,10] (Recall that the enzyme process is reported in the literature to require up to 18 hours).

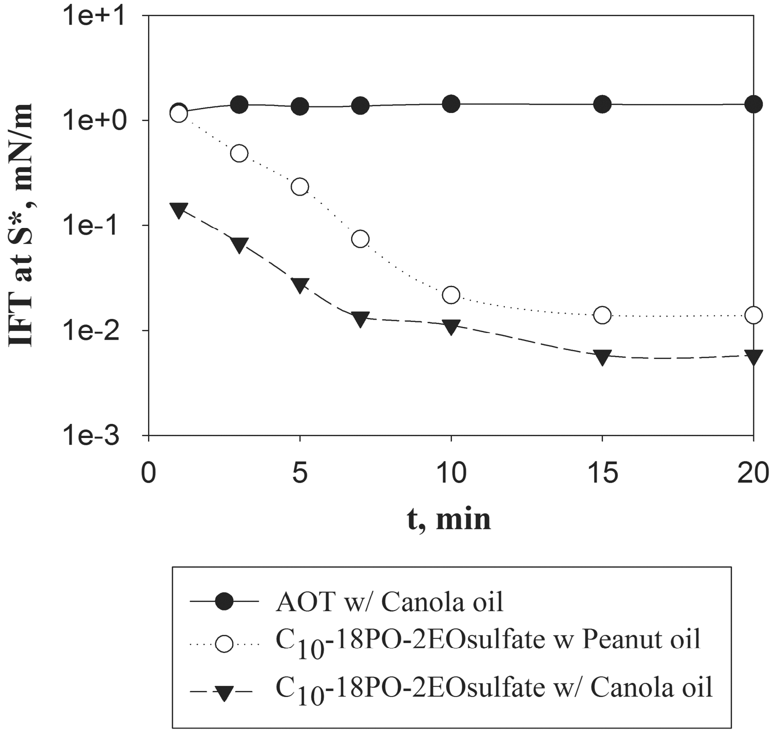


Figure 3.1: Dynamic IFT versus time of C_{10}-18PO-2EOsulfate with peanut and canola oils and AOT with canola oil at optimum salinity concentrations at 25°C. Surfactant solutions were prepared at 0.1 wt%.

In this study, we are interested in evaluating extended-surfactants for their potential use in vegetable oil extraction. Two classes of extended-surfactants were studied, namely alkyl-propoxylate-surfactant (APS) ($C_{16}H_{33}$ with varying number of POs), or, and alkyl-propoxylate-ethoxylate-surfactant (APES) ($C_{10}H_{21}$ and $C_{12}H_{25}$ with 2 EOs and varying number of POs). The APS and APES extended-surfactants studied in this work are summarized in Table 3.1. Given the uncertainty of biodegradation and human/animal consumption of these surfactants, vegetable oil extracted by this method is recommended for non-edible applications, such as biodiesel and lubrication, at this time. The aqueous surfactant-triolein IFT was measured for these extended-surfactants and recorded at 20 minutes to choose the surfactant that produced the lowest IFT, with this surfactant to be used subsequently in vegetable oil extraction experiments. Triolein 65% practical grade has often been used in the literature as the model oil for triglycerides given that it is the most abundant triglyceride species in most vegetable oils [40].

The IFT results of these extended-surfactants with triolein are summarized in Table 3.1. The results suggest that APES surfactants were able to achieve IFT values with triolein an order of magnitude lower than APS surfactants The optimum salinity (S*) varied for different surfactants. Three extended-surfactants, namely C_{16}-10.7POsulfate, C_{12}-14PO-2EOsulfate and C_{10}-18PO-2EOsulfate were chosen for the subsequent vegetable oil extraction studies since they required lowest S* which is desirable in industrial application. Between C_{16}-10.7POsulfate and C_{12}-14PO-2EOsulfate, C_{10}-18POsulfate, we could compare the extraction performance of APS surfactant versus APES surfactant. C_{12}-14PO-2EOsulfate and C_{10}-18PO-2EOsulfate were produced from alcohols of different alkyl chain lengths; therefore, we would like to investigate if the alcohol sources could impact the fraction of oil extracted.

3.3.2 Vegetable oil extraction

Effect of surfactant types

All surfactant concentrations were prepared at 0.15wt% and at optimum salt concentrations (refer to Table 3.1). The fraction of oil extracted using water alone was also evaluated. As seen in Table 3.2, the fraction of oil extracted for all cases is superior to water alone, consistent with the low IFT provided by surfactant-based systems.

Table 3.2: Effect of surfactant types on peanut oil extraction efficiency at 25^{o}C. Seed to surfactant solution liquid (S : L) ratio at 2 to 10 (g to g), 30 minute extraction time, and horizontal shaking speed at 150 shakes/min.

Extraction medium	**S*(wt%)**	**IFT* (mN/m)**	**Fraction of oil extracted[a] (wt%)**	**State of liberated oil**
Water	None	21	40	Emulsion
0.15 wt% C_{16}-10.7POsulfate	6.2	0.033	65	Emulsion
0.15 wt% C_{12}-14PO-2EOsulfate	6.1	0.0095	92	Emulsion
0.15 wt% C_{10}-18PO-2EOsulfate	6.0	0.0088	95	Free oil

[a] Amount of oil extracted via Soxhlet extraction was used as the basis

Water alone exhibited the lowest fraction of oil extracted of 40%. C_{16}-10.7POsulfate produced a somewhat higher efficiency of 65%. However, both water and C_{16}-10.7POsulfate produced stable emulsion-like phases which are not desirable in the extraction process. C_{12}-14PO-2EOsulfate and C_{10}-18PO-2EOsulfate both produced very high peanut oil extraction efficiencies of 92-95%. However, only the C_{10}-18PO-2EOsulfate produced a neat free oil phase, whereas C_{12}-14PO-2EOsulfate produced an undesirable emulsion-like phase; thus, C_{10}-18PO-2EOsulfate was chosen for study in future sections.

Effect of surfactant concentration

Figure 3.2 shows IFT values versus surfactant concentrations for C_{10}-18PO-2EOsulfate surfactant and both peanut oil and canola oil. From Figure 3.2, the CµC value of C_{10}-18PO-2EOsulfate with peanut oil is 0.15 wt% and with canola oil is 0.35wt%. Based on this, in seed extractions studies we varied the surfactant concentration below and above the CµC values to study the effect of surfactant concentration on oilseed extraction as illustrated in Figure 3.3.

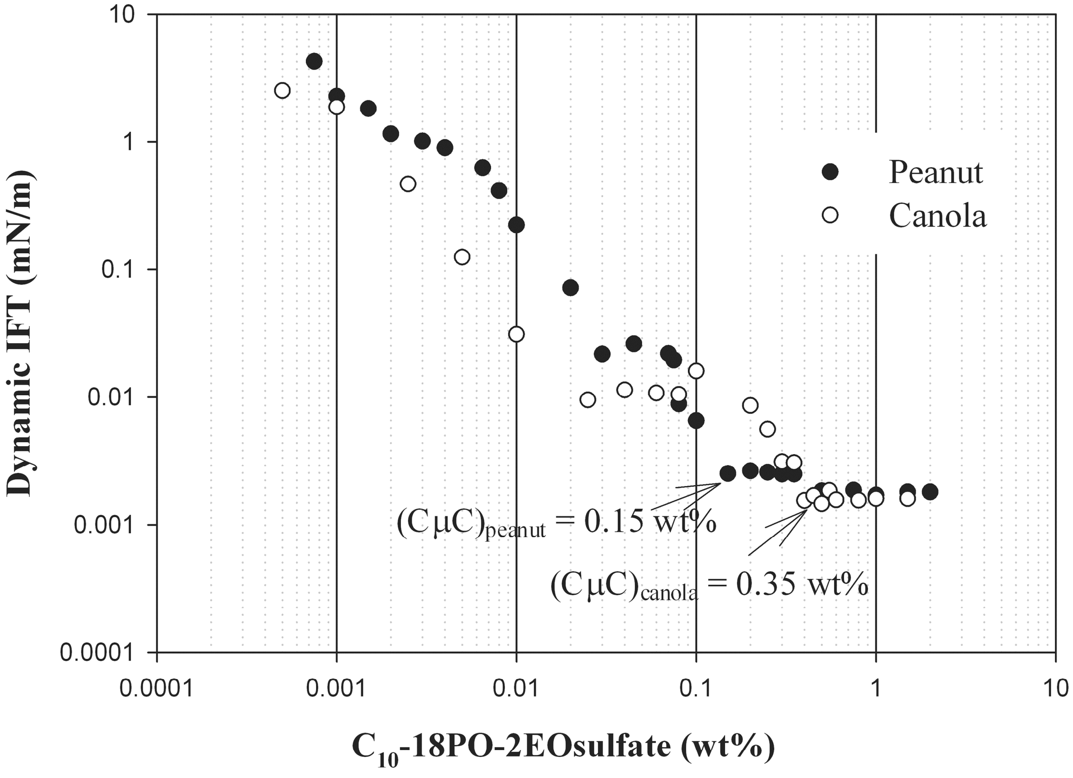


Figure 3.2: Determining the critical microemulsion concentration (CμC) using the plot of dynamic interfacial tension versus surfactant concentration at optimum electrolyte concentration for the systems C_{10}-18PO-2EOsulfate/6wt% NaCl brine/peanut oil and C_{10}-18PO-2EOsulfate/5 wt% NaCl brine/canola oil. IFT data were recorded at 20 minutes and 25°C.

From Figure 3.3 we see good agreement between the trends of the fraction of oil extracted and the CμC values reported above. With increasing surfactant concentration below the CμC, dramatic increases in both canola and peanut oil extraction efficiencies were observed. However, at surfactant concentrations higher than the CμC, the fraction of oil extracted did not change with increasing surfactant concentration. Thus, the preferred formulation for peanut oil extraction is 0.15 wt% of C_{10}-18PO-2EOsulfate and 6 wt% NaCl, and the preferred formulation for canola oil extraction is 0.35 wt% of C_{10}-18PO-2EOsulfate and 5 wt% NaCl.

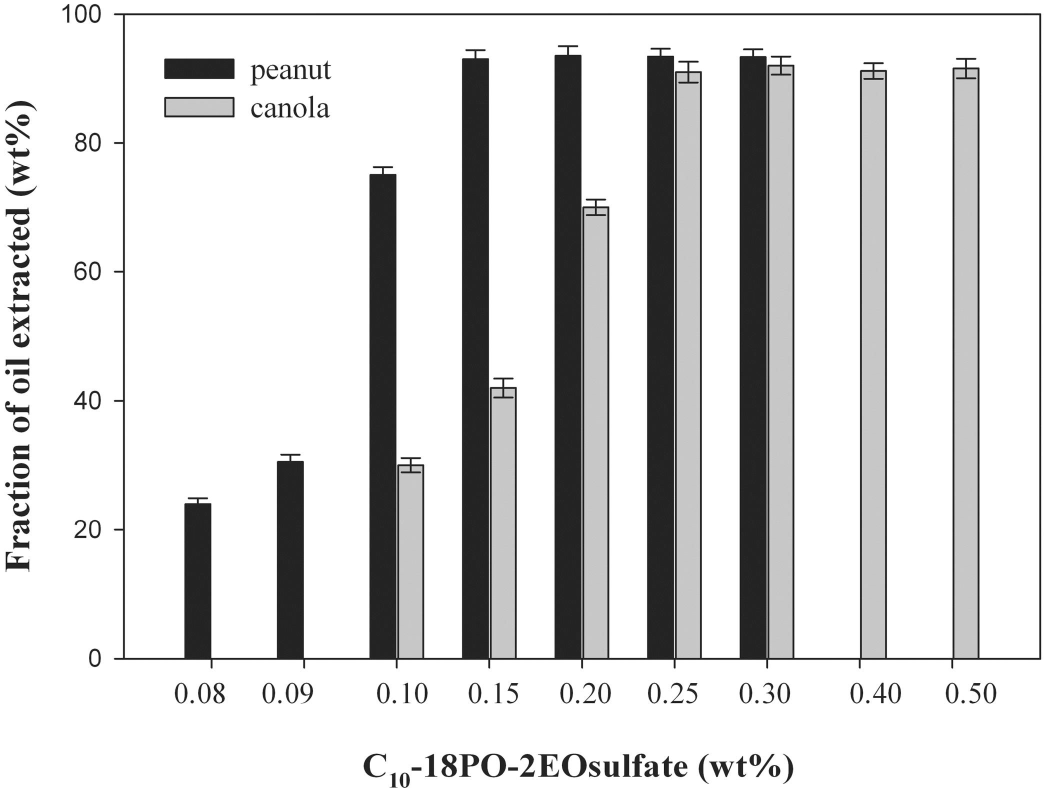


Figure 3.3: Canola and peanut oil extraction efficiency versus C_{10}-18PO-2EOsulfate concentrations. Salinity was 6 wt% NaCl with peanut oil and 5 wt% NaCl with canola oil at 25°C corresponding to S* for each. Seed to liquid ratio at 2 : 10 (g : g) for both oils, 30 minutes contact time and shaking speed at 150 shakes/min. Refer to Figure 1 for the optimum salinity (S*) of C_{10}-18PO-2EOsulfate solution with canola and peanut oils.

Effect of shaking speed

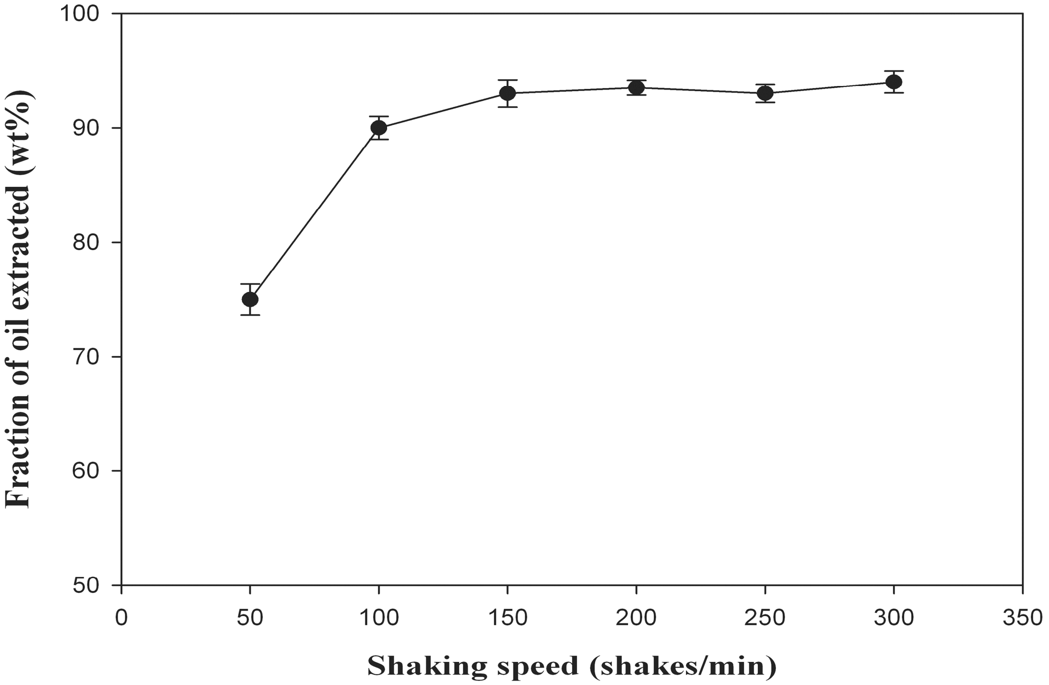


Figure 3.4: Effect of shaking speed on peanut oil extraction using 0.15 wt% of C_{10}-18PO-2EOsulfate and 6 wt% NaCl at 25^{o}C. 30 minutes contact time. Seed to surfactant solution liquid ratio at 2 : 10 (g : g).

The impact of mixing intensity (shaking speed) was evaluated as shown in Figure 3.4. The mass of the oilseed, surfactant concentration and salt concentration were fixed at 2 grams, 0.15 wt% and 6 wt%, respectively. It can be seen from the graph that at the low agitation speed (50 shakes/min) lower fraction of extracted oil was observed. However, at shaking speeds higher than 150 shakes/min, increased shaking speed no longer had a significant effect on vegetable oil extraction. It was observed that at the highest shaking speed of 300 shakes/min, stable fine solids were formed and settled slowly which led to the problem in the separation of the fine solid from the oil phase. Based on these results, a shaking speed of 100-150 shakes/min was used in subsequent experiments.

Effect of shaking time

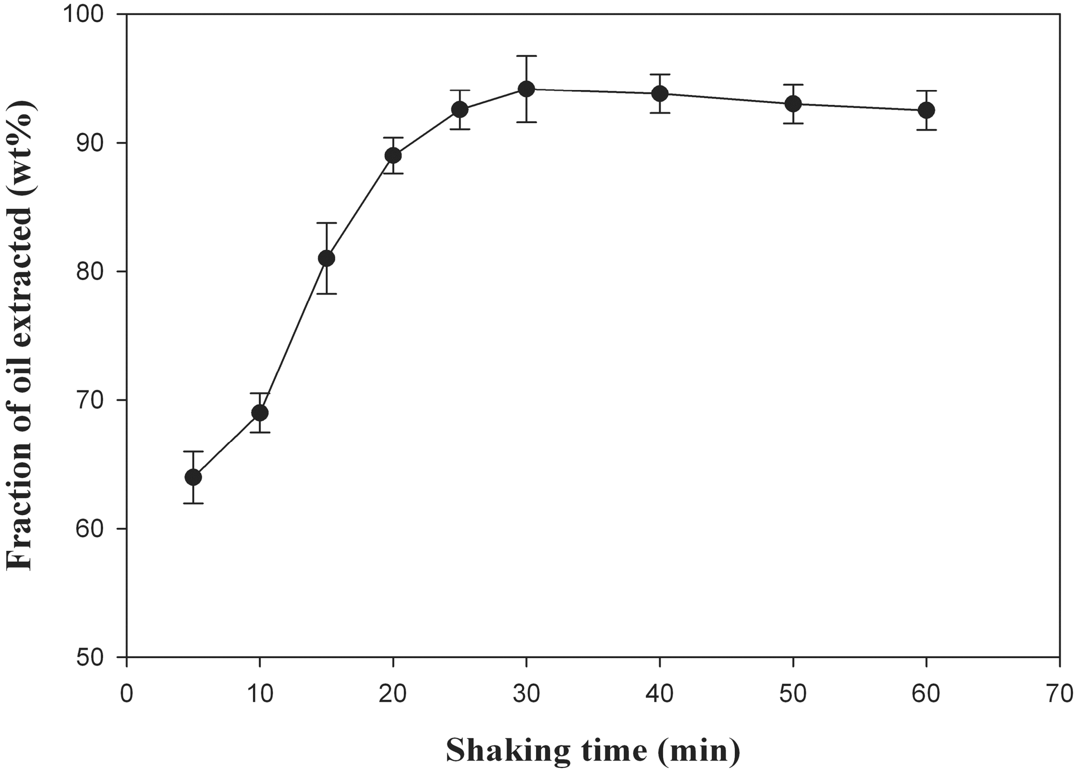


Figure 3.5: Effect of shaking time on peanut oil extraction of 0.15 wt% C_{10}-18PO-2EOsulfate and 6 wt% NaCl at 25°C. Shaking speed at 150 shakes/min. Seed to surfactant solution liquid ratio at 2 : 10 (g : g).

From the dynamic IFT results shown in Figure 3.1, equilibrium IFT was obtained between surfactant solutions and with peanut or canola oil within 20 minutes. Therefore, it is expected that the amount of oil extracted will not change after 20 minutes at 150 shakes/min. This is in good agreement with results in Figure 3.5, which shows that no further amount of oil was extracted after 25 minutes. In addition, the dynamic IFT of the post wash surfactant solution taken from the aqueous phase after centrifugation still exhibits ultralow interfacial tension with fresh vegetable oil (< 0.02 mN/m at 20 minutes); suggesting that the surfactant solution can be easily recycled as proposed in the overall process.

Effect of salt concentrations

Salinity scans were performed at a fixed C_{10}-18PO-2EOsulfate concentration of 0.15 wt%, as seen in Figure 3.6. Dynamic IFT results suggested that the lowest IFT occurred at the salt concentration of 6 wt%, in excellent agreement with S* reported in Table 3.2 and the maximum oilseed extraction results in Figure 3.6, respectively. However, from Figure 3.6 we see that 5 wt% and 8 wt% NaCl also show excellent oil extraction, demonstrating a degree of robustness relative to the NaCl concentrations.

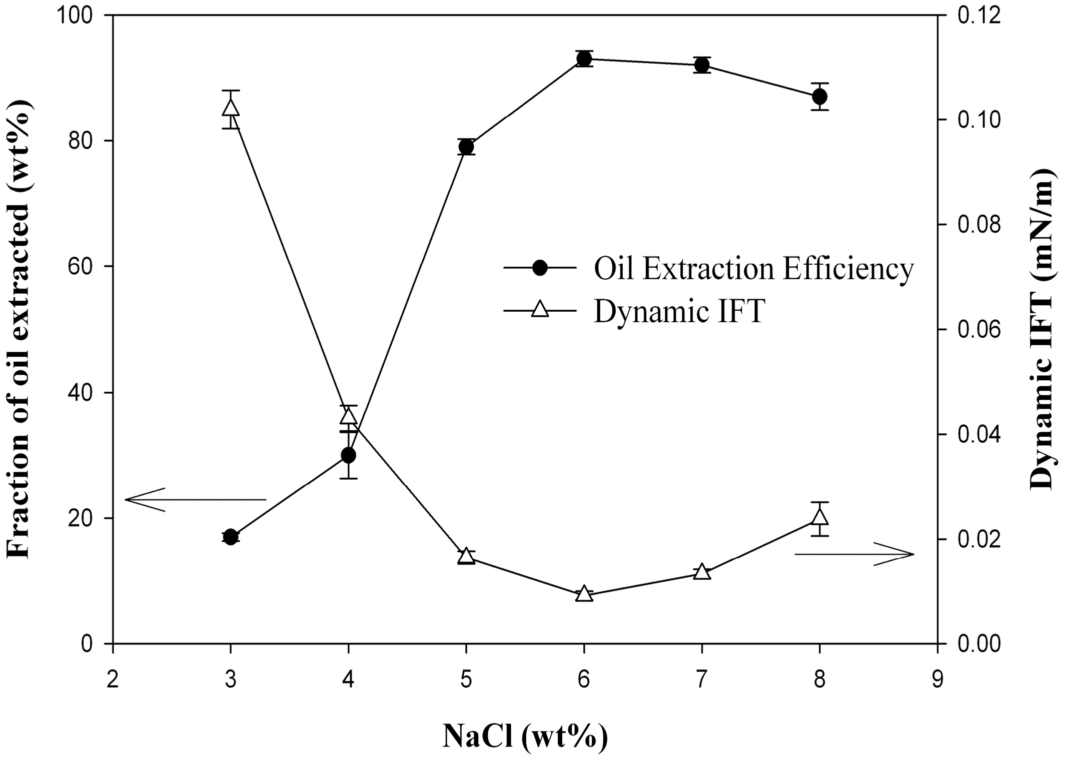


Figure 3.6: Effect of salt concentration on peanut oil extraction and dynamic IFT (data recorded at 20 minutes) using 0.15 wt% of C_{10}-18PO-2EOsulfate at 25°C. Shaking speed at 150 shakes/min for oil extraction experiments. Seed to surfactant solution liquid ratio at 2 : 10 (g : g).

Effect of solid-liquid ratio on the fraction of oil extracted

We next investigated different solid-liquid ratios of 1 to 10 to 5 to 10 (g to g), as shown in Figure 3.7. It can be seen that at low or high solid to liquid ratio, the fraction of oil extracted decreases, with the best extraction efficiency obtained at 2 : 10 (g to g) for peanut oil (Figure 3.7).

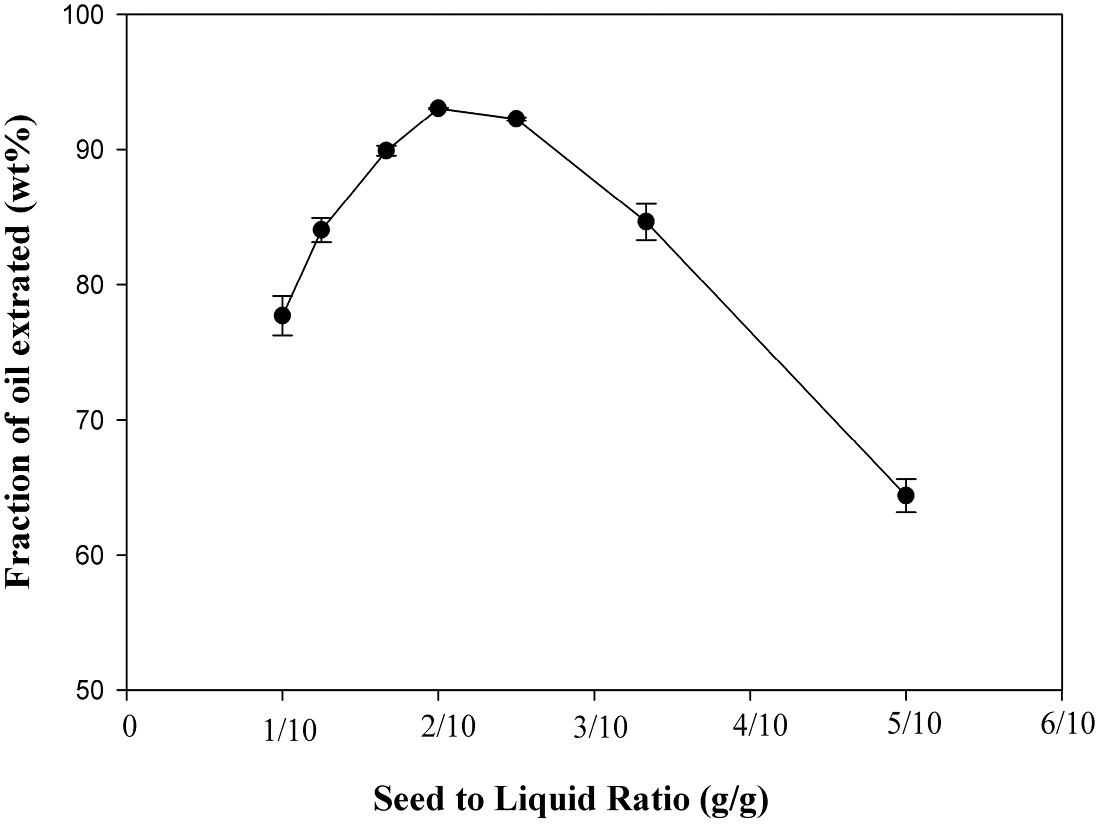


Figure 3.7: Effect of seed to liquid ratio on extractability using 0.15 wt% of C_{10}-18PO-2EOsulfate and 6 wt% NaCl at 25°C. 30 minutes contact time and shaking speed at 150 shakes/min.

The same trend was observed with canola oil (data not shown). The amount of oil extracted decreased at the highest solid - liquid ratios likely because the viscosity increase made it difficult to maintain effective mixing and to achieve surfactant-oilseed contact. Conversely, we speculate that too high of a liquid to solid ratio causes less particle collision, leading to poor extraction efficiency. It is important to note that compared to other aqueous extraction processes studied in the literature, we are able to employ a higher solid-liquid ratio; a solid to liquid ratio of 1 : 20 (g to mL) is normally observed in other studies [6,10,15].

Effect of pH on fraction of oil extracted

Peanut and canola oil extraction efficiencies were evaluated at four different pH values; 4, 7, 9 and 11 (data not shown). In contrast to aqueous extraction methods using enzymes, pH values ranging from 4 to 9 had no significant effect on the fraction of oil extracted, which is consistent with the IFT results (data now shown). At pH 11, the solution suddenly changes into green-brownish color and the extraction drops sharply since a green-brownish emulsion was observed instead of a clear oil phase. This can be explained by the solubilization of protein in the aqueous phase at pH 11.

Oil quality

The crude oil quality resulting from the aqueous surfactant-based extraction method was analyzed and compared to oil recovered using hexane as extractant. Parameters that were compared include free fatty acid concentration, triglyceride composition profile and oil clarity. The results are summarized in Table 3.3 and 3.4 for peanut oil and canola oil, respectively.

Table 3.3: Analysis of extracted peanut oil

TGC Profile[a]	**Surfactant-based process**[c]	**Hexane-based process**
LLO[b]	14.3	11.0
LOO	14.0	14.8
LOP	11.8	10.1
OOO	14.1	10.0
%FFA[d]	0.050	0.70
12 hr cold test	Pass	Not pass

[a] Reported values are in weight percentages based on total triglycerides

[b] XYZ – hydrocarbon tail for each of three triglyceride tails; the group in each tail is shown in the abbreviation (for example, LLO has two C18:2 tails and one C18:1 tail); abbreviations: Ln: Linolenic (C18:3), L: Linoleic (C18:2), O: Oleic (C18:1), S: Stearic (C18:0), P: Palmitic (C16:0)

[c] Extraction conditions: 0.15 wt% C_{10}-18PO-2EOsulfate, 6 wt% NaCl, 25ºC, seed to liquid ratio at 1: 5 (g to g), 150 shakes/min

[d] Weight percentage of free fatty acids

The hexane-extracted peanut oil has a significantly higher content of free fatty acid (0.7 wt% FFA) than aqueous surfactant-based extracted peanut oil (0.05 wt% FFA). It is important to note that, the hexane extraction was performed on the same oilseed batches used in aqueous extended-surfactant extraction. It would be interesting to investigate how the triglyceride profile might change when the oil was extracted using aqueous extended-surfactant-based versus hexane. The triglyceride composition profiles for peanut and canola oils obtained by our method are also illustrated in Table 3.3 and 3.4, respectively.

Table 3.4: Analysis of extracted canola oil

TGC Profile[a]	**Surfactant-based process**[c]	**Hexane-based process**
LnOO[b]	8.45	7.70
LOO	23.9	25.7
OOO	44.4	47.8
%FFA[d]	0.040	0.60
12 hr cold test	Pass	Not pass

[a] Reported values are in weight percentages based on total triglycerides

[b] See Table 3 for abbreviations

[c] Extraction conditions: 0.35 wt% C_{10}-18PO-2EOsulfate, 5 wt% NaCl, 25ºC, seed to liquid ratio at 1: 5 (g to g), 150 shakes/min

[d] Weight percentage of free fatty acids

Due to the aqueous extraction medium, polyunsaturated fatty acids (PUFAs) can be subject to oxidation because of the chemical active of the double bonds [41]. An analysis of triglyceride profile would provide an insight to this degradation [42]. Table 3.3 and 3.4 show the most abundant triglyceride content in peanut and canola oils. Other minor triglycerides were detected but not reported. It can be seen that the aqueous extended-surfactant-based method produced vegetable oil with triglyceride profiles similar to those obtained from conventional hexane method, indicating no significant PUFAs degradation had occurred [42]. It is worth mentioning that while the oil quality tests performed in this paper gave some information on the oil quality, more detail on oil qualities (such as information on oxidative stability, saponification value and etc.) extracted by aqueous extended-surfactant solution will be reported in a subsequent paper focusing on scaleup of this work.

3.4 CONCLUSION

In conclusion, we have shown that, among the extended-surfactants studied in this research, the alkyl-propoxylate-ethoxylate-sulfate class of surfactants is most suitable for the vegetable oilseeds evaluated in this research since it produces the lowest interfacial tension (IFT). Additionally, the C_{10}-18PO-2EO-sulfate exhibits the best performance for vegetable oil extraction in terms of low IFT, salinity values and absence of stable macroemulsions. The aqueous extended-surfactant based method proved to be effective for extracting peanut and canola oils, being able to achieve 95% and 93% oil extraction, respectively. Although the fraction of oil extracted is not as high as that of the hexane method, which achieved 98-99% efficiency, our method offers significantly better crude oil quality in terms of free fatty acid. The amount of oil extracted by aqueous extended-surfactant-based and the amount of residual oil were summed and compared to the total oil content analyzed by Soxhlet extraction. There was no statistical difference between these two values, indicating that insignificant amount of oil was lost through solubilization in the aqueous surfactant solution.

We also looked at the effects of different processing parameters on vegetable oil extraction efficiency, including pH, surfactant concentration, extraction time, shaking speed, solid-to-liquid ratio, and salinity levels. We found that surfactant concentrations at the CμC and optimum salt concentrations are the most important parameters for vegetable oil extraction efficiency. From the evaluation of crude oil quality, it was shown that our method offers better crude oil quality in terms of free fatty acid content compared to the hexane extraction method. The peanut and canola oils are clear and exhibit fresh smell. Hexane extracted oils have a burnt-like smell because the oils were heated to evaporate the hexane. Thus, we have successfully demonstrated the viability of the aqueous surfactant based extraction method for seed extraction of vegetable oils; future work will explore the scale-up of this process.

3.5 ACKNOWLEDGEMENTS

The authors would like to thank George Smith, Huntsman Petrochemical Corp. (Houston, TX) for providing us the extended-surfactant samples; Gene Neuens from Producers Cooperative Oil Mill and Plains Oilseed Products Cooperative (OKC, OK) and Wayne Janzen from Prairie Gold Oil Seeds (Okeene, OK) for providing canola seeds.

Funding for this work has been provided through the United States Environmental Protection Agency's Science to Achieve Results (STAR) program, through grant number Rd-83090301-0, the Oklahoma Secretary of Energy, and the Oklahoma Center for Advancement of Science and Technology (OCAST). Although the research described in this article has been funded by the United States Environmental Protection Agency, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Partial support was provided by industrial sponsors of the Institute for Applied Surfactant Research at the University of Oklahoma: Akzo Nobel, Clorox, Conoco/Phillips, Church and Dwight, Ecolab, Halliburton, Dow Chemical, Huntsman, Oxiteno, Procter & Gamble, Sasol North America, Shell Chemical, and from Dr. Sabatini's Sun Oil Company endowed chair and Dr. Harwell's Conoco/Dupont endowed professorship.

REFERENCES

---

1. N- Hexane Substance Technical Guidelines (accessed in May 2008). <http://ehs.ucsc.edu/lab_research_safety/pubs/facts/Hexane.pdf>
2. Juliano BO (1985) Rice: Chemistry and Technology, 2nd edn, The American Association of Cereal Chemists, Minnesota. pp 647 – 687
3. Darling ER , Yelland WEC (1952) Process of Liberating and Recovering Oil from Materials Containing Starch, Proteins, and Oil. U.S. Patent 2, 606,916

4. Hagenmaier R, Cater CM, Mattil KF (1972) Critical Unit Operation of the Aqueous Processing of Fresh Coconuts. J Am Oil Chem Soc 49: 178-181

5. Lawhon JT, Manak LJ, Rhee KC, Lusas EW (1981) Combining Aqueous Extraction and Membrane Isolation Techniques to Recover Protein and Oil from Soybeans. J Food Sci 46: 391-395

6. Diosady LL, Rubin LJ, Ting N, Trass O (1983) Rapid Extraction of Canola Oil. J Am Oil Chem Soc 60: 1658-1661

7. Hron RJ, Koltun SP, Graci AV (1982) Biorenewable Solvents for Vegetable Oil Extraction. J Am Oil Chem Soc 59(9): 674A – 684A

8. Cater CM, Rhee KC, Hagenmaier RD, Mattil KF (1974) Aqueous Extraction – An Alternative Oilseed Milling. J Am Oil Chem Soc 51: 137-141

9. Moreau RA, Dickey LC, Johnston DB, Hicks KB (2009) A Process for Aqueous Enzymatic Extraction of Corn Oil from Dry Milled Corn Germ and Enzymatic Wet Milled Corn Germ (E-Germ) J Am Oil Chem Soc 86: 469 – 474

10. Sharma A, Khare SK, Gupta MN (2002) Enzyme-Assisted Aqueous Extraction of Peanut Oil. J Am Oil Chem Soc 79(3): 215 – 218

11. Johnson LA, Lusas EW (1983) Comparison of Alternative Solvents for Oils Extraction. J Am Oil Chem Soc 60: 229 – 242

12. Rosenthal A, Pyle DL, Niranjan K (1996) Aqueous and Enzymatic Processes for Edible Oil Extraction. Enzyme Microb Technol 19: 402 – 420

---

13. Fullbrook PD (1983) The Use of Enzymes in the Processing of Oilseeds. J Am Oil Chem Soc 60: 428A – 430A
14. Latif S, Diosady LL, Anwar F (2008) Enzyme-assisted Aqueous Extraction of Oil and Protein from Canola (Brassica Napus L.) Seeds. Eur J Lipid Sci Technol 110: 887 – 892
15. Owusu-Ansah YJ (1997) Enzyme-Assisted Extractions. In: Wan PJ, Wakelyn PJ (Eds.) Technology and Solvents for Extraction Oilseeds and Nonpetroleum Oils. AOCS Press, Champaign, pp 323 – 332
16. Kapchie VN, Wei D, Hauck C, Murphy PA (2008) Enzyme-Assisted Aqueous Extraction of Oleosomes from Soybeans (Glycine max). J Agric Food Chem 56: 1766 – 1771
17. Tano-Debrah, K. and Ohta, Y. Application of Enzyme-Assisted Aqueous Fat Extraction to Cocoa Fat. (1995) J Am Oil Chem Soc 72(11):1409 – 1411
18. Nasuk A, Sabatini DA, Tongcumpou C (2009) Microemulsion-Based Palm Kernel Oil Extraction Using Mixed Surfactant Solutions. Ind Crops Prod 30(2): 194 – 198
19. Leser ME, Luisi PL, Paimieri S (1989) The Use of Reverse Micelles for the Simultaneous Extraction of Oil and Proteins from Vegetable Meal. Biotechnol Bioeng 34(9): 1140 – 1146
20. Ugolini L, Nicola GD, Palmieri S (2008) Use of Reverse Micelles for the Simultaneous Extraction of Oil, Proteins, and Glucosinolates from Cruciferous Oilseeds. J Agric Food Chem 56: 1595 – 1601

---

21. Nguyen T, Do L, Sabatini DA (2010) Biodiesel Production via Peanut Oil Extraction Using Diesel-Based Reverse-Micellar Microemulsions. Fuel DOI: 10.1016/j.fuel.2010.03.021

22. Rosen MJ (1989) Surfactants and Interfacial Phenomena. 2nd edn, John Wiley & Sons, Canada. pp 229 – 235

23. Campbell KA, Glatz CE. (2009) Mechanisms of Aqueous Extraction of Soybean Oil. J Agric Food Chem 57: 10904 – 10912

24. Do LD, Withayyapayanon A, Harwell JH Sabatini DA (2009) Environmentally Friendly Vegetable Oil Microemulsions Using Extended Surfactants and Linkers. J Surfact Deterg 12: 91 – 99

25. Salager JL, Anton RE, Sabatini DA, Harwell JH, Acosta EJ, Tolosa LI (2005) Enhancing Solubilization in Microemulsions – State of the Art and Current Trends. J Surf Deterg 8, 1: 3 – 21

26. Minana-Perez M, Graciaa, A, Lachise J, Salager JL (1995) Solubilization of Polar Oils in Microemulsion Systems. Progr Colloid Polym Sci 98: 177 – 179

27. Witthayapayanon A, Harwell JH, Sabatini DA (2008) Hydrophilic-Lipophilic Deviation (HLD) Method for Characterizing Conventional and Extended-Surfactants. J Colloid Interface Sci 325: 269 – 266

28. Withayyapayanon A, Acosta EJ, Harwell JH, Sabatini DA (2006) Formulation of Ultralow Interfacial Tension Systems Using Extended-Surfactants. J Surfact Deterg 9: 331 – 339

29. Childs JD, Acosta E, Scamehorn JF, Sabatini DA (2005) Surfactant-Enhanced Treatment of Oil-Based Drill Cuttings. J Energy Resource Technol 207(2): 153 – 162

30. McCurdy SM (1990) Effects of Processing on the Functional Properties of Canola/Rapeseed Protein. J Am Oil Chem Soc 67(5): 281 – 284

31. Carr RA (1997) Oilseed Processing. In: Wan PJ, Wakelyn PJ (Eds.) Technology and Solvents for Extraction Oilseeds and Nonpetroleum Oils. AOCS Press, Champaign, pp 101 – 120

32. Dunford NT and Temelli F (1996) Effect of Supercritical CO2 on Myrosinate Activity and Glucosinolate Degradation in Canola. J Agric Food Chem 44(8): 2372 – 2376

33. Official Method of Analysis of the Association of Official Analytical Chemists, 16th edn, AOAC International, Gaithersburg, MD (1995)

34. Mattil KF, Norris FA, Swern D(1964) Extraction of Fats and Oils. Bailey's Industrial Oil and Fat Products, 3rd edn., John Wiley & Sons, London: pp 637–717

35. Alltech Chromatography. Catalog 600, 2005: pp 499

36. Cunha SC, Oliveira MBPP (2006) Discrimination of Vegetable Oils by Triacylglycerols Evaluation of Profile Using HPLC/ELSD. Food Chem 95: 518 – 524

37. Redden PR, Huang Y, Lin X, Horrobin DF (1995) Separation and Quantification of the Triacylglycerols in Evening Primrose and Borage Oils by Reversed-Phase High-Performance Liquid Chromatography. J Chromatography A 694: 381 – 389

38. Official Method of Analysis of Association of Official Analytical Chemists (1975) 12th edn, Washington, D.C.

39. Official and Tentative Methods of the American Oil Chemists' Society. (1973) 3rd edn, American Oil Chemists' Society, Champaign, Method Cc 11-53

40. Tongcumpou C, Acosta EJ, Scamehorn JF, Sabatini DA, Yanumet N, Chavadej S (2006) Enhanced Triolein Removal Using Microemulsions Formulated with Mixed Surfactants. J Surfact Deterg 9(2): 181 – 189

41. Belitz HD, Grosch W, Schieberle P (2004) Food Chemistry. 3rd revised edn, Springer, New York, pp 159 – 168

42. Cravotto G, Boffa L, Mantegna S, Perego P, Avogadro M, Cintas P (2008) Improved Extraction of Vegetable Oils Under High-Intensity Ultrasound and/or Microwaves. Ultrason Sonochem 15: 898 – 902

Chapter 4 Pilot Scale Study of Vegetable Oil Extraction by Surfactant-Assisted Aqueous Extraction Process[1]

ABSTRACT

A number of aqueous extraction processes (AEP) have been studied as substitutes for hexane in oilseed extraction. In our previous batch-scale work, we have shown that the aqueous surfactant-based method could effectively extract up to 95% peanut and canola oils at 25°C. The goal of this work is to perform a semi-continuous pilot-scale study of the aqueous surfactant-based method for peanut and canola oil extraction. Two extraction strategies were evaluated including (1) a single extraction stage by aqueous surfactant solution and (2) two extraction stages, consisting of one aqueous surfactant wash and one de-ionized water wash. At optimum conditions, 90.6% and 88.1% oil extraction efficiencies of peanut and canola oil, respectively, were achieved in a single stage extraction, while 94.5% and 92.6% were achieved in the two-stage extraction. At the highest solid/liquid centrifuge speed, the moisture level in the extracted meal was 48%. At the optimum liquid/liquid centrifuge condition, more than 90% of the oil was recovered as free oil from the extracted-oil and surfactant-wash mixture and 39-44% of

---

[1] This chapter or portions thereof has been accepted for publication in *Journal of Separation Science and Technology* under the title “Pilot scale study of vegetable oil extraction by surfactant-assisted aqueous extraction process”. This current version has been reformatted for this dissertation.

oil was recovered from the extracted oil and DI wash mixture. Total free oil recovered after two stage extraction was 87.1% and 85.6% for peanut and canola, respectively.

Keywords: pilot scale study, vegetable oil extraction, microemulsions, extended surfactants

4.1 INTRODUCTION

Vegetable oils are typically produced from oilseeds by either hexane extraction or a combination of mechanical processing and hexane extraction. However, there are growing health concerns and increased environmental regulations regarding the use of hexane in vegetable oil extraction. Exposure to hexane at 15 ppm/day for three months has been shown to cause peripheral nerve damage, and hexane is also a potential hazardous explosive material [1]. In 2001, the U.S. Environmental Protection Agency (EPA) established regulations on hexane emission due to growing environmental concerns. In addition, oils produced by hexane extraction are high in free fatty acid, wax and unsaponifiable matter, and can also exhibit a dark greenish-brown color [2].

The use of aqueous extraction processes (AEP) for vegetable oil has been studied widely [3,4,5,6]. AEP for oilseed extraction eliminate the potential for explosion and emissions of the volatile organic solvent hexane. Simultaneous recovery of oil and protein by AEP is possible with lower equipment costs and energy consumption than by hexane extraction [7 ,8]. Because of the immiscibility of water and vegetable oil, AEP consistently been reported to produce vegetable oil superior in quality (lower phosphatide levels and peroxide values) to that produced by hexane-based processes [9,10]. In general, when employing AEP, the extracted oil and protein in the liquid phase distribute among three portions which are the free oil, cream (oil in water emulsions) and skim (protein and sugar-rich aqueous phase)[11]. Limiting the utility of AEP is the fact that vegetable oil recovery is typically low (33-68%) [12].The vegetable oil is trapped inside the porous matrix of the meal due to high capillary forces. Low oil extraction efficiency can be attributed to the high interfacial tension between the water phase and the vegetable oil (8 - 10 mN/m for canola and peanut oil) making the oil unable to diffuse through the porous matrix of the meal [13,14]. By definition, interfacial tension is the surface tension caused by intermolecular interactions at the surface separating two immiscible fluids [15] – in this case vegetable oil and the extracting aqueous solution.

Several approaches have been tested in an effort to improve the oil extraction efficiency of AEP including mechanical treatment (flaking and extruding to obtain smaller grain size) [12], enzyme assisted treatment (EAEP) [16,17] and surfactant enhanced extraction [14,18]. Mechanical treatment by grinding has improved the oil recovery from 33% to 66% when flour particles were reduced from 0.4 mm to 0.1 mm [5]. Similar oil recovery (68%) was achieved when employing flaking and extruding treatment to soybean flours [12]. However, mechanical treatment alone still results in insufficient oil extraction efficiency. Consistently high oil extraction efficiency (> 90%) has been reported in the literature when using enzyme assisted [8] or surfactant enhanced AEP [14,18]. In the study of AEP extraction mechanisms of soybean oil, Campbell et al. reported that both Protease enzyme and sodium dodecyl sulfate (SDS) surfactant enhanced AEP were able to achieve similar and higher oil extraction efficiency than AEP alone [13]. In the microscopic study [13], it was found that when employing AEP alone, the unextracted oil was trapped in an insoluble matrix of denatured proteins. The coalesced oil size was too large to diffuse through the disrupted cellular matrix [13]. Further, it was found that the mechanism of oil release using Protease enzyme is by proteolytic digestion of insoluble cellular matrix [13]. Alternatively, the oil release mechanism when aqueous using surfactant is to disrupt the oil/water interface by lowering the interfacial tension between the surfactant solution and the oil, thereby facilitating the oil droplet breakup and making it possible for the oil to diffuse through the disrupted cell [13].

The use of surfactant enhanced AEP extraction has been investigated by our group in batch scale studies using alkyl propoxylate-ethoxylate-sulfate surfactants [14,18]. In batch studies, we have achieved up to 94% oil extraction efficiency for peanut, canola and palm oils when the interfacial tension between the surfactant solution and the oil phase was less than 0.05 mN/m [14,18]. Alkyl propoxylate-ethoxylate-sulfate surfactants are extended-surfactants, a new class of surfactant that has intermediate polar groups (i.e. propoxylate or ethoxylate) inserted between the head and tail of the surfactant molecule [19]. Due to this unique structure, extended surfactants have consistently produced ultralow interfacial tension (IFT) with a wide range of vegetable oils, which is critical in oilseed extraction [14, 19]. We define ultralow IFT as IFT << 0.1 mN/m [14]. The surfactant enhanced AEP (SAEP) for vegetable oil is particularly attractive due to the short contact time between the surfactant medium and the oilseeds (about 30 minutes), ambient temperature extraction and high solid to liquid ratios (SLR of 1 to 5 g solids/g liquid), which are desirable in industrial application [14,18]. Another advantage is that the surfactant concentrations are at the critical microemulsion concentration (cμc) which are relatively low (less than 0.5 wt%) [14]. Cμc is defined as the lowest surfactant concentration capable of producing ultralow IFT. At this concentration, the vegetable oil is removed mainly due to the mobilization mechanism in which the oil is liberated as a separate phase rather than solubilized into the aqueous surfactant phase [14,20] It is important to note that, when employing EAEP, the incubation time is more than one hour and the slurry temperature is in the range of 50 - 60°C [8,11]. It is important to note that only a limited number of scaleup studies on AEP and EAEP oil extraction in the literature [11,21]. Rhee et al. studied the AEP pilot plant scale production of peanut protein concentrate, with little emphasis on oil extraction efficiency [21]. The peanut protein and oil recovery processes were carried out at 60°C and pH of 4 for one hour incubation time. Up to 88.8% oil was recovered as free oil after four consecutive washes with a SLR of 1 to 10 for the first wash and SLR of 1 to 5 for other three consecutive washes [21]. It was shown that dry grinding the peanuts gave free oil while wet grinding the peanuts gave lower oil extraction efficiency and most emulsion phases [21]. Moura et al. studied the scale-up of EAEP extraction of soybeans in a two stage counter-current process using extruded soybean flakes [11]. One pilot scale run was carried out over a two day period [11]. In the two stage counter-current processes with a SLR of 1 to 6, at 50°C and 1 hr incubation time, up to 99% soybean oil extraction efficiency was achieved; however, most oil was distributed among cream and skim fractions after centrifugation, requiring an additional step to obtain free oil [11]. Although the oil extraction efficiency is very promising, this study did not use a continuous process (i.e. use of funnel separation to recover free oil from cream [11]). The objectives of the current research are (1) to study the effect of processing parameters on extraction efficiency and (2) to identify potential problems related to the scale-up system of SAEP. We thus seek to extend our prior research work in the present study, we decided to evaluate semi-continuous laboratory-based SAEP using laboratory-scale processing equipment similar to that used in industrial processes. The SAEP was scaled up from 2 grams to 150 grams of peanut and canola flours.

4.2 MATERIALS AND METHODS

4.2.1 Materials

$C_{10}H_{21}$-18PO-2EOsulfate surfactant (19.9 active%) was kindly provided by Huntsman Chemical Co. (Houston, TX) and used as received. Blanched peanut seeds were purchased from the local market. Canola seeds were kindly provided by Producers Cooperative Oil Mill, Plains Oilseed Products Cooperative (Oklahoma City, OK) and Prairie Gold Oil Seeds (Okeene, OK). Sodium chloride (99%+ purity) was purchased from Sigma Aldrich and used as received.

4.2.2 Methods

Oilseed pretreatment

Blanched peanut seeds were dehulled, whereas canola seeds were not since it is not economically feasible to dehull canola seeds [22]. Peanut and canola seeds were ground using a food processor. The particle size used in this study was in the range of 0.21 to 0.42 mm size by using US Sieve size No. 40 and No.70, which is in the recommended range for oilseed extraction [23].

Oilseed extraction by SAEP

Figure 4.1 illustrates the schematic diagram of the pilot scale process utilized in this research and Figure 4.2 shows selected products at different SAEP stages using optimized extraction conditions.

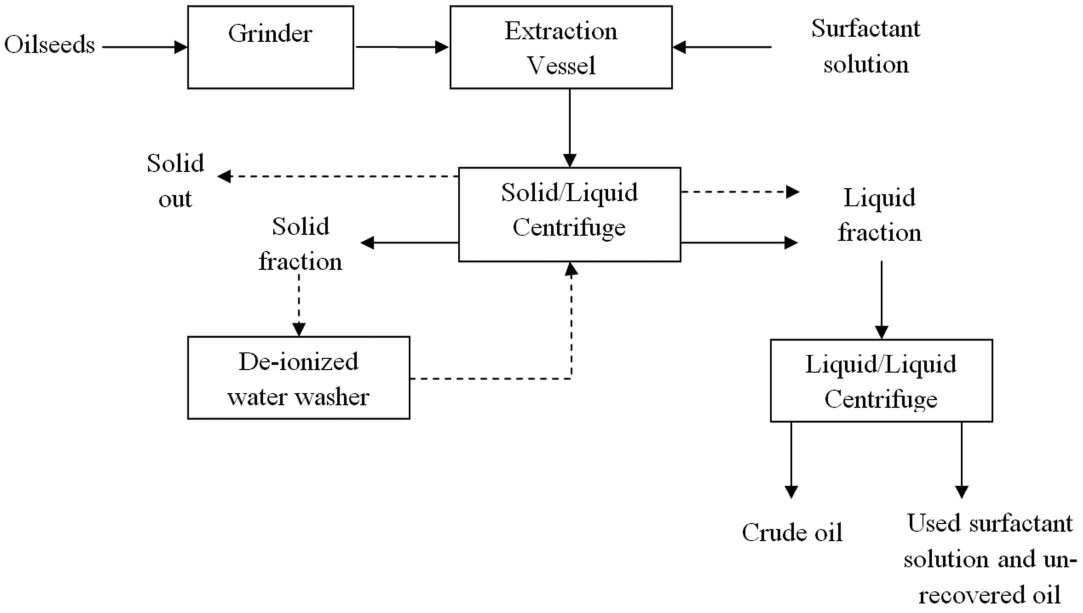


Figure 4.1: Schematic diagram of laboratory–based pilot scale processing of peanut and canola oil extraction. Solid line (—): surfactant wash step; Dash line (– –): DI washing step

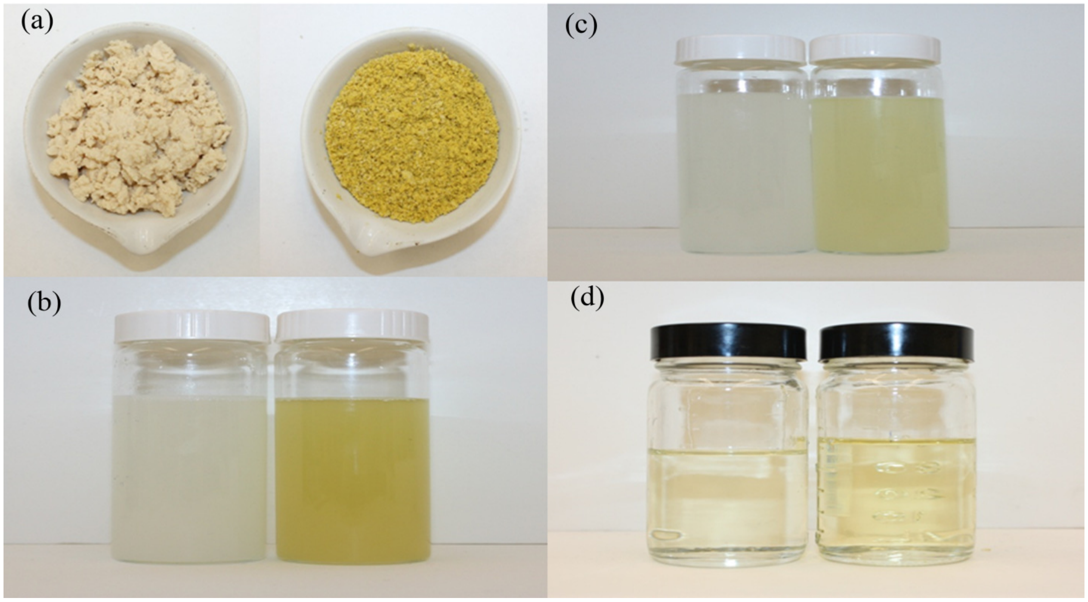


Figure 4.2: Selected products at different stages of SAEP and DI washing at optimum conditions for peanut and canola from left to right, respectively. (a) peanut and canola flours (b) liquid fraction from L/L centrifuge of surfactant wash step (c) liquid fraction from L/L centrifuge of DI washing step (d) free oil crude oil recovered from L/L centrifuge

First, 750 grams of solution containing surfactant ($C_{10}H_{21}$-18PO-2EO-sulfate) and sodium chloride (NaCl) at concentrations specified below were placed in a two liter stainless steel extractor vessel. Next, 150 grams of seed flours were dispensed into the solution to produce a SLR of 1 to 5 (g to g). For peanut oil extraction, $C_{10}H_{21}$-18PO-2EO-sulfate was fixed at 0.15 wt% and NaCl at 6 wt%, while for canola oil extraction, the surfactant concentration was 0.35 wt% with NaCl at 5 wt%. These are optimum conditions found from our previous study [14]. Dispersion of the flours in the extraction solution was performed by a four-blade 1 inch mixer attached to the Talboys light duty mixer overhead (model 101). Oilseed flours were directly fed into the surfactant solution in the extraction vessel. The slurry was agitated at 500 rpm to ensure gentle mixing and sufficient dispersion of the flour in the solution. Preliminary studies were conducted at three agitation speeds - 500, 750 and 1000 rpm. There was no statistically significant difference in the oil extraction efficiency when varying the agitation speeds (data not shown); therefore, an agitation speed of 500 rpm was used throughout the study. After 30 minutes of extraction, the slurry was pumped by a chemical metering pump (Precision Control Products, AMF CUNO metering pump, model 8311-11) at varying flowrates into a semi-continuous solid/liquid centrifuge (Lavin centrifuge, model L2, see reference [24] for details including picture of equipment) equipped with a 4" stainless steel bowl. The bowl was custom perforated and used in conjunction with a 200 mesh filter cloth and a 200 mesh filter plastic to keep the filter cloth in place. They were placed inside the bowl to improve the solid/liquid (S/L) separation. The S/L centrifuge speed was varied at 1029, 2100 and $4116\times g$.

The liquid portion (oil/surfactant/electrolyte/water mixture) from the S/L centrifuge was collected in a two-liter glass beaker. After collecting the liquid fraction (i.e. no more liquid was collected from the S/L outlet), the solution was then pumped by a Masterflex L/S peristaltic pump (Easyload, model 7518-00) into a continuous liquid/liquid (L/L) centrifuge (CINC model V02, see reference [25] for details/picture of the equipment) at flowrates varying from 1 – 5 mL/min. The L/L centrifuge was pre-filled with 150 mL of heavy phase solution (de-ionized water) in order to obtain the best separation performance (recommended by the manufacturer). It is important to note that in the continuous large scale operation, this step will not be necessary. The L/L centrifuge speed was varied to study the efficiency in oil/surfactant solution separation. The oil from the light phase outlet was collected in a 500 mL glass beaker and the skim fraction (most often oil in water emulsions [11]) from the heavy phase outlet was collected in a one-liter glass beaker. The solids obtained from S/L centrifuge process were carefully scooped out. The oil residual content in the solid fraction was further analyzed. The water content in the oil or cream fraction obtained from the light phase outlet of the L/L centrifuge was also analyzed. These test methods are discussed below. For the de-ionized water washing step, the SAEP extracted meal (solid fraction) obtained from S/L separation process was carefully scooped out and re-suspended in 450 mL of de-ionized water held in a two liter stainless steel extractor vessel. The slurry was resent to the S/L and L/L centrifuges. All data reported are average values from triplicates.

Oil content

Total oil content in crude oilseeds and in residual meal obtained from S/L separation were analyzed using hexane solvent in a Soxhlet extraction apparatus following the Association of Official Analytical Chemists (AOAC) standard procedure (Method 948.22) [26]. The residual meal was dried overnight in a forced oven at 104oC and re-ground for solvent extraction. In the second Soxhlet extraction step, no more oil was collected. Total oil analysis gave 46.7% ± 0.86% peanut oil and 42.5 ± 0.92% canola oil content based on dry weight basis, consistent with values reported in the literature [27]. Oil extraction efficiency was calculated as weight percentage of oil extracted divided by the total oil present in the seeds as determined by this method. It is important to note that in order to avoid variation in oil content and removal efficiency in different runs, the total oil content was analyzed in each run and the oil removal efficiency was calculated based on the corresponding oil content of the same run. Oil content in the light phase obtained from the liquid/liquid centrifuge was analyzed by the temperature modified Babcock method adapted from reference [28].

Moisture content

The moisture level in the oilseeds was determined by AOAC standard procedure (Method 925.40) [33]. Moisture levels in both peanut and canola seeds were in the range of 4 - 6 wt% which is well within the recommended range [31]. The moisture content in the residual meal after S/L separation was determined by the weight difference after placing the meal in the forced oven overnight at 104^{o}C. Water content in the extracted oil obtained from the L/L separation was determined by Karl Fischer volumetric titration method using TitroLine KF (Schott instruments).

Interfacial tension experiments

Interfacial tension (IFT) experiments were carried out using a spinning drop tensiometer (University of Texas, model 500). To measure the IFT value between the post wash solution and peanut and canola oils, 15 mL of the slurry obtained from S/L centrifuge were transferred into a glass tube and centrifuged at $2170\times g$ (IEC centrifuge, model HN). The aqueous portion obtained after the centrifuge was used for IFT measurements. IFT values were recorded at 20 minutes [14].

Statistical analysis

One way ANOVA was used for data statistical analysis and compared with p-value at 0.05.

4.3 RESULTS AND DISCUSSION

Table 4.1 shows the effect of the S/L centrifuge speeds and inlet flowrate on the moisture of the meal and the total oil extraction efficiency by SAEP. The S/L centrifuge speeds were varied at 1029, 2100 and 4116×g (the maximum allowable speed of the equipment), and at each centrifuge speed, the inlet flowrate was evaluated at 8, 10 and 12 mL/min. It is important to note that, due to the bowl design of the S/L centrifuge, a slurry flowrate higher than 12 mL/min resulted in a significant amount of solids loss.

Table 4.1: Effect of process parameters on peanut oil extraction efficiency – solid/liquid (S/L) separation

Speed (rpm)	**speed (x g)**	**Inlet flowrate (mL/min)**	**Meal moisture content (wt%)**	**Oil residual[a] (wt%)**	**Total oil recovery[a] (wt%)**
3500	1029	8	78.6±0.66	19.8±0.87	80.1
		10	80.6±1.64	20.8±0.96	79.2
		12	78.5±0.69	19.6±1.10	80.4
5000	2100	8	64.8±0.81	14.3±1.20	85.6
		10	63.5±2.31	15.9±0.63	84.1
		12	65.9±1.32	15.0±1.34	85.6
7000	4116	8	44.8±2.50	9.44±0.90	90.6
		10	46.9±3.73	9.22±1.33	90.1
		12	48.3±1.81	9.65±1.50	90.2

[a] Amount of oil extracted via Soxhlet extraction was used as the basis.

Sample calculation:

$$\begin{aligned} &Percentage\ of\ oil\ residual\ (wt\%) \\ &= \frac{mass\ of\ oil\ residual\ (g)}{mass\ of\ total\ oil\ determined\ by\ Soxhlet\ extraction\ (g)} \times 100\% \\ &= \frac{6.64\ g}{70.35\ g} \times 100\% = 9.44\ wt\% \end{aligned}$$

From Table 4.1, it can be seen that, while the inlet flowrate had little effect on the recovery of extracted oil, the S/L centrifuge speed had a more pronounced effect. As the centrifugation speed increased, the moisture level in the meal was reduced and total extracted oil in the liquid fraction increased. At 4116×g (7000 rpm), the moisture level of the meals shows the lowest value at 44.8 wt% and the total oil extracted in the liquid shows the maximum value to be 90.6 wt% for peanut and 88.1 wt% for canola oil (Table 4.2).

Table 4.2: Total oil extracted at optimum conditions at 25°C[a]

	Fraction of oil extracted from surfactant wash[b] (wt%)	Fraction of oil extracted from[b] DI wash (wt%)	Total oil extracted[b] (wt%)
peanut	90.6	3.98	94.5
Canola	88.1	4.54	92.7

[a] 30 minute surfactant solution extraction, 5 minute DI wash, S/L centrifuge at 4116xg and 8 mL/min inlet flowrate

[b] Amount of oil extracted via Soxhlet extraction was used as the basis

These values are somewhat lower than those obtained in the batch scale, which were 95 wt% and 93 wt% for peanut and canola oil, respectively. This difference might be due to the fact that in the batch scale we used a three phase centrifuge, while in the pilot scale we separated this process into two different steps using the S/L separator and L/L centrifuge, suggesting that the separation of the liquid in S/L separator was not as effective in the three phase batch centrifuge. However, it is important to note that the use of a three phase decanter for a slurry of high solid content (up to 20 wt%) is impractical [21].

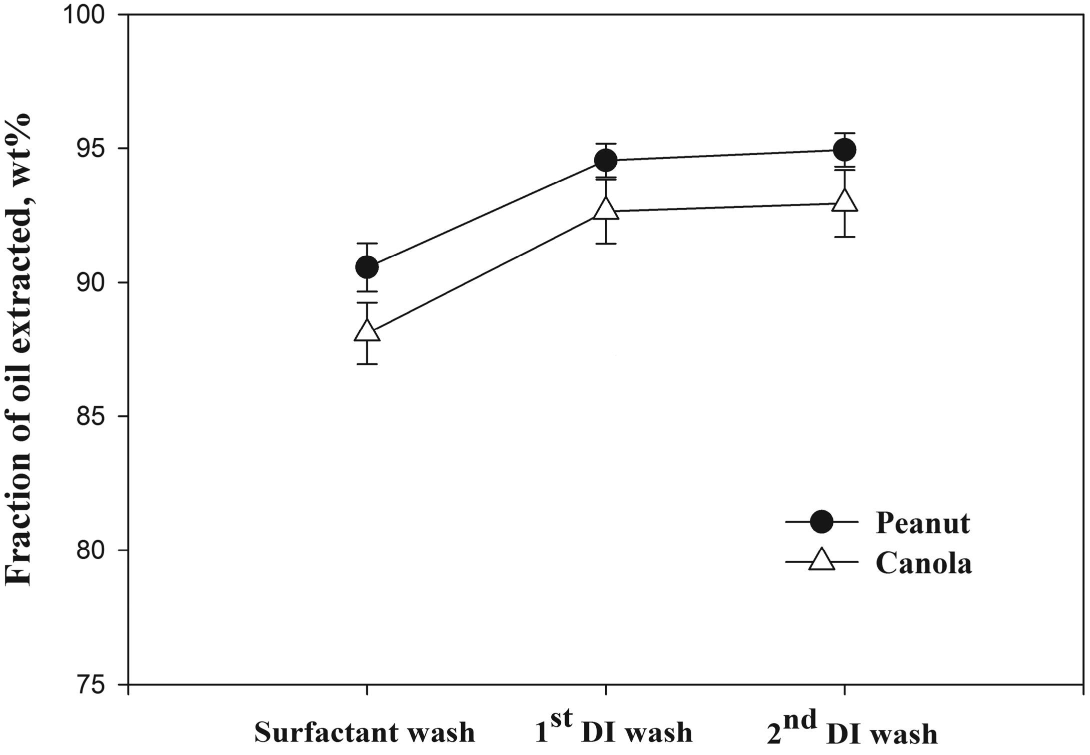


Figure 4.3: Oil extraction efficiency for different consecutive extraction trials at 25°C. Extraction condition: 30 minute wash, S/L centrifuge at 4116xg and 8 mL/min inlet flowrate. Amount of oil extracted via Soxhlet extraction was used as total oil

The washing step using de-ionized water was introduced to recover more oil from the SAEP extracted meal. Figure 4.3 shows the effect of the surfactant washing, and the first and second DI washing on the total oil extraction efficiency. It can be seen that an additional 4 to 5 wt% of total oil was recovered by the first washing step and no more appreciable amount of oil was recovered in the second washing step. The oil obtained from the washing step brought the total oil extraction efficiency to 94.5 wt% and 92.6 wt% for peanut and canola oil, respectively, approaching the results obtained in the batch scale. These results confirm that the oil was extracted effectively in the surfactant wash step but was not fully separated in the S/L separation step.

The DI water in the wash step recovered the oil that was already released and stayed outside the cell structure. Table 4.3 shows the IFT between the peanut and canola oil with the extraction media at different washing stages by SAEP and AEP. The IFT value of the extracted oils with the first DI washing solution was about 2 mN/m for both peanut and canola oils, indicating that there was some surfactant remaining in the meal from the surfactant wash. The IFT values of the extracted oils with the second DI washing solution was 5 – 6 mN/m; similar to the IFT values of peanut and canola oils with DI washing only solution, which indirectly indicated that there was no appreciable amount of surfactant left in the meals. The basket centrifuge was used here because it was the only option available at the scale we needed for our system but is not the best option when operating the oilseed extraction in large scale processes because it has limited solid holding capacity and will prevent the system from operating continuously. In large scale operating facility, we envision the use of the solid bowl scrolling centrifuge or continuous pusher centrifuge which has been used widely in solid-liquid separation processes [29]. However, this equipment was not available at our operational scale.

Table 4.3: IFT prewash and postwash extraction solution with refined peanut and canola oil measured at 20 minutes

	prewash IFT (mN/m)	postwash IFT (mN/m)	1st DI postwash IFT (mN/m)	2nd DI postwash IFT (mN/m)
canola[a]	0.015	0.018	2.1	6.1
peanut[a]	0.011	0.011	2.2	5.0
peanut[b]	10.0	5.0	NA	NA

[a] SAEP

[b] AEP

Figure 4.4 shows the effect of the inlet flowrate on the oil recovery and the water content in the oil phase at a constant centrifugation speed of 680×g of the L/L centrifuge. The extracted-oil and surfactant-washed solution had 7 - 10 wt% of canola and peanut oil. It can be seen that the oil recovery decreased and the water content in the oil increased as the feed rate increased. The maximum moisture standard for crude peanut oil is 0.25 wt% [30] and for canola oil is 0.3 wt% [31]. The highest oil recovery was achieved at the lowest inlet flowrate of 1 mL/min, corresponding to the longest residence time of 150 minutes. At this condition, the water content in the crude peanut and canola oils were 0.15 wt% and 0.22 wt%, respectively, and met the standard requirement (0.25 wt% for peanut oil and 0.30 wt% for canola oil). The longer residence time allowed the oil droplet to more efficiently separate from the emulsions [32].

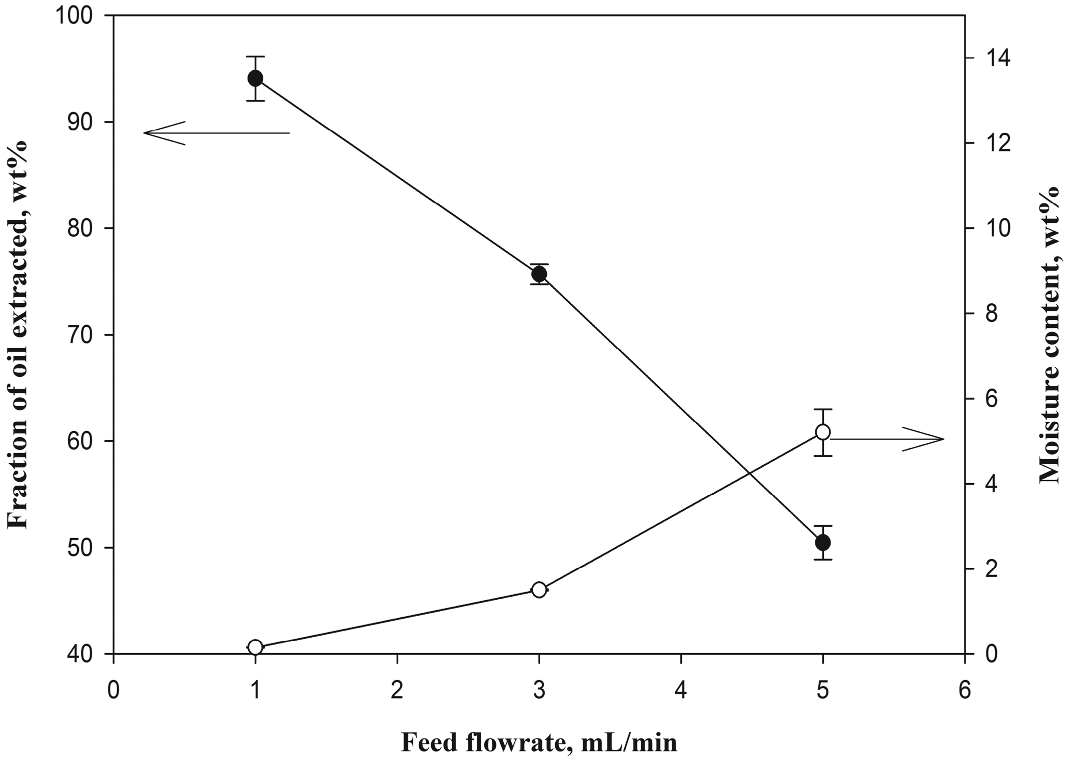


Figure 4.4: Effect of feed flowrate on peanut oil recovery from liquid fraction at constant liquid/liquid centrifuge speed at 25°C. Extraction condition: 30 minute wash, S/L centrifuge at 4116xg and 8 mL/min inlet flowrate, L/L centrifuge at 680xg

Free crude peanut and canola oils obtained from the L/L centrifuge at 1 mL/min and 680xg are shown in Figure 4.2(d). The extracted oils have excellent clarity with canola oil being more yellowish than peanut oil due to the color pigment of the oilseeds (Figure 4.2a). In addition, the SAEP peanut and canola had fresh smell, whereas the hexane-extracted oil had a burnt smell. At a feed rate of 5 mL/min, there was a dramatic decrease in the free oil recovery to 51 wt% and an increase in water content of the oil phase to 5.2 wt% as the residence time decreased to 30 minutes. Although the long retention time for demulsification process is a drawback in the aqueous-based extraction process, it might be offset by the high energy consumption and relatively long retention time to evaporate the hexane solvent and to obtain free crude oil in the hexane extracted process. In addition, the oil obtained from aqueous-based process has been consistently reported to have superior qualities and required less refining step than the oil from the hexane extraction process [3,8,14,18].

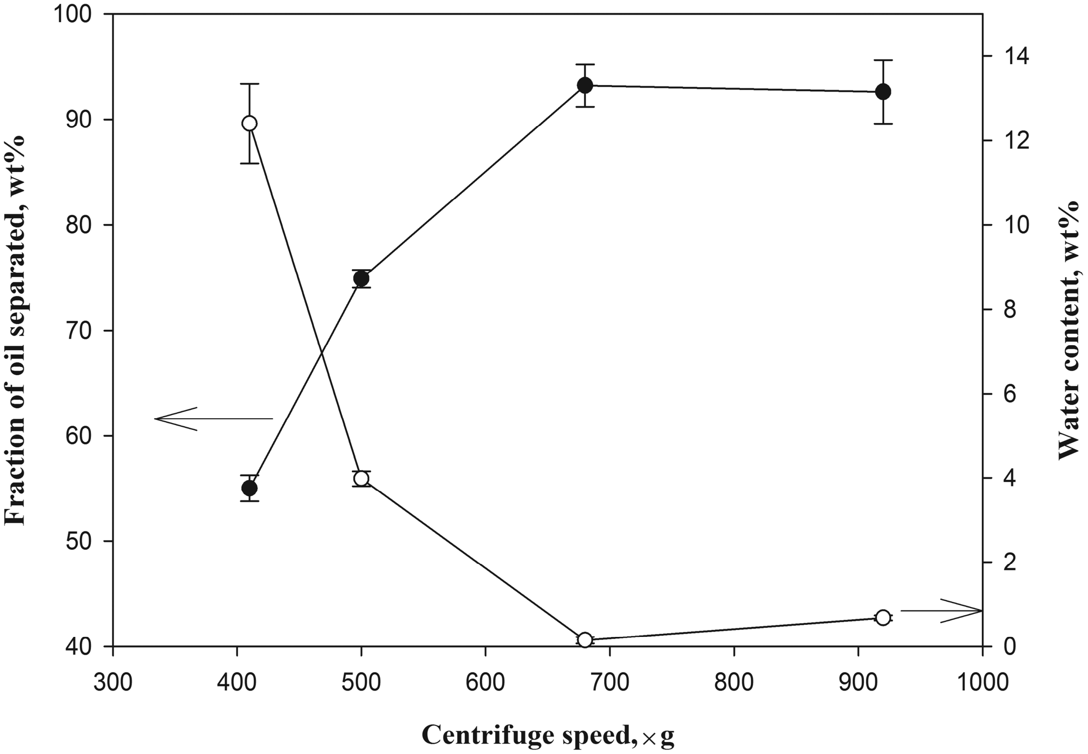


Figure 4.5: Effect of centrifuge speed on peanut oil recovery from liquid fraction at a constant feed flowrate of 1 mL/min at 25°C. Extraction condition: 30 minute wash, S/L centrifuge at 4116xg and 8 mL/min inlet flowrate

Figure 4.5 shows the effect of centrifugation speed (410, 500, 680 and 920×g) on the oil recovery and moisture level in the oil at a constant feed rate of 1 mL/min. The effect of the centrifugation speed on the oil in water emulsion demulsification can be understood by the following equation [32]:

$$v_o = \frac{(\rho_w - \rho_o) \times r\omega^2 \times D^2}{18\mu_w}$$

(Equation 4.1)

where v_o is the settling velocity of oil, ρ_w is the density of water, ρ_o is the density of oil, r is the radius of rotation, ω is the angular velocity of centrifugation, D is the diameter of the droplets and μ_w is the viscosity of continuous phase, which is the aqueous surfactant solution in our case. From the equation, it is expected that the emulsion separation will be more efficient at higher centrifugation speed.

The mechanism of oil in water emulsions separation by centrifugation was explained by Nour et al. [32]. Higher centrifuge rotation (ω) generates heat, increasing the temperature of the fluid. The ratio of $\frac{(\rho_w - \rho_o)}{\mu_w}$ increases as the temperature increases because the water viscosity decreases much faster than the density difference [32], thereby increasing the settling velocity of the oil. When increasing temperature from 20^{o}C to 40^{o}C, we measured the viscosity of the aqueous phase, μ_w, (surfactant/NaCl/water mixture) to be reduced by 60% whereas the change of $(\rho_w - \rho_o)$ was reduced by only 4% (data not shown). In addition, during the gravimetrical separation process, oil droplets collide with each other and coalesce to form larger oil droplets, which also enhanced the oil/water separation process. From Figure 4.5, it can be seen that when the centrifugation speed was increased from 410 to 680×*g*, higher oil recovery and lower water content in the oil phase were obtained. However, at 920×*g*, while there was no difference in the oil recovery ($p > 0.05$), the water content at 920×*g* was higher than that at 680×*g*. This was due to the rotor design of the CINC centrifuge, which was initially designed to operate as a contactor [25, 33]. In this case, the fluid was premixed and accelerated in a circumferential direction between the housing and the spinning rotor before entering the separation zone. Increasing the rotation speed ω too high caused the fluid premixing to become too vigorous, resulting in smaller oil droplets which are more stable, causing poorer separation efficiency [33].

Table 4.4 shows the free crude oil recovery obtained from the surfactant wash and DI wash step from the best runs. At similar L/L centrifuge condition, only 44.9% peanut oil and 38.5% canola oil was recovered as free oil phase from the extracted oil - DI washing mixture versus more than 90% of free oil recovery from the extracted oil – surfactant washing mixture. This result was expected because in the oil extracted – DI washing mixture, there was much lower oil content (1 – 2 wt%), therefore, the oil in water emulsion was much more stable and harder to separate [11]. The total crude oil recovery was at 87.1 wt% for peanut oil and 85.6 wt% for canola oil, which were lower than those obtained from the batch scale [14].

Table 4.4: Free crude oil recovery at optimum conditions[a]

	Fraction of free oil recovered from SAEP[b] (wt%)	Fraction of free oil recovery from DI[b] washing (wt%)	Total free oil recovery[b] (wt%)
peanut	85.3	1.79	87.1
canola	83.9	1.75	85.7

[a] 30 minute surfactant solution extraction, 5 minute DI wash at 25°C, S/L centrifuge at 4116xg and 8 mL/min inlet flowrate, and L/L centrifuge at 680xg and 1 mL/min inlet flowrate

[b] Amount of oil extracted via Soxhlet extraction was used as the basis. Free crude oil has moisture level less than 0.25 wt% for peanut oil and 0.30 wt% for canola oil

It is worth mentioning that mechanical treatment of the oilseeds for cell wall rupture is also a critical parameter in improving the oil extraction efficiency. An approximately 50% increase in oil extraction efficiency was achieved for soybean oil when the flour size was reduced from 0.40 mm to 0.10 mm [34]. Therefore, we decided to grind the peanut to a finer size of less than 0.15 mm (mesh 120) versus the 0.21 – 0.42 mm (mesh 35 – 70) studied above to test the extraction efficiency. Table 4.5 shows the effect of particle size on total oil extracted and total free oil recovery.

Table 4.5: Effect of particle size on fraction of oil extracted and free crude oil recovery for peanut at 25°C[a]

Mesh size	Flour size (mm)	Fraction of oil extracted from surfactant wash [b] (wt%)	Fraction of free oil crude recovery efficiency[c] (wt%)
40 – 70	0.21 - 0.42	90.6	94.2
larger than 100	< 0.15	93.2	71.2

[a] Extraction condition: 30 minute surfactant wash, S/L centrifuge at 4116xg and 8 mL/min inlet flowrate

[b] Amount of oil extracted via Soxhlet extraction was used as the basis

[c] Total amount of oil in liquid fraction was used the basis; moisture level is less than 0.25wt%

It can be seen that while grinding improved the extraction efficiency to 93.2 wt% of oil from SAEP, the free oil recovery dramatically decreased to 71 wt%. We attributed this result to the effect that excessively fine grinding will produce smaller oil globules, causing more stable emulsions which are harder to break [12]. Recently, Lamsal et al. studied a mechanical treatment of oilseeds, where by flaking the oilseeds first and then extruding the flakes, they could enhance the oil extraction efficiency without causing stable emulsions. While this could avoid the formation of stable emulsions, it also denatured the proteins due to the high temperature of the extruding process. This method can be employed in the case where protein recovery is not an important parameter.

4.4 CONCLUSION

In conclusion, we have demonstrated that a semi-continuous pilot scale system of aqueous surfactant enhanced vegetable oil extraction was able to achieve a total oil extraction efficiency similar to that obtained from batch scale [14] after aqueous surfactant and DI washing steps (25°C). However, the total crude oil recovery was at 87.1 wt% for peanut oil and 85.6 wt% for canola oil, which were lower than those obtained from batch scale. The S/L and L/L separation steps are critical parameters in oil extraction by SAEP, EAEP and AEP. Further free oil recovery from the skim of the L/L centrifuge outlet is very challenging. It will be worth studying the effect of SAEP on vegetable oil extraction of extruded flakes, in which the proteins were denatured, resulting in less stable emulsion problems. It is also worth studying the de-emulsification efficiency of extracted oil – surfactant solution mixture at higher temperatures, which was not within the scope of this study. Compared to other AEP processes, the SAEP process is very competitive because it achieves oil extraction efficiency at 25°C similar to other AEP methods at 50–70 °C in a reasonable time frame (30 minutes).

The scope of this study is to evaluate the pilot scale process of vegetable oil extraction by aqueous-surfactant based process. Protein recovery from this process should be investigated in the future research to evaluate the economic feasibility of this technology. Protein recovery from aqueous-based method has been reported to have superior quality to that recovered from hexane-based process [23] and can be used in human consumption which has a higher market value compared to the protein produced from hexane extraction process which can only be used for cattle consumption. Similar to other aqueous-based process, the adaption of this technology was motivated by environmental issues. The vegetable oil extraction industry has contributed the primary VOC emissions in the food industry [3]. The annual hexane loss in the soybean oil extraction process alone in the US could be as high as 210 – 430 million liters [3]. Although the capitol cost of the aqueous-based extraction process is relatively higher than hexane extraction process [3], the low surfactant concentrations (less than 0.5 wt%) and ambient operating condition might be advantageous compared to the hexane concentration at higher than 95 wt%. This should be further evaluated in the future research.

4.5 ACKNOWLEDGEMENTS

The authors would like to thank George Smith, Huntsman Petrochemical Corp. (Houston, TX) for providing us with the extended-surfactant samples; Gene Neuens from Producers Cooperative Oil Mill and Plains Oilseed Products Cooperative (OKC, OK) and Wayne Janzen from Prairie Gold Oil Seeds (Okeene, OK) for providing the canola seeds. Funding for this work has been provided through the Oklahoma Secretary of Energy, and the Oklahoma Center for Advancement of Science and Technology (OCAST). Partial support was provided by industrial sponsors of the Institute for Applied Surfactant Research at the University of Oklahoma: Akzo Nobel, Clorox, Conoco/Phillips, Church and Dwight, Ecolab, Halliburton, Huntsman, S.C. Johnson & Son, Oxiteno, Procter & Gamble, Sasol North America, Shell Chemical, and from Dr. Sabatini's Sun Oil Company endowed chair and Dr. Harwell's Conoco/Dupont endowed professorship. Brittany Pritchett and Nicole Rowlette are acknowledged for experimental assistance.

REFERENCES

---

1. N- Hexane Substance Technical Guidelines (accessed in May 2008). <http://ehs.ucsc.edu/lab_research_safety/pubs/facts/Hexane.pdf>
2. Juliano BO (1985) Rice: Chemistry and Technology, 2nd edn, The American Association of Cereal Chemists, Minnesota. pp 647 – 687
3. Rosenthal A, Pyle DL, Niranjan K (1996) Aqueous and Enzymatic Processes for Edible Oil Extraction. Enzyme and Microbial Technology 19: 402 – 420.
4. Hagenmaier R, Cater CM, Mattil KF (1972) Critical Unit Operation of the Aqueous Processing of Fresh Coconuts. J Am Oil Chem Soc 49: 178-181.
5. Rosenthal A, Pyle DL, Niranjan K (1998) Simultaneous aqueous extraction of oil and protein from soybean: mechanisms for process design. Trans Inst Chem Eng Part C 76: 215 -218.
6. Kim SH (1989) Aqueous Extraction of Oil from Palm Kernel. J Food Sci 54, 2:491-492.
7. Cater CM, Rhee KC, Hagenmaier RD, Mattil KF (1974) Aqueous extraction – an alternative oilseed milling. J Am Oil Chem Soc 51: 137-141.
8. Sharma A, Khare SK, Gupta MN (2002) Enzyme-assisted aqueous extraction of peanut oil. J Am Oil Chem Soc 79(3): 215 – 218.

9. Johnson LA, Lusas EW (1983) Comparison of alternative solvents for oils extraction. J Am Oil Chem Soc 60: 229 – 242.
10. Embong MB, Jelen P (1977) Technical feasibility of aqueous extraction of rapeseed oil – a laboratory studies. J Inst Can Sci Technol Aliment 10: 239 – 243.
11. Moura JMLN, Almeida NM, Johnson LA (2009) Scale-up of Enzyme-Assisted Aqueous Extraction Processing of Soybeans. J Am Oil Chem Soc 86: 809 – 815.
12. Lamsal BP, Murphy PA, Johnson LA (2006) Flaking and extrusion as mechanical treatments for enzyme-assisted aqueous extraction of oil from soybeans. J Am Oil Chem Soc 83, 11: 973 – 979.
13. Campbell KA, Glatz CE. (2009) Mechanisms of Aqueous Extraction of Soybean Oil. J Agric Food Chem 57: 10904 – 10912.
14. Do LD, Sabatini DA (2010) Aqueous Extended-Surfactant Based Method for Vegetable Oil Extraction: Proof of Concept. J Am Oil Chem Soc 87: 1211 – 1220.
15. Rosen MJ (1989) Surfactants and Interfacial Phenomena. 2nd edn, John Wiley & Sons, Canada. pp 229 – 235
16. Sharma A, Khare SK, Gupta MN (2002) Enzyme-assisted aqueous extraction of peanut oil. J Am Oil Chem Soc 79(3): 215 – 218.
17. Moreau RA, Dickey LC, Johnston DB, Hicks KB (2009) A Process for Aqueous Enzymatic Extraction of Corn Oil from Dry Milled Corn Germ and Enzymatic Wet Milled Corn Germ (E-Germ) J Am Oil Chem Soc 86: 469 – 474.

18. Nasuk A, Sabatini DA, Tongcumpou C (2009) Microemulsion-based palm kernel oil extraction using mixed surfactant solutions. Industrial Crops and Products 30(2): 194 – 198.

19. Do LD, Withayyapayanon A, Harwell JH and Sabatini DA (2009) Environmentally Friendly Vegetable Oil Microemulsions Using Extended Surfactant and Linkers J Surf Deterg 12(2): 91 – 99

20. Childs JD, Acosta E, Scamehorn JF, Sabatini DA (2005) Surfactant-enhanced treatment of oil-based drill cuttings. J Energy Resouce Technol 207(2): 153 – 162.

21. Rhee KC, Cater CM, Mattil KF (1973) Aqueous Process for Pilot Plant-Scale Production of Peanut Protein Concentrate. J Food Sci 38: 126 – 128.

22. McCurdy SM (1990) Effects of processing on the functional properties of canola/rapeseed protein. J Am Oil Chem Soc 67(5): 281 – 284.

23. Carr RA (1997) Oilseed Processing. In: Wan PJ, Wakelyn PJ (Eds.) Technology and Solvents for Extraction Oilseeds and Nonpetroleum Oils. AOCS Press, Champaign, pp 101 – 120.

24. Lavin Centrifuge. Model L2. < http://www.lavincentrifuge.com/products/l2.html>.

25. CINC Centrifuge. Model V02.

<http://www.cincmfg.com/Model_V02_Centrifuges_s/29.htm>.

26. Official Method of Analysis of the Association of Official Analytical Chemists, 16th edn, AOAC International, Gaithersburg, MD (1995).

27. Mattil KF, Norris FA, Swern D(1964) Extraction of Fats and Oils. Bailey's Industrial Oil and Fat Products, 3rd edn., John Wiley & Sons, London: pp 637–717.

28. Lynch JM, Barbano DM, Fleming JR (1997) Modification of Babcok Method to Eliminate Fat Testing Bias Between Babcock and Ether Extraction Methods (Modification of AOAC Official Methods 989.04 and 995.18): Collaborative Study. J AOAC Int 80(4): 907 -940.

29. Anlauf H (2007) Recent developments in centrifuge technology. Separation and Purification Technology 58: 242 – 246.

30. Sanders TH (2002) Groundut (Peanut) Oil. In: Gunstone FD (Ed.) Vegetable Oils in Food Technology: Composition, Properties and Uses. CRC Press, Blackwell Publishing, USA/Canada, pp 231 – 244.

31. Przybylski R, Mag T (2002) Canola/Rapeseed Oil. In: Gunstone FD (Ed.) Vegetable Oils in Food Technology: Composition, Properties and Uses. CRC Press, Blackwell Publishing, USA/Canada, pp 98 – 124.

32. Nour AH, Mohammed FS, Yunus RM, Arman A (2009) Demulsfication of Virugin Coconut Oil by Centrifugation Method: A Feasibility Study. Int J Chem Technol 1(2): 59 – 64.

33. CINC Centrifuge. How it works.
< http://www.cincmfg.com/How_our_Centrifuges_Work_s/108.htm>.

34. Rosenthal A, Pyle DL, Niranjan K (2001) Simultaneous aqueous extraction of oil and protein from soybean: Mechanisms for process design. Trans Inst Chem Eng Part C 76: 224 – 230.

Chapter 5 Algae, Canola or Palm Oils – Diesel Microemulsion Fuels: Phase Behaviors, Viscosity and Combustion Properties[1]

ABSTRACT

Vegetable oils (VG) are being considered as a renewable energy alternative for diesel. The high viscosity of VG causes injector operation and durability problems in compression-ignition engines. To alleviate this microemulsification can be considered as a simple method for reducing vegetable oil viscosity without the complex chemical transformation processes such as transesterification, which also produce undesirable byproducts such as glycerol. The goal of our work is to formulate reverse micellar microemulsions (ME) of vegetable oils and No 2 diesel (DF) blend with ethanol using different combinations of surfactant and co-surfactants. Ethanol, also a renewable fuel, was used as a viscosity modifier. We studied three VGs to blend with DF: canola, palm and algae oils. The ME fuels were tested for temperature stability, viscosity, water tolerance and their combustion performance in terms of flame radiation and pollutant (CO, NOx) emissions. With appropriate surfactant and co-surfactant systems, we were able to formulate canola and algae/diesel blend ME fuels with cloud points and pour points that satisfy the ASTM standards. Among all formulations, palm/diesel ME fuels

---

[1] This work or portions of thereof is the collaboration work with Mechanical Engineering Department and will be submitted to International Journal of Green Energy

solidified at 6 – 6.5°C due to high saturated triglyceride content. While the formulated ME fuels had approximately 10% lower heating value than DF, their CO emission and flame radiation were superior to those of DF. NO_x emissions also were lower with the blends containing no nitrate additives, but were higher than with DF in the presence of nitrate additives. Thus, these results show that microemulsification is a viable technology for producing biofuels with desirable viscosity and that fuel properties can be adjusted via formulation variables without chemical processes.

Keyword: Algae, palm, canola, biofuels, microemulsions, combustion test, phase behaviors, emissions, viscosity

5.1 INTRODUCTION

Due to increasing energy demands and a desire to reduce our dependence on petroleum fuels, research on alternative fuels has received increased attention. The proposed US renewable fuels initiative targets increasing the domestic supply of alternative fuels to 36 billion gallons by 2022 [1].Trucks and agricultural vehicles are typically operated with diesel fuel. In 1909, Rudolf Diesel ran a diesel-powered car using peanut oil for the first time [2]. Since then many research studies have focused on the use of vegetable oils as an alternative fuel. Research has shown that vegetable oils can be used as an alternative to diesel fuel. Vegetable oil contains primarily triglycerides, the triacylglyceryl esters of various fatty acids with glycerol. Vegetable oils are becoming more attractive as alternative fuels since they have similar energy content to diesel fuel and they are renewable, non-toxic and environmentally carbon neutral [3]. However, vegetable oils have high viscosities, low volatilities and often freeze at low temperature.

Due to their high viscosities, long-term use of pure vegetable oils causes engine problems such as coking of injector nozzles, sticking of piston rings, and lubricating oil contamination [4]. These disadvantages inhibit the use of vegetable oil as a direct substitute for diesel. In order to overcome the problem of high viscosity, four possible solutions have been proposed, including: dilution (or blending) of vegetable oils with diesel fuel, transesterification of vegetable oils to fatty methyl esters (FAMES) or biodiesels, microemulsification of vegetable oils and pyrolysis [4].

The simplest method to reduce viscosity is the dilution method which involves the direct blending of vegetable oils with diesel fuel. Although dilution decreases the viscosity, these fuels have similar problems to that of neat vegetable oils such as coking of injector nozzles, sticking piston rings and lubricating oil contamination [4]. Dilution of vegetable oils with diesel also shows no appreciable decrease in the pour point compared to neat vegetable oils [5]. Pour point, defined as the lowest temperature at which the fuel will flow, is a very important property of fuel, particularly in cold climate conditions. The use of vegetable oil blended with diesel fuel is limited because of this problem. Another way to reduce vegetable oil viscosity is by pyrolysis [6,7]. The pyrolysis method is the thermal degradation of vegetable oils to deoxygenate them and obtain an enriched diesel-like hydrocarbon product [6]. The drawback of this method is that it is very hard to control the product quality. The reaction might not be complete, resulting in undesirable products such as tri-, di-, and mono-glycerides. The products can also have a wide range of hydrocarbons that might require additional reactions [7]. Further, the viscosity of pyrolyzed soybean oil was found to be 10.2 cSt at 38^{o}C, which exceeds the specified value of 4.1 cSt for diesel fuel [8].

Transesterification of vegetable oils to biodiesel is by far the most widely studied approach to reduce viscosity [9]. Biodiesel is formed by the transesterification of triglycerides with alkyl alcohols in the presence of a basic or acidic catalyst to produce alkyl esters and glycerol. Biodiesel has many fuel properties comparable to No. 2 diesel fuel such as kinematic viscosity, specific gravity, cetane number and gross heat of combustion. However, biodiesel also has many drawbacks; it has a higher cloud point and pour point than those of the parent oils [10], limiting the use of biodiesel in cold environments. Cloud point is defined as the temperature at which the fuel becomes cloudy due to the formation of crystals which can clog fuel filters and supply lines. As mentioned above, pour point is the lowest temperature at which the fuel can flow by itself. For example, the cloud point of methyl soyate is 15-20^{o}C which is higher than that of No. 2 diesel fuels; therefore, only a blend of less than 10% of methyl soyate with No. 2 diesel can tolerate low temperature conditions [3]. In addition, there is evidence showing that combustion of methyl esters increases the nitrogen oxides (NO_x) in the exhaust emissions [11]. Another major drawback of biodiesel is the production cost. It is reported that it costs up to 5 times more (before taxes) to produce methyl soyate than petroleum-based fuels [3].

Microemulsification, the method of interest in our research work, is another way to reduce vegetable oil viscosity. While this method offers many advantages, it has received only limited research attention. The microemulsification method involves mixing two immiscible fluids, which are a low molecular weight alcohol with a vegetable oil-diesel mixture, to reduce the vegetable oil viscosities using surfactants to stabilize the mixture [4]. By definition, microemulsions are thermodynamically stable dispersions of oil and water stabilized by a film of surfactant [12]. These fuels appear isotropic [12] because of the small size of the equilibrium reverse micelles (10 to 100 nanometers). The advantages of the microemulsification method include low production costs, simple and easy implementation, no engine modification requirement, and no chemical reactions. Although there is a slight loss in heating value for microemulsion fuels, microemulsion fuels incorporating ethanol have shown lower combustion temperature, resulting in a drastic reduction in the emissions of thermal NOx, CO, as well as black smoke and particulate matter [13].

There are very limited number of studies on vegetable oil/diesel-based microemulsion fuels in the literature. Only some systems containing water-monoglycerides (or triglycerides) have been studied [12,14]. Dantas et al. [14] demonstrated the feasibility of forming reverse micelle microemulsions of alcohols and water with different ratios of vegetable oil/diesel mixtures using coconut fatty acids diethanol-amide (Comperlan SCD) and sodium lauryl sulfate (Texapon HBN) at 25°C. However, no further microemulsion fuel properties, such as viscosity or temperature stability, have been studied.

The overall goal of our work is to formulate reverse micelle microemulsions containing a vegetable oil/diesel blend with ethanol which can be used as an alternative fuel to neat diesel fuels. To achieve this goal, three specific objectives were pursued: (1) to formulate reverse micellar microemulsion fuels with a good temperature stability, (2) to study the viscosity of the formulated microemulsion fuels, and (3) to evaluate combustion properties of selected stable microemulsion fuels. In this research work, we studied three different types of triglyceride oils, including canola oil, palm kernel oil and algae oil (Liminaria Digita species). To date, the authors have not found a publication reporting the phase behavior or combustion properties of algal-based microemulsion fuels. In this work, oleyl alcohol and oleyl amine were chosen as the main surfactants. Fatty surfactants are hydrophobic; therefore, they can be used to formulate reverse micellar microemulsions according to Winsor premises [12]. In addition, fatty surfactants can be produced from renewable sources and have 90% energy content of diesel fuels, making them attractive to use [15]. In this work, we combined the fatty surfactant(s) with fuel improving co-surfactants. These include 2-ethylhexylnitrate and 2-ethylhexanol, 1-octanol, and ethylene glycol butyl ether as cetane enhancers and/or anti-freezing additives.

5.2 MATERIALS AND METHODS

5.2.1 Materials

Oleyl alcohol (OA, 85% active), oleyl amine (OAM, 70% active), 2-ethylhexylnitrate (EHN, 99%), 2-ethylhexanol (EHL, 99.6%) and ethylene glycol butyl ether (EGBE) were purchased from Sigma Aldrich (City and State). 1-Octanol (OCT, 99%) was purchased from Fischer Scientific (Fair Lawn, NJ). Ethyl alcohol (200 proof, absolute anhydrous) was purchased from PHARM-AAPER (Brookfield, CT). All materials were used as received. Properties of surfactant and co-surfactants are shown in Table 5.1.

Table 5.1: Properties of studied surfactant and co-surfactants[a]

Materials	Assigned symbol	Molecular formula	Molecular weight (g/mole)	Density (g/mL)	Melting point (°C)
oleyl alcohol	OA	$C_{18}H_{36}O$	268.5	0.849	0 - 5
oleyl amine	OAM	$C_{18}H_{37}N$	267.5	0.813	18 - 26
2ethylhexanol, isooctanol	EHL	$C_8H_{18}O$	130.2	0.833	-76
2ethylhexylnitrate	EHN	$C_8H_{17}NO_3$	175.2	0.963	< -45
n-octanol	OCT	$C_8H_{18}O$	130.2	0.827	-15
ethylene glycol butyl ether	EGBE	$C_6H_{14}O_2$	118.2	0.902	-75

[a]Data provided by the manufacture

Crisco® pure canola oil (The J.M Smucker Company, Orrville, OH) was purchased from Walmart (Norman, OK). Refined palm kernel oil was purchased from Mountain Rose Herbs (Eugene, OR) and algae oil (>99%) of Liminaria Digita species was purchased from Pure Spa Direct (Hicksville, NY). Fatty acid (FA) analysis of these oils is provided in Table 5.2. No. 2 Diesel fuel was purchased from a local gas station (Norman, OK).

Table 5.2: Fatty acid methyl ester (FAME) composition of studied oils[a]

Fatty acid		**MW** (g/mole)	**Palm Kernel** % molar	**Canola** % molar	**Algae** % molar
Caprylic	C8:0[b]	144.21	1.89	-	-
Capric	C10:0	172.27	7.15	-	0.12
Lauric	C12:0	200.32	48.04	-	0.25
Myristic	C14:0	228.37	16.23	0.05	5.25
Pentadecanoic	C15:0	242.40	-	-	1.47
Palmitic	C16:0	256.43	7.46	4.00	16.25
Palmitoleic	C16:1	254.41	-	0.18	3.55
Margaric	C17:0	270.45	-	-	-
Heptadecenoic	C17:1	268.44	-	-	-
Stearic	C18:0	284.48	2.20	2.65	0.59
Oleic	C18:1	282.46	16.05	56.00	7.90
Linoleic	C18:2	280.45	-	26.00	5.35
Linolenic	C18:3	278.43	0.98	10.00	6.62
Stearidonic	C18:4	276.42	-	-	14.48
Arachidic	C20:0	312.53	-	0.46	0.16
Gadeleic	C20:1	310.52	-	0.02	-
Eicosedienoic	C20:2	308.50	-	-	3.44
Eicosatrienoic	C20:3	306.49	-	-	0.60
Arachidonic	C20:4	304.47	-	-	14.60
Eicosapentaenoic	C20:5	302.46	-	-	19.37
Behenic	C22:0	340.59	-	0.32	-
Erucic	C22:1	338.57	-	0.33	-
Lignoceric	C24:0	368.64	-	-	-

[a] Data provided by the manufacture

[b] Cx:y: x is the number of carbons; y is the degree of saturation. For example, C18:1 means that the fatty acid has 18 carbons and 1 double bond (unsaturation)

5.2.2 Methods

Vegetable oil properties

Triglyceride profiles of studied vegetable oils were predicted based on the Antoniosi Filho et al.'s method [16]. When using this method, two rules are applied. First, within the isomers, only the principal triglyceride with the highest composition is shown, and the presented percentage value is the sum of all the individual isomers [16]. For example, palmitoyl-dioleoyl-glycerol (POO) and palmitoyl-linoleoyl-stearoyl-glycerol (PLS) are isomers with the same number of carbons and double bonds (52:2). If the composition of POO is higher, the computer program will only show POO, but the percentage value shown is the sum of POO and PLS percentage composition. Second, individual triglycerides with a composition of less than 0.5% of the total were ignored from the computer program [16].

Reverse microemulsion phase behavior study

In order to formulate reverse microemulsions, the fraction of vegetable oil/diesel blend to ethanol was always kept higher than one. In order to study the effect of surfactant/co-surfactant (S/C) molar ratios and concentrations on the stability of the fuels at different temperatures, a titration method was applied in which the surfactant/cosurfactant at fixed mole ratios (4:1, 1:1, 1:4, 1:8 and 1:16) was gradually added into a 15 mL glass vial containing 5 mL of vegetable/diesel blend (50 vol%) and 2 mL of ethanol (200 proof) and then gently shaken. The choice of vegetable oil/diesel fuel blend to ethanol volumetric ratio of 5:2 was based on the viscosity of the final microemulsion fuels as discussed later in the text. Several combinations of the surfactant

(OA or OAM) with co-surfactants (EHN, EHL, EGBE and OCT) were chosen to determine the best combination. The microemulsion fuel samples were placed inside the waterbath at different temperatures (-10°C, -5°C, 0°C, 5°C, 10°C, 25°C, 30°C, 40°C, 50°C) and observed for two weeks. The microemulsion fuel samples were also placed in a freezer at -23°C for two weeks to study the phase behaviors. At each temperature, the minimum total concentration of surfactant and co-surfactant required to completely solubilize ethanol into the vegetable/diesel fuel reverse microemulsion blend was recorded. Microemulsion fuels that had the best temperature stability properties were chosen for further study.

Cloud point determination

The stable microemulsion fuels chosen from phase behavior study were tested for their cloud points (CP). The standard CP for No.2 winter diesel fuels (November, December, January and February) is -10°C max and -4°C max for No 2 summer diesel fuel (March – October) [17]. CP was determined by cooling the microemulsion fuels at 1°C intervals [18]. The temperature at which cloudiness was observed was reported as CP (ASTM method D 2500) [18].

Pour point determination

Pour point (PP) is defined as the lowest temperature at which fluid movement is still detected. It is important to note that the standard PP for No.2 winter diesel fuels (November, December, January and February) is -17.8°C max, and -9.4°C max for No 2 summer diesel fuels (March – October) [17]. PP was determined by cooling the microemulsion fuels at 3 °C intervals; the temperature at which no movement was detected when tilting the sample was reported as PP (ASTM method D 97) [18].

Effect of water on phase behavior

Since the maximum allowable water content in the No 2 diesel fuel is 0.05 vol% [17], the stable microemulsion fuels selected from above were tested for the water tolerance within this standard range. De-ionized water was added into the fuels so that the final water content in the fuels was at 0.05 vol%. The samples were placed in a freezer at -23°C and observed for phase separation.

Viscosity study

The dynamic viscosity of microemulsion fuels was measured using a Brookfield LV III+ viscometer adapted with a Brookfield small sample adapter (SSA). The SSA consisted of a chamber-spindle set (Brookfield, SC4-18/13R) with a water-jacket connecting to a circulating temperature bath (MGW LAUDIA, model S – 1). 6.7 mL of microemulsion fuel sample (recommended by the manufacture) was transferred into a viscometer chamber and the spindle rate was set at 30 rpm. The dynamic viscosity was recorded when the temperature stabilized at the desired value . The kinematic viscosity was calculated by dividing the dynamic viscosity by the microemulsion fuel density. The impact of the fraction of vegetable oil to diesel, ethanol, surfactant and co-surfactant, and water in the blend on the viscosity of the microemulsion fuels was studied. The temperatures were varied from -4°C to 40°C. For No 2 diesel fuels, the standard viscosity at 40°C is 1.9 – 4.1 cSt [17]. Microemulsion fuels that have the best temperature stability and viscosities within the range of required standard values were chosen for combustion/emission study.

Combustion Test Setup

The aforementioned microemulsion fuels were tested in laminar flame configuration for their global emissions (NOx, CO) and global radiation. This technique developed by Love et al. [19,20] yields combustion properties that are attributable to only to the fuel chemical structure on a relative basis. The parameters studied include the effect of different additive formulations, vegetable oil type, vegetable oil to diesel fraction in the blend, and total surfactant and co-surfactant concentrations.

Figure 5.1 shows the schematic diagram of the combustion experimental setup, which is identical to that of Love et al. [19,20]. Air (a mixture of oxygen and nitrogen at molar ratio of 1 to 3.76) was introduced into a preheated pipe through a calibrated flowmeter. The air was heated to 410^{o}C using high-temperature heating tapes wrapped around the pipe. At this temperature, the microemulsions fuels were completely vaporized.

The liquid fuel was injected at 1.6 mL/min into the preheated gas mixture using a compact infusion pump (Havard Apparatus, Model 975). The air temperature in the pipe and fuel vapor-gas mixture temperature at the burner exit were monitored and maintained using K-Type thermocouples connected to proportionate controllers.. The vaporized fuel was ignited using a propane pilot flame, which was removed after ignition. For this study, the equivalence ratio, the ratio of the fuel-to-oxidizer ratio $\left(F/A\right)_{actual}$ to the stoichiometric fuel-to-oxidizer ratio $\left(F/A\right)_{ST}$, was fixed at 7. This value for the equivalence ratio was chosen so that the flame would be laminar, attached to the burner, and simulate the gas-phase combustion regions in diesel engines. [20].

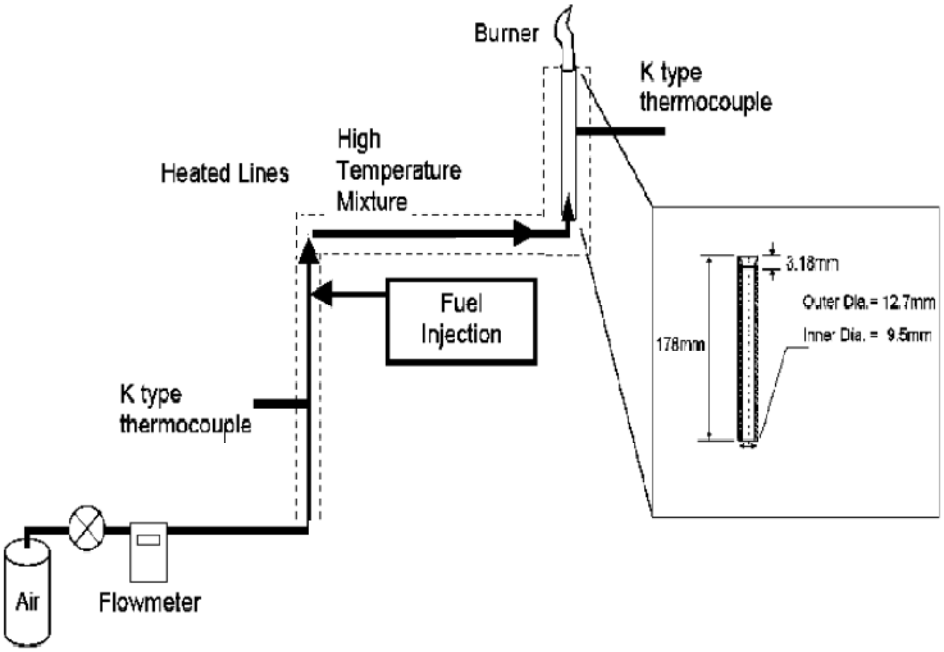


Figure 5.1: Schematic diagram of the combustion experiment set-up. Adapted from reference [19]

Flame imaging

Visible flame images were taken using a digital camera (EOS Digital Rebel XT/EOS 350D). The images were captured under room lighting with a dark background.

Global flame radiation

The method for measuring the flame radiation was previously described in detail elsewhere [19,20]. Although the radiation emitted from a flame may be attributed to the gases CO_2, and H_2O, and solid soot particles, at the conditions of the present experiments the main contributor would be the latter [21]. Thus, flame radiation can also be considered as a good indicator of soot concentration in the flame. A quick method to compare the soot emission of microemulsion fuels relatively to No. 2 diesel fuels can be through radiative heat fraction (F) which is defined in Equation (5.1) [19,22,23]:

$$F = \frac{\bar{q}''_{\mathrm{mod}} \times 4\pi L^2}{m_{fuel} \times LHV_{fuel}} \qquad \text{(Equation 5.1)}$$

where F is ratio of the radiative heat transfer to the total energy content of the fuel consumed in the flame, $\bar{q}''_{\mathrm{mod}}$ is the time integrated heat flux due to radiation from the burning fuel incident on the radiometer, L is the distance from the radiometer to the flame, m_{fuel} is the mass of fuel that is injected into the setup, and LHV_{fuel} is the lower heating value of the fuel injected. The lower heating value of individual components in the microemulsion fuels was calculated using the Mendeleyev's formula [24], and the lower heating value of the blend was calculated using the method adapted from reference [25].

Global pollutant emissions

The global emissions of NO_x and CO of microemulsion fuels were investigated. The setup and method for this study were previously reported [19,20]. The emission index, which is the mass of pollutant released per unit mass of the fuel burnt, is calculated using Equation (5.2):

$$EI_i = \frac{X_i}{(X_{CO_2} + X_{CO})} \times \left(\frac{N \times MW_i}{MW_f} \right) \qquad \text{(Equation 5.2)}$$

where EI_i (grams of pollutant/kilogram of fuel burnt) is the emission index of species i; MW_i and MW_f are the molecular weight of species i and the microemulsion fuels, respectively; X_i, X_{CO2} and X_{CO} are the mole fraction of species i, CO_2 and CO, in the combustion products respectively; and N is number of carbon atoms of the microemulsion fuels. It was assumed that when burning the microemulsion fuels, all carbon appeared as CO and CO_2 in the flame exhaust. Given that tested flames were not liberating black smoke, there was no solid carbon deposit on the sample collector, and the amount of carbon radical concentration level was in parts per million, this assumption is justified [19].

5.3 RESULTS AND DISCUSSIONS

5.3.1 Vegetable oil properties

Figure 5.2 shows the estimated triglyceride composition profile of canola, palm and algae oils with the x-axis representing the number of carbons in the triglyceride, followed by the degree of unsaturation (Cx:y).

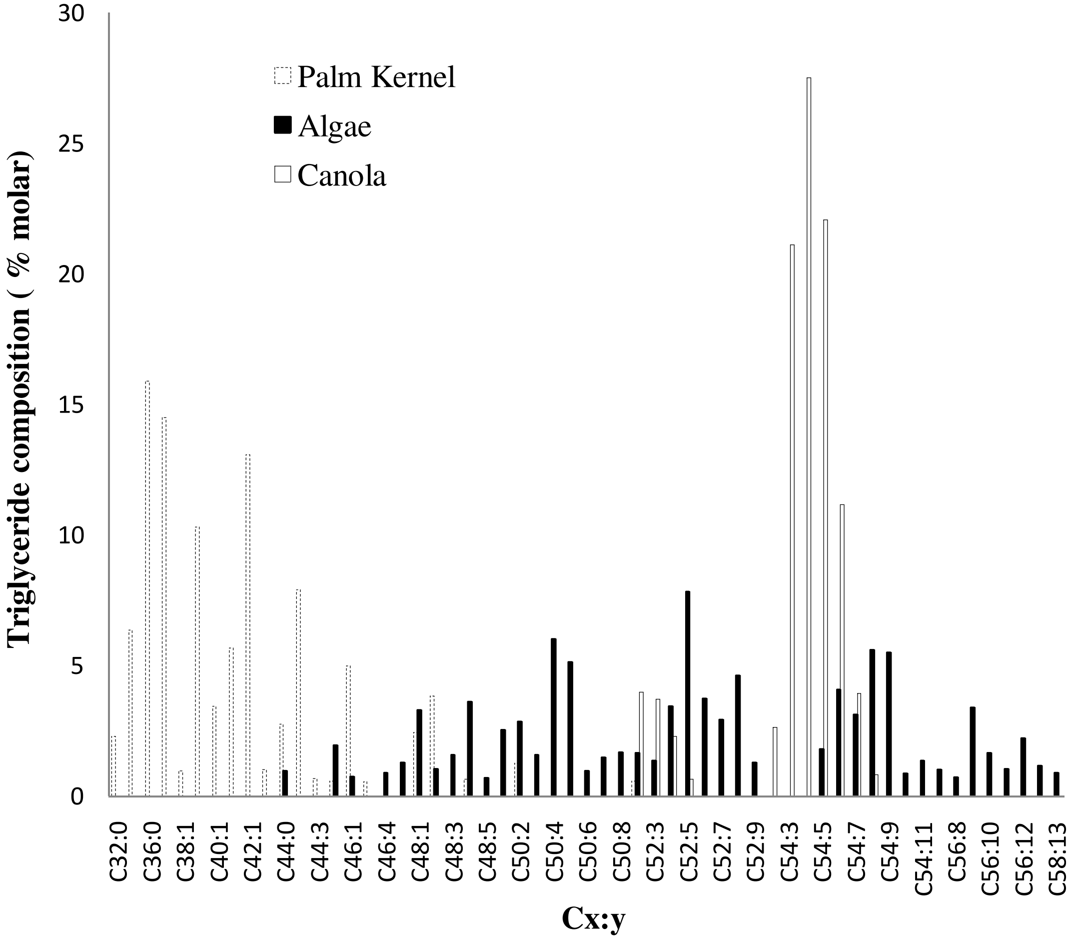


Figure 5.2: Triglyceride profile of studied oils. The y-axis is the %molar composition and x-axis is the triglyceride structure (Cx:y means #carbon : degree of unsaturation)

The triglyceride profile of the vegetable oils shows a very interesting distribution. Palm oil has higher saturated triglyceride and relatively lower alkyl chain length, with the dominant triglycerides having carbon numbers ranging from 32 to 48. Canola oil has relatively higher unsaturated triglycerides and relatively higher alkyl chain length, with the dominant triglycerides having carbon numbers ranging from 50 to 54. Algae oil has mostly unsaturated triglycerides with the triglyceride profile being spread over carbon numbers range from 44 to 58. The triglyceride profile is in agreement with the physical state of the studied oils. At 25°C palm oil is in solid phase due to its high content of saturated triglycerides, whereas canola and algae oils are in liquid phase due to their high content of unsaturated triglycerides. The viscosities at 40°C of canola, palm and algae oils were 37, 30.4 and 12.6 cSt, respectively, which is consistent with their corresponding triglyceride profile, since the viscosities of vegetable oils generally decrease with the increasing degree of unsaturation and decreasing alkyl chain length [26]. Based on their triglyceride profiles, the molecular weights were estimated to be 880 g/mole for canola, 756 g/mole for palm, and 848 g/mole for algae oil with the corresponding molecular structures: $C_{56.8}H_{101.3}O_6$ for canola, $C_{43.5}H_{81.8}O_6$ for palm, and $C_{54.8}H_{91.4}O_6$ for algae oils. The predicted molecular weights and molecular structures are in agreement with data published in the literature [27,28]. These values were subsequently used for the calculation of microemulsion fuel properties.

5.3.2 Microemulsion phase behavior study

Effect of surfactant to co-surfactants mole ratio on the microemulsion phase behaviors

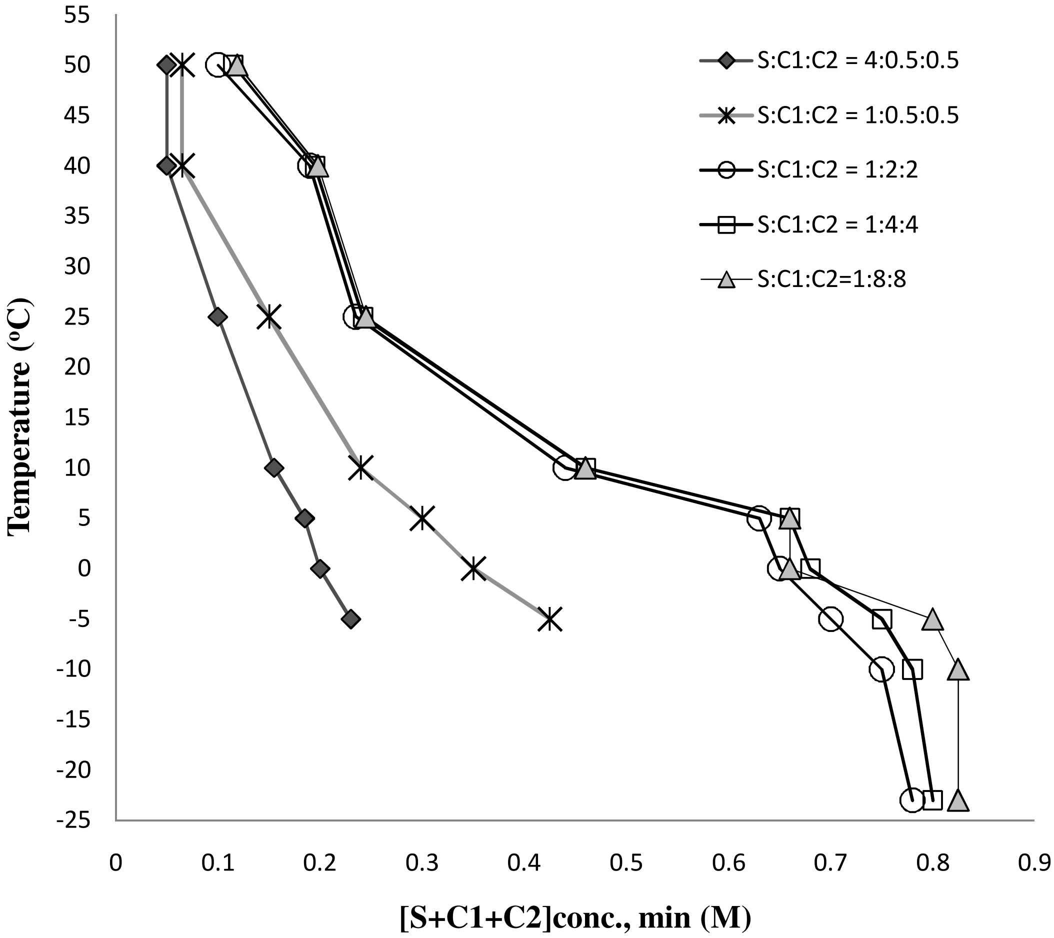


Figure 5.3: Effect of OA(S): EHL(C1): EGBE(C2) mole ratio on the phase behaviors of canola/diesel/ethanol microemulsions at different temperature. Canola/diesel blends at equal volumetric ratio. Oil phase was 5 mL and ethanol was 2 mL. See Table 5.1 for abbreviations. For system S:C1:C2 at 4:0.5:0.5 and 1:0.5:0.5, gel formation was observed at temperature below $-5^{o}C$

Figure 5.3 shows the effect of surfactant (S) to co-surfactant (C1, C2) mole ratio on the phase behavior of canola oil/diesel/ethanol microemulsions at temperatures ranging from -23°C to 50°C. System at S:C1:C2 = 4:0.5:05 means that the mole ratio of S to C1 and C2 are both 4:0.5. Formulations shown in this figure are comprised of OA as the surfactant, EHL and EGBE as co-surfactants. The x-axis shows the minimum total molar concentrations of surfactant and co-surfactants required to completely solublize 2 mL of ethanol in 5 mL of vegetable diesel blend at 50 vol% at each studied temperature. This means that to the right of the boundary, the microemulsion phase is homogenous, and to the left of the phase boundary two separate phases exist. From the figure, it can be seen that as the surfactant fraction in the mixture decreases at a fixed temperature (e.g., 4:0.5:0.5 to 1:8:8), higher total surfactant and co-surfactant concentration is required to obtain a homogenous phase. This trend is expected since decreasing surfactant to co-surfactant mole ratios decreases the amount of surfactant to make reverse micelles, thereby reducing the solublizing power.

Regarding the effect of temperature on phase behaviors, a general trend was observed for all systems; when decreasing the temperature, higher amount of surfactant and co-surfactants were needed to solublize the ethanol into the oil blend. An explanation for this phase behavior is that when the temperature decreases, the ethanol becomes more hydrophilic and tends to separate from the oil phase, which was also observed for ethanol/diesel blend systems [29]. Higher amounts of surfactant in reverse micelles are required to solublize the same amount of ethanol into the reverse micellar core at lower temperature. For systems having S:C1:C2 ratio at 4:0.5:0.5 and 1:0.5:0.5, the phase boundaries stopped at temperature at -5°C because below this temperature, gel phases were experienced due to crystallization of the surfactant; this type of separation is also known as Type I separation [29]. Type II separation occurs when the microemulsion phase is separated into two phases upon decreasing temperature [29]. Systems of S:C1:C2 mole ratio at 1:2:2, 1:4:4 and 1:8:8, show great temperature stability over the studied temperature range. The surfactant effect of phase behaviors becomes less pronounced when the number of co-surfactant moles exceed those of the surfactant. Decreasing the oleyl alcohol content to that of the co-surfactants reduces the heating value of the resulting microemulsion fuels. Therefore, among the last three systems, formulation with S:C1:C2 mole ratio at 1:2:2 was chosen for further study.

Effect of vegetable oil type on microemulsion phase behavior

Figure 5.4 shows the effect of vegetable oil type (canola, palm, and algae) on the microemulsion phase behavior at different temperatures. The surfactant/co-surfactant system is OA/EHL/EGBE at mole ratio of 1:2:2. The vegetable/diesel blend was 5 mL and mixed at equal volumetric ratio; the ethanol volume was fixed at 2 mL. The effect of temperature on all of the microemulsion phase behaviors on all systems were similar to the trend observed above, in which higher total surfactant and co-surfactant concentrations were required at lower temperature to completely solubilize the same amount of ethanol into the vegetable/diesel oil phase.

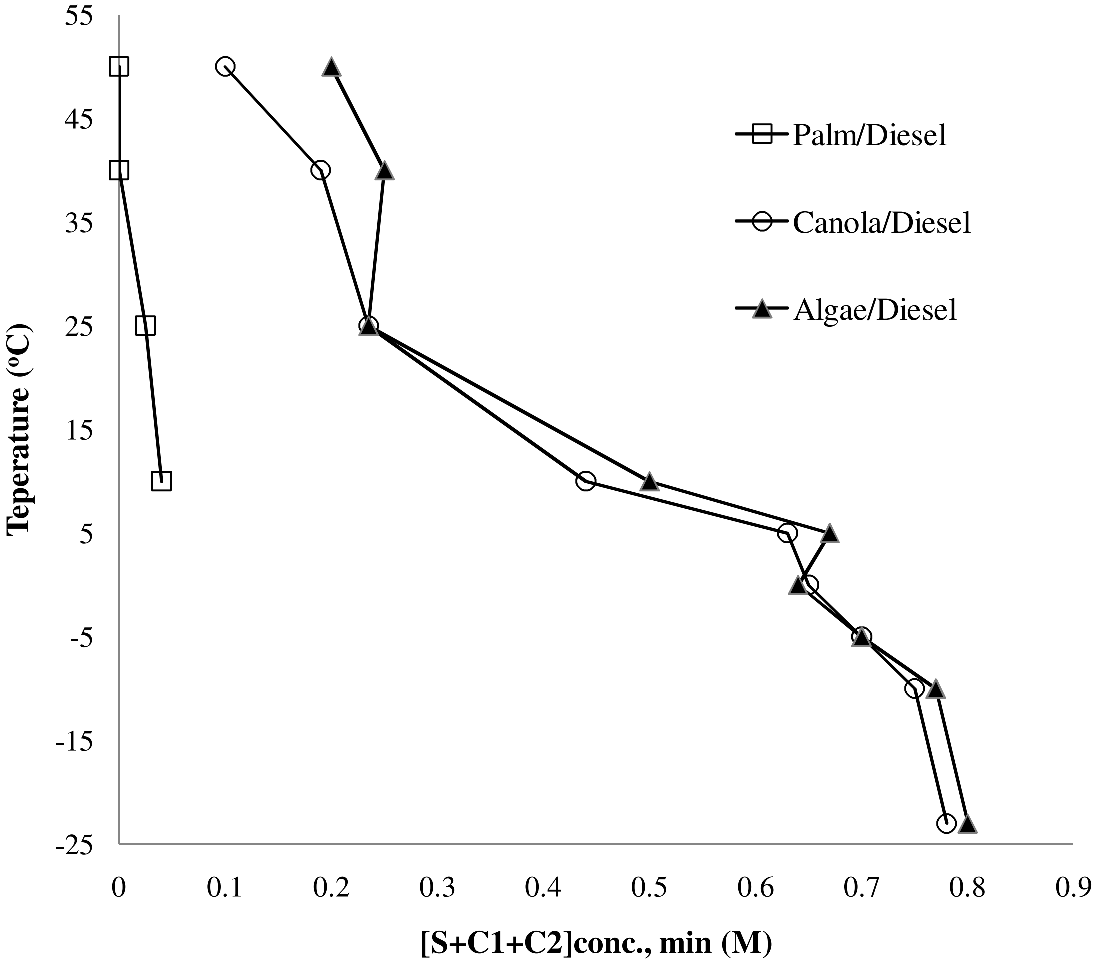


Figure 5.4: Effect of vegetable oil type on microemulsion phase behaviors of OA(S): EHL(C1): EGBE(C2) (mole ratio at 1:2:2)Vegetable oil/diesel blends at equal volumetric ratio. Oil phase was 5 mL and ethanol was 2 mL. Gel formation was observed for palm/diesel blend microemulsions at temperature below 6.5°C. See Table 5.1 for abbreviations.

From Figure 5.4, it can be seen that at temperatures above 40°C, the palm/diesel blend is completely miscible with ethanol. This supports the explanation of the ethanol affinity towards the oil phase at higher temperature as discussed above. In comparison, among the three types of studied oil blends, the palm/diesel blend microemulsions required the lowest total surfactant and co-surfactants to solubilize the same amount of ethanol . The palm oil has the lowest average alkyl chainlength which makes the oil blend relatively more hydrophilic. However, gel formation was observed for the palm/diesel blend microemulsions at relatively high temperature (6.5°C) due to the high saturation content in the palm oil. Palm oils are generally produced in tropical countries (i.e. Malaysia, Thailand, Vietnam, etc), where the temperature is rarely less than 10°C for most of the time in the year; therefore, the formulated diesel/palm microemulsion fuels can be implemented in these countries. From Figure 5.4, it can be seen that canola and algae/diesel blend microemulsions have superior temperature stability (no gel phases observed).

Cloud point and pour point of selected microemulsion fuels

Table 5.3 represents the cloud point and pour point of selected microemulsion fuels. In all formulations, the S:C1:C2 mole ratio was fixed at 1:2:2, and the total surfactant and co-surfactant concentration was 0.82 - 0.84 M or 13.94 - 15.49 wt%.

Table 5.3: Cloud point and pour point of selected microemulsions:

MF[a]	**S/C1/C2**[b]	**Total conc. (M)**	**Total conc. (wt%)**	**Vegetable oil type in the blend**[c]	**CP**[e] **(°C)**	**PP**[f] **(°C)**
1	OA/EHL/EGBE[d]	0.83	14.9	canola	-11	<-23
2	OAM/EHL/EGBE	0.83	14.0	canola	-5	-16
3	OA/OCT/EGBE	0.83	14.9	canola	-10	<-23
4	OAM/OCT/EGBE	0.83	13.9	canola	-6	-13
5	OA/EHN/EGBE	0.84	15.0	canola	-10	<-23
6	OAM/EHN/EHL	0.82	15.5	canola	-8	-17
7	OA/EHL/EGBE	0.83	14.9	algae	-11	<-23
8	OA/OCT/EGBE	0.83	14.9	algae	-10	<-23
9	OA/EHL/EGBE	0.83	14.9	palm	6.5	6.0

[a] Assigned microemulsion fuel#

[b] S:C1:C2 mole ratio at 1:2:2

[c] Fraction in the vegetable/diesel blends at 50 vol%

[d] See Table 5.1 for abbreviations

[e] CP standard for No 2 diesel fuel is -10°C max (November - February) and -4°C max (March – October)

[f] PP standard for No 2 diesel fuel is-17.8°C ma (November – February) and -9.4°C max (March – October)

Two general trends were observed. In all microemulsion fuels, the cloud point (CP) is lower than the pour point (PP) and the CP and PP are higher in microemulsion fuels comprised of OAM. Because OAM has higher melting point than OA (see Table 5.1), this trend is expected. Microemulsion fuels (MF)1,3,5,7,8 have superior quality that meet the standard CP and PP requirement of winter No. 2 diesel fuels (see Table 5.3 for requirements), and all microemulsion fuels in Table 5.2 but MF9 meet the standard CP and PP requirement for summer No. 2 diesel fuels [17].

Effect of water on phase behavior

Up to 0.05 vol% of water was added into the microemulsion fuels at 25^{o}C. No separation was observed for any of the microemulsion fuels in Table 5.3, indicating great water tolerance of the formulated microemulsion fuels. The water tolerance of these microemulsion fuels are superior to those of EB-diesel microemulsions [29], in which phase separation occurred instantly upon the addition of water.

5.3.3 Microemulsion fuel viscosity study

Effect of ethanol on microemulsion fuel viscosity

Figure 5.5 illustrates the effect of ethanol content on the viscosity of the formulated microemulsion fuels for canola/diesel, algae/diesel, and palm/diesel oil blend at equal volume ratio and S:C1:C2 at 1:2:2 mole ratio and constant number of moles. The vegetable oil/diesel blend was 50 vol%. For all systems, increasing the ethanol content in the blend decreased the viscosity of the microemulsion fuels. However, others have shown that increasing ethanol fraction decreases the heating value of the fuels [30] and the cetane number of the fuels since ethanol has such a low cetane number of 8 [31]. Therefore, the desirable microemulsion fuels should have the lowest ethanol fraction that still meets the ASTM standard. The ASTM viscosity for No 2 diesel fuel (shown in horizontal dashline) is 4.1 cSt [17]. For canola and palm oil/diesel blend MF, the minimum ethanol requirement to be 4.1 cSt is 24 vol%, whereas that for algae/diesel blend MF at the lowest ethanol amount was 14 vol%. This is expected because the viscosities of algae oil (15.2 cSt at 40°C) is much lower than those of palm (32.3 cSt at 40°C) and canola oils (37 cSt at 40°C). For the later combustion test, the ethanol fraction in the MF was kept at 24 vol% for ease of comparison between vegetable oil types.

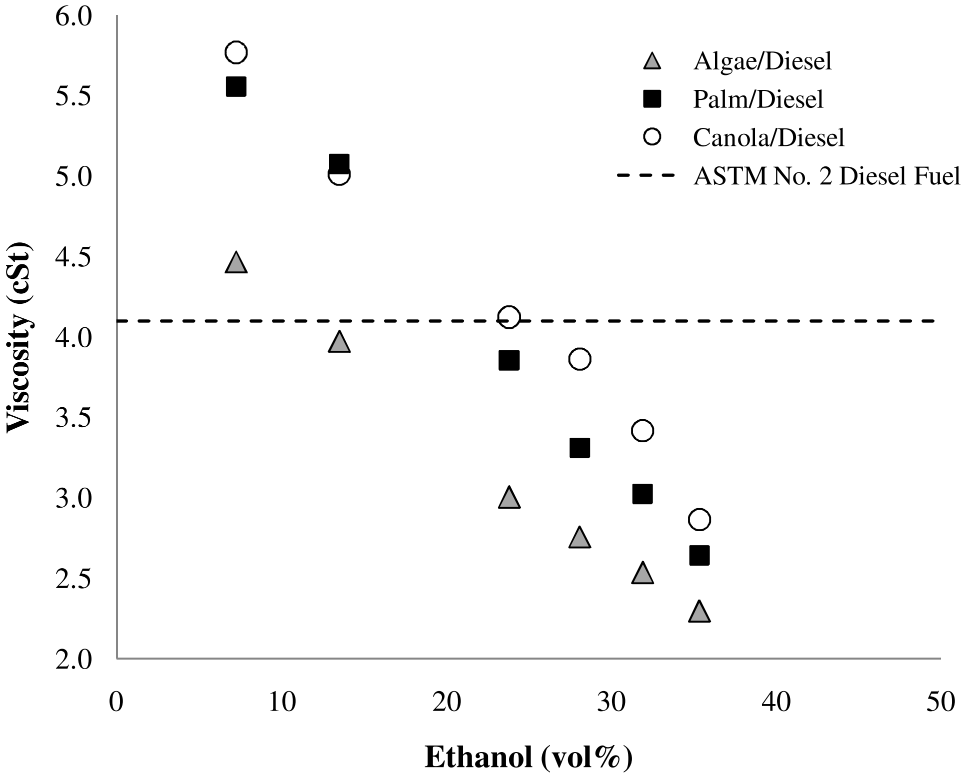


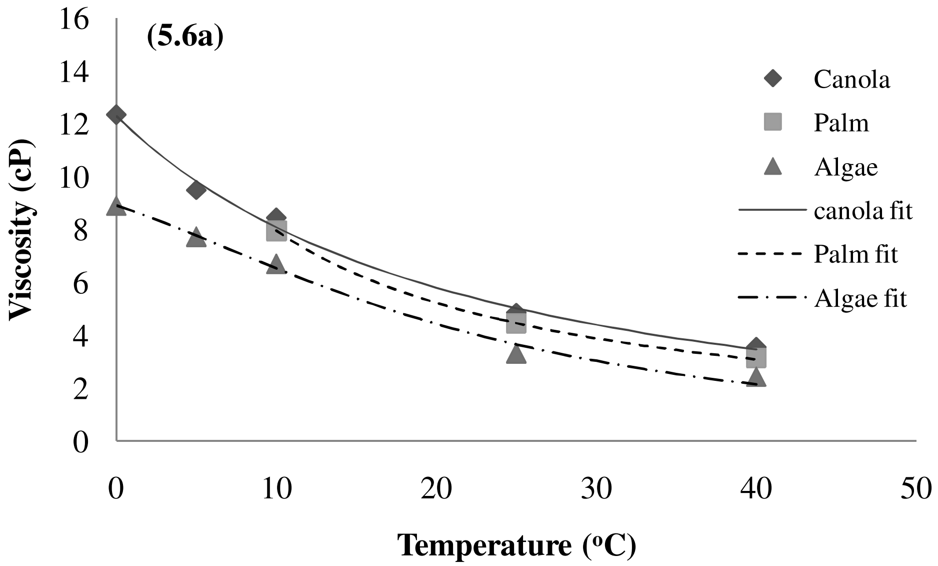
Figure 5.5: Effect of ethanol on microemulsion viscosities of studied vegetable oil/diesel blends at 40°C. Surfactant and co-surfactant system is OA/EHL/EGBE at 1:2:2 mole ratio. See Table 5.1 for abbreviations.

Effect of temperature on microemulsion fuel viscosity

Figure 5.6a shows the effect of temperature (0 – 40^{o}C) on the MF dynamic viscosities (cP) for three vegetable oil/diesel blends. Figure 5.6b shows the effect of fraction of algae oil in algae/diesel blend on viscosities over the same range of temperature. A general trend in which the viscosity increases as the temperature decreases was observed for all microemulsion fuels. This trend is as expected because as the temperature decreases in liquids, the cohesive forces of the molecules increase causing the molecules in the liquids to become more packed, thereby increasing the viscosity of the fuels [32]. In liquids, temperature effect on dynamic viscosities generally follows the following empirical equation:

$$\mu = \frac{\mu_o}{1+\alpha T+\beta T^2} \qquad \text{(Equation 5.3)}$$

where μ is the dynamic viscosity (cP) of the liquids at T degree Celsius; μ_o is the dynamic viscosity (cP) of the liquid at 0^{o}C; and α and β are constants. The fitting plot, which was plot against the data in 5.6a and 5.6b, shows a well fit with R^2 from 0.95 – 0.99. It is also important to note that the viscosity of No. 2 diesel fuel was 9.76cP at 0^{o}C. At this temperature the canola/diesel blend MF had a viscosity slightly higher than diesel fuels, while the viscosity of algae/diesel at 50 vol% blend was similar to that of No. 2 diesel fuel.



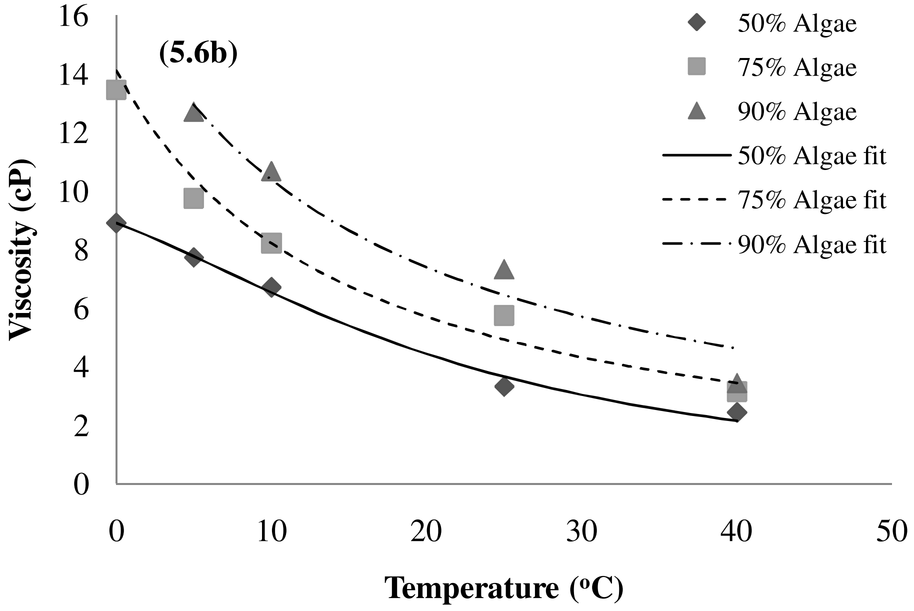


Figure 5.6: Effect of temperature on dynamic viscosity of microemulsion fuels. The oil phase in all formulations consists of 50 vol% vegetable oil and 50 vol% of diesel fuel; Fig 5.6a: Effect of vegetable oil type in the blends. Fig 5.6b: Effect of algae oil fraction in the blends. 50% algae means the oil phase consists of 50 vol% algae and 50 vol% diesel.

5.3.4 Combustion properties of microemulsion fuels

Flame imaging of microemulsion fuels


Canola MF (MF1) Palm MF (MF9) Algae MF (MF7) Diesel Canola CME

Figure 5.7: Flame images at frequency ratio of 7 for selected microemulsion fuels, diesel fuel and B100 canola biodiesel. Surfactant and co-surfactants system is OA(S) : EHL(C1) : EGBE(C2) (mole ratio at 1:2:2 and total concentration at 0.83 M). CBD is 100% canola biodiesel. See Table 5.3 for microemulsion fuel abbreviations.

Figure 5.7 shows the flame images of the canola, palm and algae microemulsion fuels in comparison to No 2 diesel and B100 canola biodiesel (CBD). As mentioned above, the combustion was in a laminar flame at equivalence ratio of 7, in which the flame characteristics depend only on the fuel chemistry [19]. From Figure 5.7, it can be seen that No. 2 diesel fuel flame is completely yellow; whereas all microemulsion flames (for abbreviation, see Table 5.3) and the CBD flame have a small blue region near the burner exit followed by yellow region downstream. The blue region is an indication of - gas phase combustion of the fuels with higher degree of oxidation, and was expected for the microemulsion fuels due to the presence of oxygen in the fuel molecule [19]. These results thus demonstrate the desirable combustion properties of the microemulsion fuels.

Heating value of microemulsion fuels

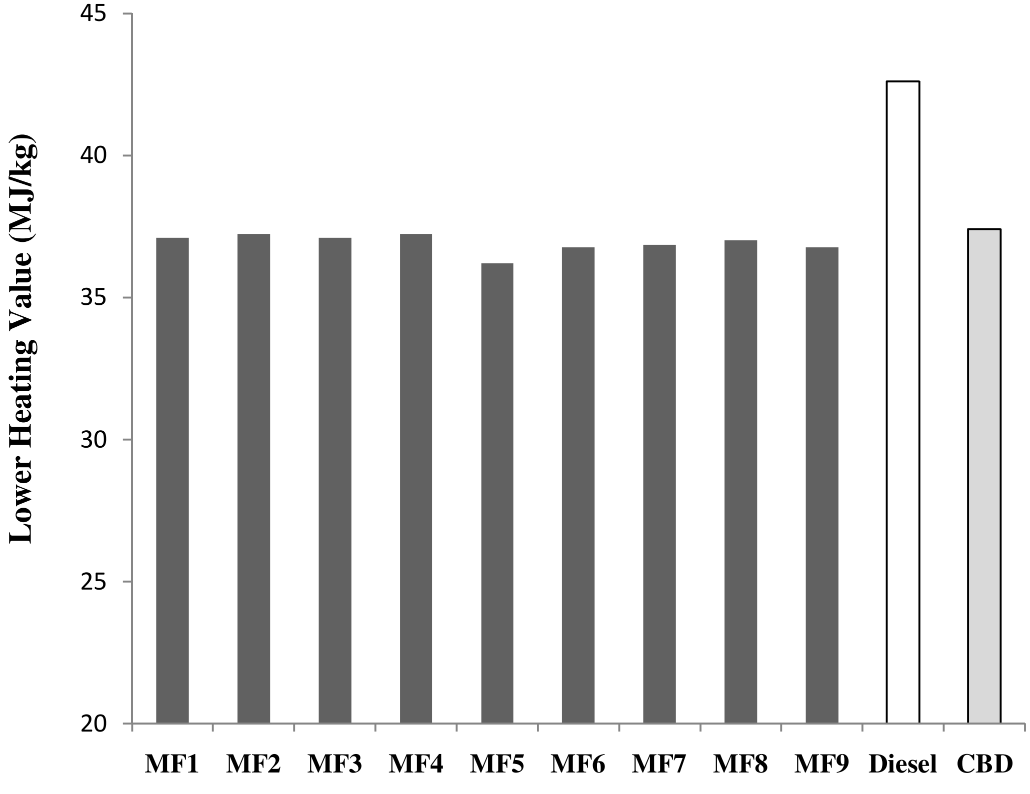


Figure 5.8: Lower heating values of selected microemulsion fuels, B100 canola biodiesel (CBD) and diesel fuel. See Table 5.3 for microemulsion fuel abbreviations.

Figure 5.8 shows the lower heating value (LHV) of microemulsion fuels estimated using Mendeleyev's formula for MF1 to MF9 (for abbreviations, see Table 5.3). LHV of No 2 diesel fuel is 42.6 MJ/kg. The formulated microemulsion fuels have LHV ranging from 36 – 37 MJ/kg, which is slightly less than LHV of No 2 diesel fuel (about 10% less); this is similar to the LHV of canola biodiesel (CBD, 37.4 MJ/kg) [33,34].

Global radiation emissions of microemulsion fuels

Figure 5.9 shows the radiative fraction F of microemulsion fuel flames compared to canola biodiesel (CBD) flame and No. 2 diesel fuel flame Since with the tested microemulsion fuels, no smoke was released , F can be used as an indication of the soot concentration in the flame, where a higher F means higher soot concentration [19, 20]. From Fig. 5.9, it can be seen that microemulsion fuels produce much lower F than No 2 diesel and slightly lower F than CBD. This trend is expected because diesel has a high fraction of aromatic compounds, causing a large amount of soot, whereas the oxygen atoms present in the microemulsion fuels promote soot oxidation and suppress the soot concentration, resulting in a more complete combustion [35]. The low radiation and soot production of microemulasion fuels make them ideal candidates for gas turbine engines.

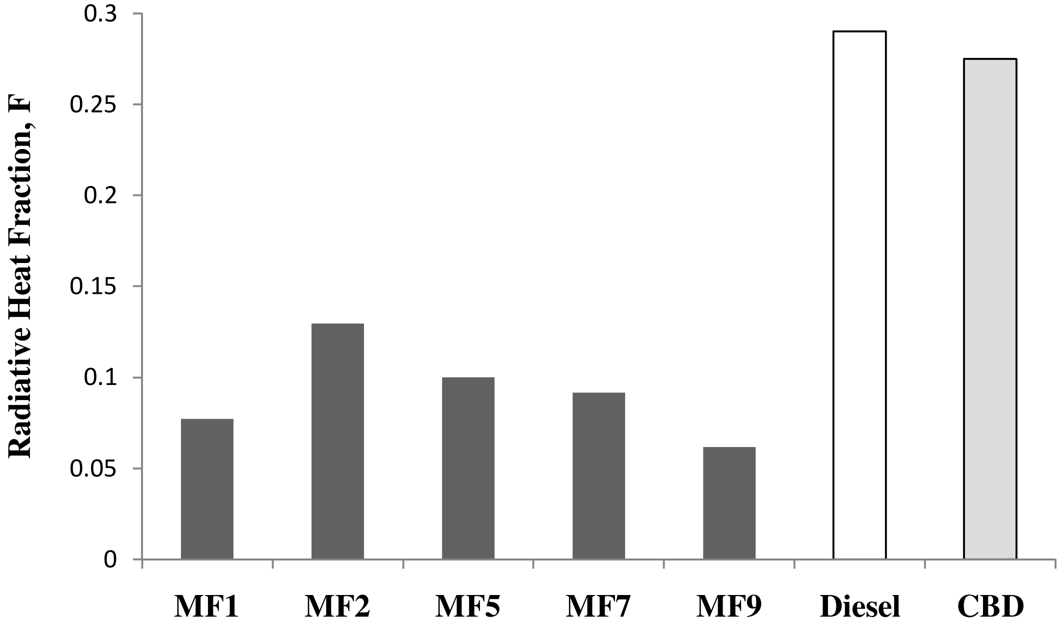


Figure 5.9: Radiative heat fraction of selected microemulsion fuels, B100 canola biodiesel (CBD) and diesel fuel. See Table 5.3 for microemulsion fuel abbreviations.

Global pollutant emissions of microemulsion fuels

The global emissions of CO and NO_x from the combustion of microemulsion fuels as well as No 2 diesel fuel and CBD are shown in Figure 5.10 and 5.10b, respectively.

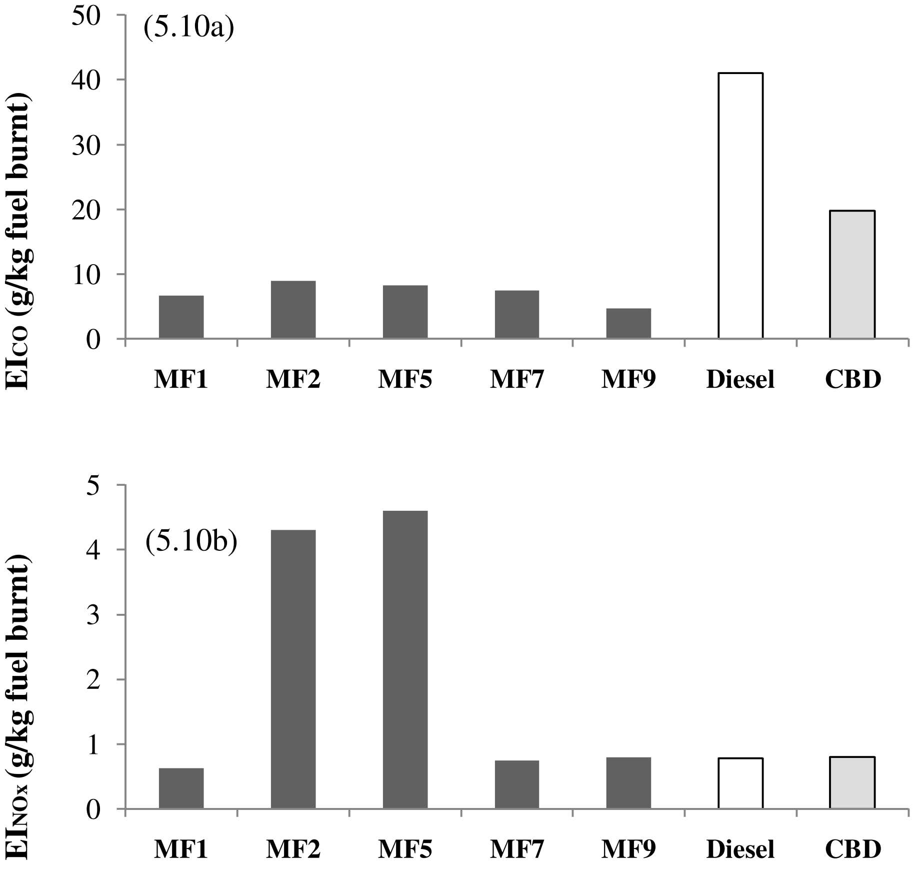


Figure 5.10: Global pollutant emissions of selected microemulsion fuels, B100 canola biodiesel and diesel fuel: (a) Emission index of CO; (b) Emission index of NO_x. See Table 5.3 for microemulsion fuel abbreviations.

From Fig. 10a, it can be concluded that the microemulsion fuels burn much cleaner than both No 2 diesel fuel and CBD, with the CO emission, only 20%, of the corresponding values for diesel fuel. However, in Fig.10b, the NO_x emissions of microemulsion fuels MF2 and MF5 are greater than the values for diesel and CBD. In contrast, MF1, 3, 7 and 8 have the lowest NO_x emissions among the studied microemulsion fuels, and they are also similar to or lower than for diesel fuel or CBD.

MF2 and MF5 produce higher NO_x emissions because of the nitrogen containing OAM and EHN in them. MF1, 3, 7 and 8 do not use nitrogen containing compounds, thereby accounting for their lower NO_x emissions.

5.4 CONCLUSION

We have demonstrated the use of surfactants and cosurfactants in formulating reverse micellar microemulsions of vegetable oil/diesel blends with ethanol. The palm/diesel ME fuels at 50 vol% palm oil in palm/diesel blend solidified at 6°C regardless of the surfactants or co-surfactants used. Algae and canola/diesel-based ME fuels formulated with oleyl alcohol showed better temperature stability than those formulated with oleyl amine. With appropriate surfactant and co-surfactant systems, we were able to formulate canola and algae/diesel-based ME fuels that meet the ASTM cloud point and pour point specifications for No 2 diesel fuel. At 50 vol% blend of vegetable oils in diesel fuel, 24 vol% of ethanol is needed to decrease the canola/diesel and palm/diesel-based ME fuel viscosity to meet the ASTM standard for No 2 diesel (4.1 cSt); whereas, only 15 vol% of ethanol is needed in algae/diesel-based ME fuel. The ME fuels have heating values similar to that of biodiesel and 10% less than that of No. 2 diesel fuel due to the presence of the ethanol. Global radiation and global CO emission of ME fuel flames are lower than those of both diesel fuel and canola biodiesel flames. NO_x emissions greatly depend on the surfactant/co-surfactant used. NO_x emissions are much higher in MFs contain oleyl amine and ethyl hexyl nitrate; whereas, NO_x emissions are similar to diesel fuels in ME fuels absence of nitrate compounds.

5.5 ACKNOWLEDGEMENTS

The authors would like to thank Norman Love, Megan Salisbury and Anh Mai for the experimental assistance. Funding for this work has been provided through the Oklahoma Center for Advancement of Science and Technology (OCAST) and Oklahoma Bioenergy Center. Partial support was provided by industrial sponsors of the Institute for Applied Surfactant Research at the University of Oklahoma: Clorox, Conoco/Phillips, Church and Dwight, Ecolab, GlaxoSmithKline, Halliburton, Huntsman, S.C. Johnson & Son, Oxiteno, Procter & Gamble, Sasol North America, Shell Chemical, and from Dr. Sabatini's Sun Oil Company endowed chair and Dr. Harwell's Conoco/Dupont endowed professorship.

REFERENCES

---

1. Renewable Fuel Standard (RFS) Access 10/2010: http://www.epa.gov/otaq/fuels/renewablefuels/index.htm

2. Goering CE, Schwab AW, Campion RM (1983) Soyoil-Ethanol Microemulsions as Diesel Fuel. Trans ASAE 26(6): 1602-1607.

3. Dunn RO, Bagby MO (2000) Low-Temperature Phase Behavior of Vegetable Oil/ Co-solvent Blends as Alternative Diesel Fuel. J Am Oil Chem Soc 77(12): 1315 – 1323.

4. Dunn RO (2004) Other Alternative Diesel Fuels from Vegetable Oils. In: Knothe G, Jurgen K, and Van GJ (Eds.) The Biodiesel Handbook, AOCS Press, Champaign, pp 241 – 263.

5. Strayer RC, Blake JA and Craig WK (1983) Canola and high erucic rapeseed oil as substitues for diesel fuel: Preliminary tests. J Am Oil Chem Soc 60(8): 1587-1592.

6. Alencar JW, Alves PB, Craveiro AA (1983) Pyrolysis of Tropical Vegetable Oils. J Agric Food Chem, 31(6): 1268 – 1270.

7. Lima DG, Soares VCD, Ribeiro EB, Carvalho DA, Cardoso ECV, Rassi FC, Mundim KC, Rubim JC, Suarez PAZ (2004) Diesel-like fuel obtained by pyrolysis of vegetable oils J Anal Appl Pyrolysis 71: 987 – 996

8. Schwab, G. J.; Selke, E.; Sorenson, S. C. and Pryde, E. H. (1988). "Diesel fuel from thermal decomposition of soybean oil." J Am Oil Chem Soc 65(11): 1781-1786.

9. Demirbas A (2005) Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. Prog Energ Comb Sci 31: 466 – 487

10. Knothe G, Dunn RO, Bagby MO. The use of vegetable oils and their derivatives as alternative diesel fuels. Oil Chemical Research, National Center for Agricultural Utilization Research, Agricultural Research Service, U.S. Department of Agriculture, Peoria, I L 61604. (accessed in July 2010)

< http://www.biodieselgear.com/documentation/VegetableOilsAsAlternativeDieselFuels.pdf>

11. Ali U, Hanna MA (1994) Alternative diesel fuels from vegetable oils. Bioresource Technol 50: 153 – 163

12. Rosen MJ (2004) Surfactants and Interfacial Phenomena. John Wiley & Sons, Inc. New Jersey, p. 208 – 242.

13. Lif A, Holmberg K (2006) Water-in-Diesel Emulsions and Related Systems. Adv Colloid Interface Sci 123-126: 231 – 239

14. Dantas TNC, Silva AC, Neto AAD (2001) New Microemulsion System Using Diesel and Vegetable Oils. Fuel 80: 75-81.

15. Knothe G (2005) Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. Fuel Process Technol 86: 1059 – 1070

16 . Antoniosi Filho NR, Mendes OL, Lancas FM (1995) Computer Prediction of Triacylglycerol Composition of Vegetable oils by HRGC. J Am Oil Chem Soc 40 (9/10): 557 – 562

17. No 2 Diesel Fuel MSDS. Tosco Refining Company (accessed in October 2010) < http://www.petrocard.com/Products/MSDS-ULS.pdf>

18. Dunn RO (2004) Cold Weather Properties and Performance of Biodiesel. In: Knothe G, Jurgen K, and Van GJ (Eds.) The Biodiesel Handbook, AOCS Press, Champaign, pp 83 – 125

19 . Love N, Parthasarathy R, Gollahalli S (2009) Rapid Characterization of Radiation and Pollutant Emissions of Biodiesel and Hydrocarbon Liquid Fuels. J Energ Resour Tech, 131(012202): 1 – 9.

20. Love N.D, Parthasarathy R.N., Gollahalli S.R. (2009) Effect of Iodine Number on NOx Formation in Laminar Flames of Oxygenated Biofuels. Int J Green Energy 6 (4): 323 – 332.

21. Baukal C, Schwartz R (2001) The John Zink Combusion Handbook, CRC, New York, p 101

22. Brzustowski TA, Gollahalli SR, Gupta MP, Kaptein M, Sllivan HF (1975) Radiant Heating from Flares. ASME Paper No. 75-HT-4.

23. Iwata Y, Koseki H, Janssens M, Takahashi T (2001) Combustion Characteristics of Crude Oils. Fire Mater, 25: 1 – 7.

24. Khovakh M (1979) Motor Vehicle Engines. Moscow: MIR Publishers.

25. Bayraktar H (2008) An Experimental Study on the Performance Parameters of an Experimental CI Engine Fueled with Diesel-Methanol-Dodecanol Blends. Fuel, 87: 158 – 164.

26. Rodrigues JA, Cardoso FP, Lachter ER, Estevao LRM, Lima E, Nasimento RSV (2006) Correlating Chemical Structure and Physical Properties of Vegetable Oil Esters. J Am Oil Chem Soc 83 (4): 353 – 357.

27. Batista E, Monnerat S, Kato K, Stragevitch L, Meirelles AJA (1999) Liquid-Liquid Equilibrium for Systems of Canola Oil, Oleic Acid and Short-Chain Alcohols. J Chem Engr Data 44(6): 1360 – 1364.

28. Rabelo J, Batista E, Cavaleri FW, Meirelles AJA (2000) Viscosity Prediction for Fatty Systems. JAOCS 77(12): 1255 – 1262.

29. Fernando S (2004) Development of a Novel Biofuel Blend Using Ethanol-Biodiesel-Diesel Microemulsions: EB-Diesel. Energ Fuel 18: 1695 – 1703.

30. Dunn RO, Bagby MO (1994) Solubilization of Methanol and Triglycerides: Unsatrated Long-Chain Fatty Alcohol/Medium-Chain Alkanol Mixed Amphiphile Systems. J Am Oil Chem Soc 71(1): 101 – 108.

31. Li D, Zhen H, Xingcai L, Wu-gal Z, Jian-guang Y (2004) Phsico-Chemical Properties of Ethanol-Diesel Blend Fuel and Its Effect on Performance and Emissions of Diesel Engines. Renew Energ 30(6): 967 – 976.

32. Bansal RK (2005) Fluid Mechanics and Hydraulic Machines. Laxmi publications, pp 1 – 6

33. Issariyakul T, Kulkarni MG, Meher LC, Dalai AK, Bakhshi NN (2008) Biodiesel production from mixtures of canola oil and used cooking oil. Chem Engr J, 140 (1-3): 77 – 85.

34. Erazo Jr JA, Parthasarathy R, Gollahalli S (2010) Atomization and combustion of canola methyl ester biofuel spray. J Fuel, 89(12): 3735 – 3741.

35. McCormick R, Graboski M, Alleman T, Herring A (2001) Impact of Biodiesel Source Material and Chemical Structure on Emissions of Criteria Pollutants from a Heavy-Duty Engine. EnvironSci Technol, 35: 1742 – 1747

Chapter 6 CONCLUSION

This chapter summarizes the concluding remarks of this work and the knowledge gained from the previous chapters. Future recommendations and potential applications are also discussed. The overall goal of this research work was to formulate vegetable oil microemulsions without alcohol or co-oil addition using a series of extended-surfactants, to apply the ultra low interfacial tension property of aqueous based extended-surfactants solution with vegetable oils to extract oil from oilseeds and to formulate temperature insensitive reverse micellar microemulsion fuels. This dissertation also investigated the laboratory pilot scale study of oilseed extraction using aqueous-surfactant-based method and the combustion properties of microemulsion fuels.

In Chapter 2, we have demonstrated the ultralow interfacial tension properties of a series of extended-surfactants with a wide range of vegetable oils. Equilibrium IFT values were reached within 15 minutes, which is relatively fast. We have also shown that hydrophobic/hydrophilic linkers can be used in combination with extended-surfactants to form microemulsions with a wide range of vegetable oils. Both Winsor Type III and Type IV microemulsions were formed at ambient condition without the addition of co-oil and/or alcohols and at relatively low electrolyte concentrations. Our proposed formulations can form environmentally benign microemulsions with a wide range of oils, regardless of the triglyceride compositions, and can obtain high solubilization parameters, up to 10 ml/g. These microemulsion formulations are particularly attractive in pharmaceuticals, cosmetics and cleaning technology applications.

In Chapter 3, we have shown that among the extended-surfactants studied in this chapter, the alkyl-propoxylate-ethoxylate-sulfate class of surfactants is most suitable for the vegetable oilseeds evaluated in this research since it produces the lowest interfacial tension (IFT). Additionally, the C_{10}-18PO-2EO-sulfate exhibits the best performance for vegetable oil extraction in terms of low IFT, salinity values and absence of stable macroemulsions. The aqueous extended-surfactant based method proved to be effective for extracting peanut and canola oils, being able to achieve 95% and 93% oil extraction, respectively. Although the fraction of oil extracted is not as high as that of the hexane method, which achieved 98-99% efficiency, our method offers significantly better crude oil quality in terms of free fatty acid. The amount of oil extracted by aqueous extended-surfactant-based and the amount of residual oil were summed and compared to the total oil content analyzed by Soxhlet extraction. There was no statistical difference between these two values, indicating that insignificant amount of oil was lost through solubilization in the aqueous surfactant solution.

We also looked at the effects of different processing parameters on vegetable oil extraction efficiency, including pH, surfactant concentration, extraction time, shaking speed, solid-to-liquid ratio, and salinity levels. We found that surfactant concentrations at the CμC and optimum salt concentrations are the most important parameters for vegetable oil extraction efficiency. From the evaluation of crude oil quality, it was shown that our method offers better crude oil quality in terms of free fatty acid content compared to the hexane extraction method. The peanut and canola oils are clear and exhibit fresh smell. Hexane extracted oils have a burnt-like smell because the oils were heated to evaporate the hexane. Thus, we have successfully demonstrated the viability of the aqueous surfactant based extraction method for seed extraction of vegetable oils; future work will explore the scale-up of this process.

In Chapter 4, we have demonstrated that a semi-continuous pilot scale system of aqueous surfactant enhanced vegetable oil extraction was able to achieve a total oil extraction efficiency similar to that obtained from batch scale after aqueous surfactant and DI washing steps (25^oC). However, the total crude oil recovery was at 87.1 wt% for peanut oil and 85.6 wt% for canola oil, which were lower than those obtained from batch scale. The S/L and L/L separation steps are critical parameters in oil extraction by SAEP, EAEP and AEP. Further free oil recovery from the skim of the L/L centrifuge outlet is very challenging. It will be worth studying the effect of SAEP on vegetable oil extraction of extruded flakes, in which the proteins were denatured, resulting in less stable emulsion problems. It is also worth studying the de-emulsification efficiency of extracted oil – surfactant solution mixture at higher temperatures, which was not within the scope of this study. Protein recovery from this process should be investigated in the future research to evaluate the economic feasibility of this technology.

Finally, in Chapter 5, we have demonstrated the use of surfactants and cosurfactants in formulating reverse micellar microemulsions of vegetable oil/diesel blends with ethanol. The palm/diesel microemulsion fuels at 50 vol% palm oil in palm/diesel blend solidified at 6^oC regardless of the surfactants or co-surfactants used. Algae and canola/diesel-based ME fuels formulated with oleyl alcohol showed better temperature stability property than those formulated with oleyl amine. With appropriate surfactant and co-surfactant systems, we were able to formulate canola and algae/diesel-based ME fuels that meet the ASTM cloud point and pour point for No 2 diesel fuel. At

50 vol% blend vegetable oils in diesel fuel, 24 vol% of ethanol is needed to decrease the canola/diesel and palm/diesel-based microemulsion fuel viscosity to meet the ASTM standard for No 2 diesel (4.1 cSt); whereas, only 15 vol% of ethanol is needed in algae/diesel-based ME fuel. The ME fuels have heating value similar to that of biodiesel and 10% less than that of diesel fuel due to the presence of the ethanol. Global radiation and global CO and CO_2 emissions of ME fuels are superior to both diesel fuel and canola biodiesel. NO_x emissions greatly depend on the surfactant/co-surfactant used. NO_x emissions are much higher in MFs contain oleyl amine and ethyl hexyl nitrate; whereas, NO_x emissions are similar to diesel fuels in ME fuels absence of nitrate compounds.

APPENDIX A Supplement materials for Chapter 1

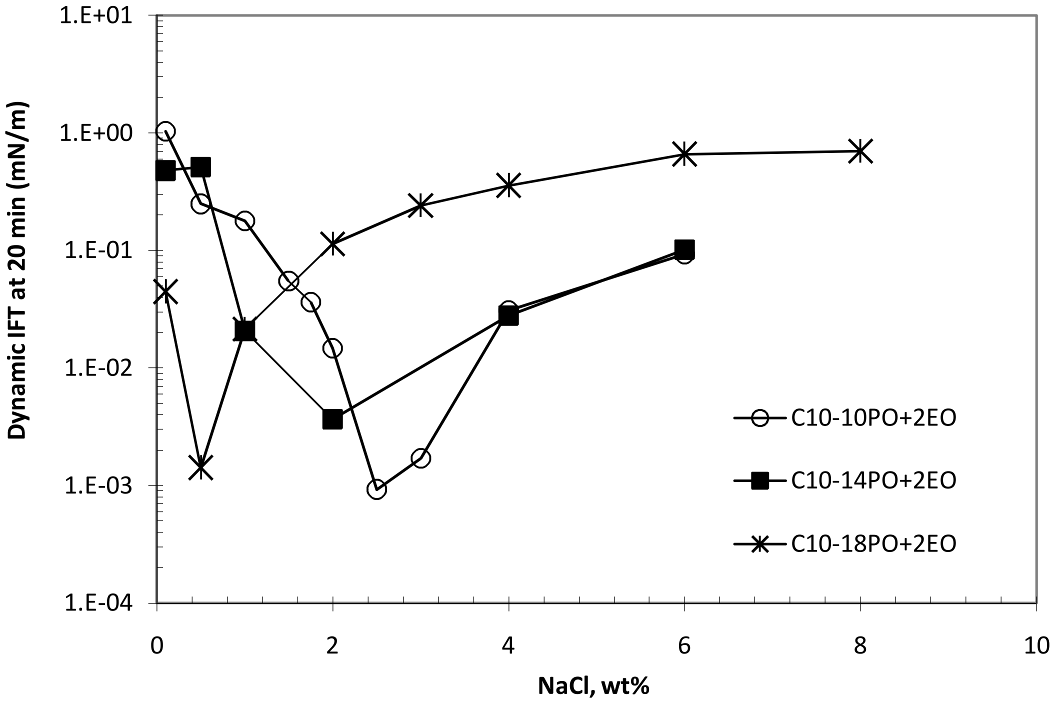


Figure A.1: Effect of NaCl on dynamic IFT at 20 minutes of C_{10}-xPO-2EO-$NaSO_4$ series on triolein oil (65% grade) at 27°C.

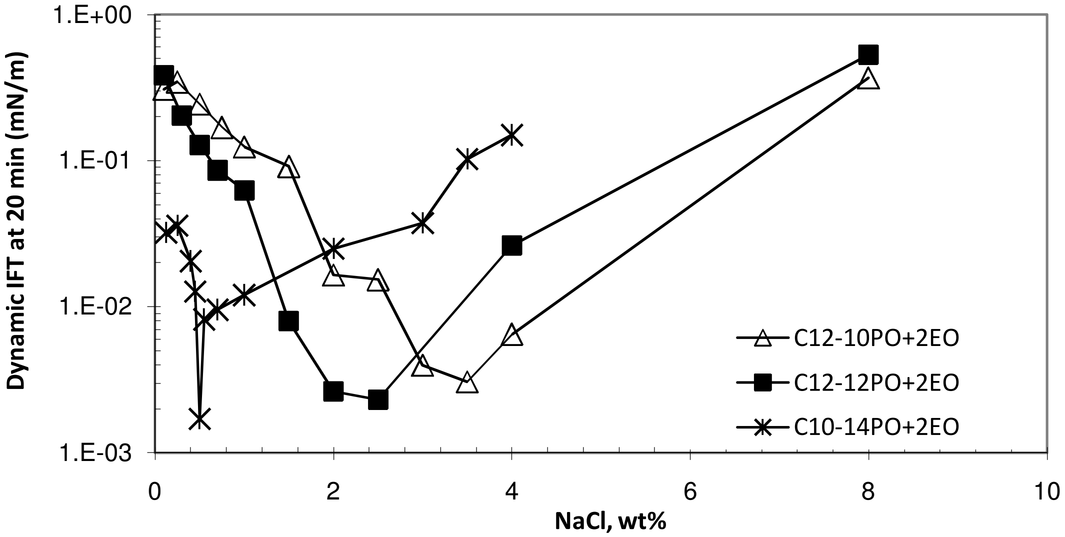


Figure A.2: Effect of NaCl on dynamic IFT at 20 minutes of C_{12}-xPO-2EO-$NaSO_4$ series on triolein oil (65% grade) at 27°C.

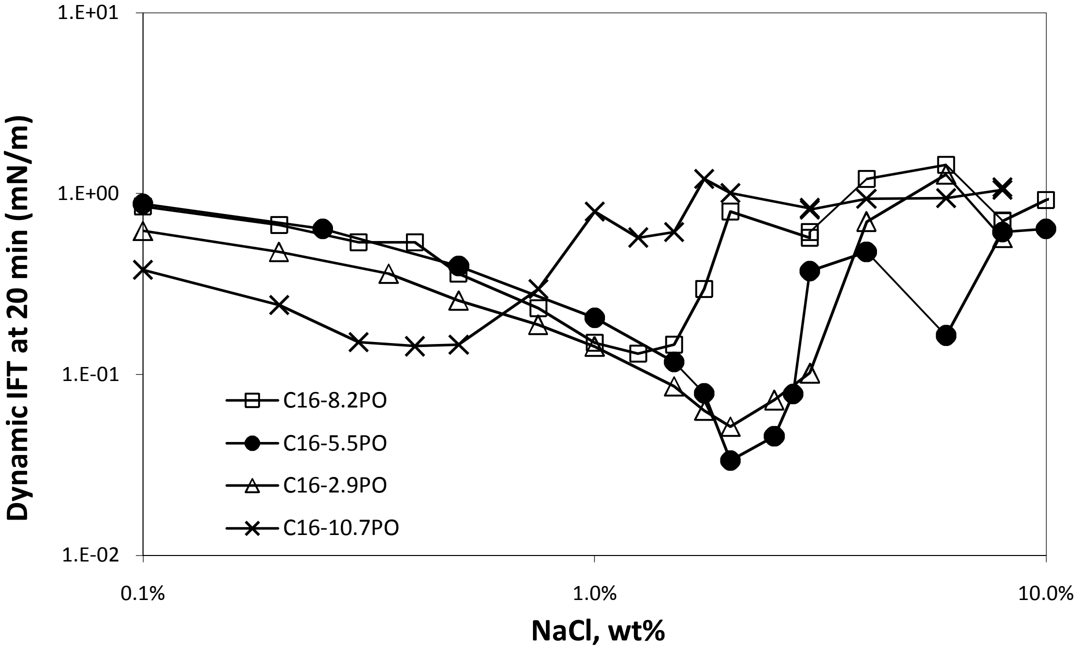


Figure A.3: Effect of NaCl on dynamic IFT at 20 minutes of C_{16}-xPO-$NaSO_4$ series on triolein oil (65% grade) at 27°C.

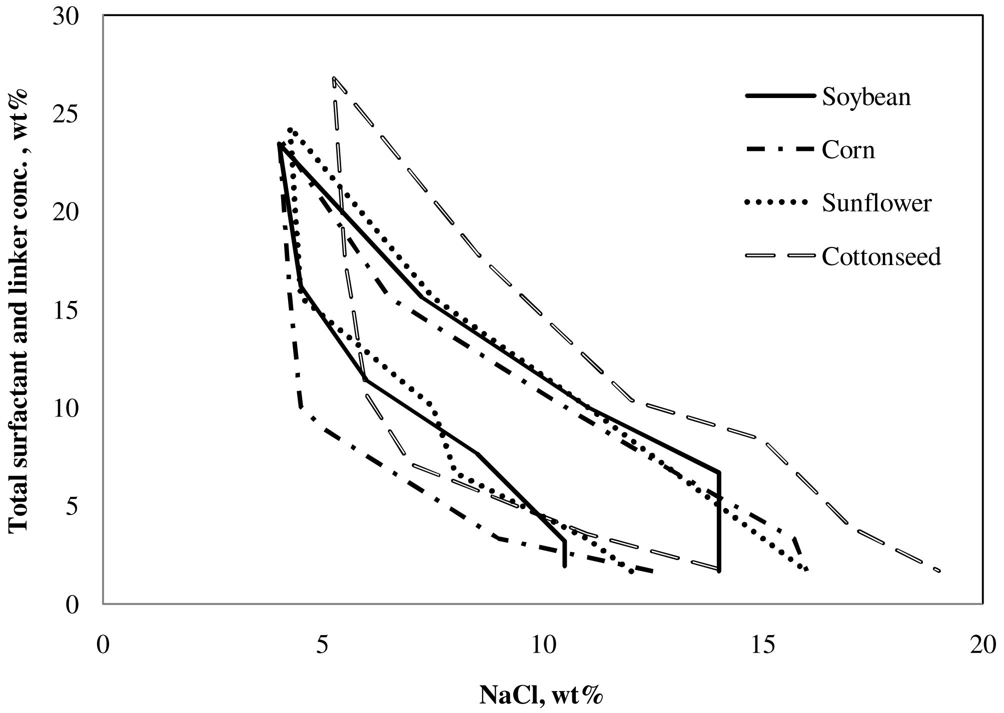


Figure A.4: Partial "fish" phase diagram of soybean, corn, sunflower and cottonseed oils at 27^{o}C. Surfactant and linker system is C10-18PO-2EONaSO4/Oleyl alcohol/Glucopon at weight ratio of 3/2.5/1.2

APPENDIX B Supplement materials for Chapter 3

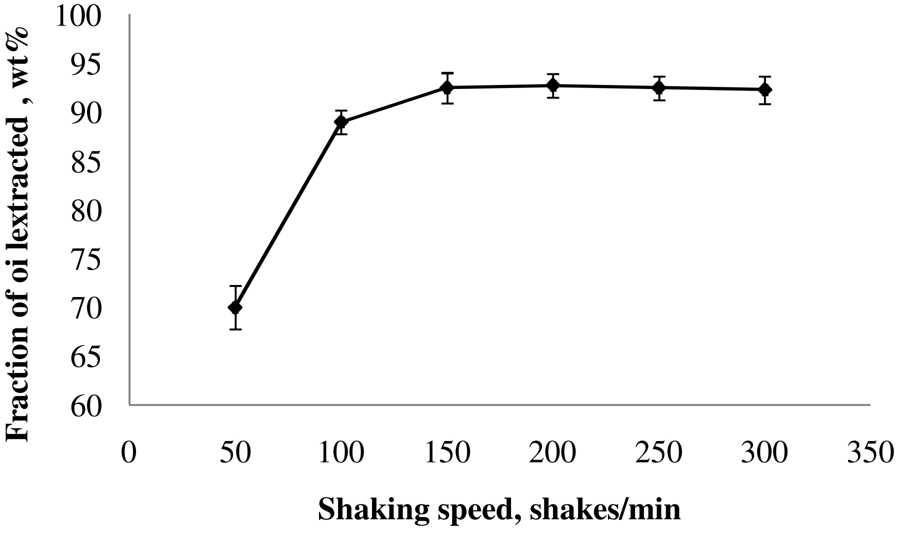


Figure B.1: Effect of shaking speed on canola oil extraction using 0.35 wt% of C_{10}-18PO-2EOsulfate and 5 wt% NaCl at 25°C. 30 minutes contact time. Seed to surfactant solution ratio at 2 : 10 (g : g)

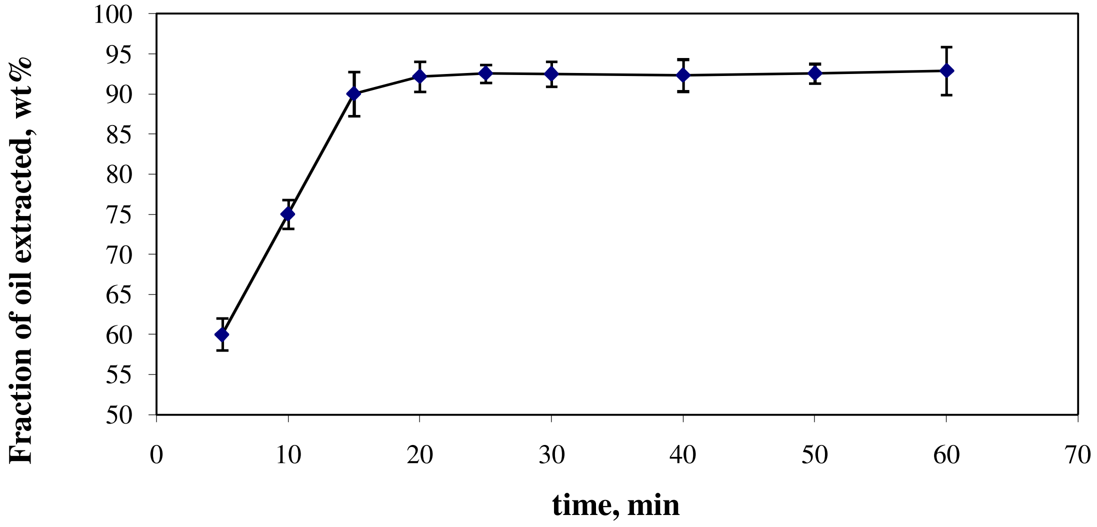


Figure B.2: Effect of shaking time on canola oil extraction of canola oil extraction using 0.35 wt% of C_{10}-18PO-2EOsulfate and 5 wt% NaCl at 25°C. Shaking speed at 150 shakes/min. Seed to surfactant solution ratio at 2 : 10 (g : g)

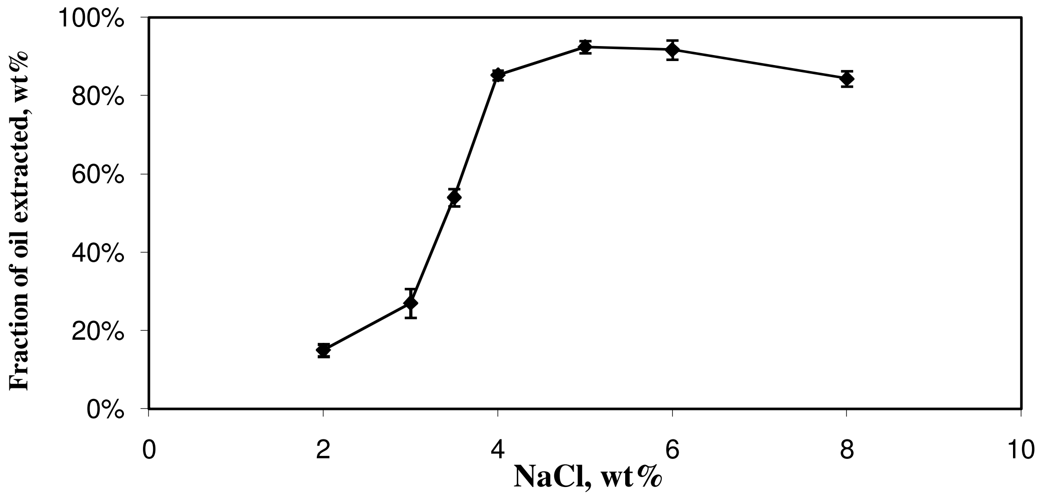


Figure B.3: Effect of salt concentration on canola oil extraction and dynamic IFT (data recorded at 20 minutes) using 0.35 wt% of C_{10}-18PO-2EOsulfate and 5 wt% NaCl at 25°C. Shaking speed at 150 shakes/min for oil extraction experiments. Seed to surfactant solution ratio at 2 : 10 (g : g)

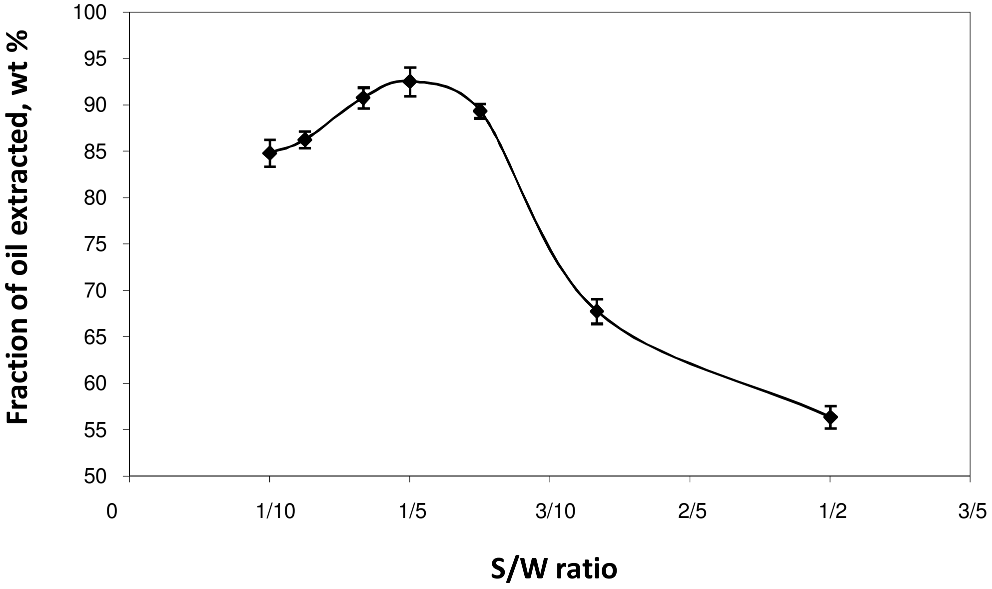
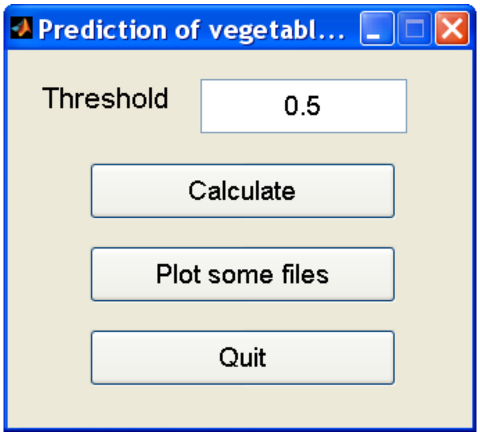


Figure B.4: Effect of seed to liquid ratio on extractability using 0.35 wt% of C_{10}-18PO-2EOsulfate and 5 wt% NaCl at 25°C. 30 minutes contact time and shaking speed at 150 shakes/min.

APPENDIX C Supplement materials for Chapter 5

C.1 Computer program (MATLAB) for vegetable oil triglyceride profile prediction (chapter 5)

C.1.1 Code of the graphic user interface



Threshold 0.5

Figure C.1.1: Illustration of the User Interface

```
function varargout = veg_tri_gui(varargin)
% VEG_TRI_GUI M-file for veg_tri_gui.fig
%      VEG_TRI_GUI, by itself, creates a new VEG_TRI_GUI or raises the existing
%      singleton*.
%
%      H = VEG_TRI_GUI returns the handle to a new VEG_TRI_GUI or the handle to
%      the existing singleton*.
%
%      VEG_TRI_GUI('CALLBACK',hObject,eventData,handles,...) calls the local
%           function named CALLBACK in VEG_TRI_GUI.M with the given input arguments.
```

```
%
%      VEG_TRI_GUI('Property','Value',...) creates a new VEG_TRI_GUI or raises the
%      existing singleton*.  Starting from the left, property value pairs are
%      applied to the GUI before veg_tri_gui_OpeningFunction gets called.  An
%      unrecognized property name or invalid value makes property application
%      stop.  All inputs are passed to veg_tri_gui_OpeningFcn via varargin.
%
%      *See GUI Options on GUIDE's Tools menu.  Choose "GUI allows only one
%      instance to run (singleton)".
%
% See also: GUIDE, GUIDATA, GUIHANDLES

% Edit the above text to modify the response to help veg_tri_gui

% Last Modified by GUIDE v2.5 02-Aug-2010 12:13:48

% Begin initialization code - DO NOT EDIT
gui_Singleton = 1;
gui_State = struct('gui_Name',       mfilename, ...
                   'gui_Singleton',  gui_Singleton, ...
                   'gui_OpeningFcn', @veg_tri_gui_OpeningFcn, ...
                   'gui_OutputFcn',  @veg_tri_gui_OutputFcn, ...
                   'gui_LayoutFcn',  [] , ...
                   'gui_Callback',   []);
if nargin && ischar(varargin{1})
    gui_State.gui_Callback = str2func(varargin{1});
end
```

```
if nargout
    [varargout{1:nargout}] = gui_mainfcn(gui_State, varargin{:});
else
    gui_mainfcn(gui_State, varargin{:});
end
% End initialization code - DO NOT EDIT



% --- Executes just before veg_tri_gui is made visible.
function veg_tri_gui_OpeningFcn(hObject, eventdata, handles, varargin)
% This function has no output args, see OutputFcn.
% hObject    handle to figure
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)
% varargin   command line arguments to veg_tri_gui (see VARARGIN)

% Choose default command line output for veg_tri_gui
handles.output = hObject;

% Update handles structure
guidata(hObject, handles);

% UIWAIT makes veg_tri_gui wait for user response (see UIRESUME)
% uiwait(handles.figure1);
```

```
% --- Outputs from this function are returned to the command line.
function varargout = veg_tri_gui_OutputFcn(hObject, eventdata, handles)
% varargout  cell array for returning output args (see VARARGOUT);
% hObject    handle to figure
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Get default command line output from handles structure
varargout{1} = handles.output;



% --- Executes on button press in pb.
function pb_Callback(hObject, eventdata, handles)
% hObject    handle to pb (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

[inFileName,inPathName] = uigetfile({'*.xlsx'},'Select the excel file');
[outFileName,outPathName] = uiputfile({'*.xls'},'Save to...');
inFile = inFileName;
outFile1 = outFileName;
outFile2 = [outFile1(1:length(outFile1)-4),'sum.xls'];
threshold = str2num(get(handles.edThresh,'String'));
% perform the calculation
tri_veg_pre(inFile,outFile1,outFile2,threshold);

msgbox('The calculation is finished!');
```

```
% --- Executes on button press in pbQuit.
function pbQuit_Callback(hObject, eventdata, handles)
% hObject    handle to pbQuit (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

delete(handles.figure1)

 function edThresh_Callback(hObject, eventdata, handles)
% hObject    handle to edThresh (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of edThresh as text
%        str2double(get(hObject,'String')) returns contents of edThresh as a double

% --- Executes during object creation, after setting all properties.
function edThresh_CreateFcn(hObject, eventdata, handles)
% hObject    handle to edThresh (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: edit controls usually have a white background on Windows.
%       See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
end
```

```
% --- Executes on button press in pbPlot.
function pbPlot_Callback(hObject, eventdata, handles)
% hObject    handle to pbPlot (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

[inFileName,inPathName] = uigetfile({'*.xls'},'Select the excel file','MultiSelect','on');
if(ischar(inFileName))
   temp = inFileName;
   clear inFileName
   inFileName{1} = temp;
end
for i = 1:length(inFileName)
   lengthFile = length(inFileName{i});
   if(lengthFile<=6)
      errordlg('Please choose a file ending with word "sum"','Wrong file!')
      return;
   else
      fileSelType = inFileName{i}(lengthFile-6:lengthFile-4);
      if(fileSelType~='sum')
         errordlg('Please choose a file ending with word "sum"','Wrong file!')
         return;
      end
   end
end
```

```
[outFileName,outPathName] = uiputfile({'*.xls'},'Save to...');
% plot the result
tri_veg_plot(inFileName,outFileName);
```

C1.1.2 Code of the triglyceride prediction program

```
function [] = tri_veg_pre(inFile,outFile1,outFile2,threshold)

% size of inputs is vector of 17 elements
[num,txt,a] = xlsread(inFile);

numX = 0;
for i = 1:length(a)
   if(a{i,2}~=0)
      numX = numX + 1;
      x{numX,1} = a{i,1};
      x{numX,2} = a{i,2};
      x{numX,3} = a{i,3};
      x{numX,4} = a{i,4};
      x{numX,5} = a{i,5};
   end
end

totalNumCom = factorial(numX)/factorial(numX-3)+numX*numX;
id = cell(totalNumCom,1);
com = cell(totalNumCom,1);
sum1 = cell(totalNumCom,1);
sum2 = cell(totalNumCom,1);
```

```
numCom = 0;
for i = 1:numX
    numCom = numCom + 1;
    com{numCom,1} = [x{i,1},x{i,1},x{i,1}];
    id{numCom,1} = sort([i i i]);
    sum1{numCom,1} = sum([x{i,3},x{i,3},x{i,3}]);
    sum2{numCom,1} = sum([x{i,4},x{i,4},x{i,4}]);
end
for i = 1:numX
    for j = 1:numX
        if(j~=i)
            numCom = numCom + 1;
            com{numCom,1} = [x{i,1},x{i,1},x{j,1}];
            id{numCom,1} = sort([i i j]);
            sum1{numCom,1} = sum([x{i,3},x{i,3},x{j,3}]);
            sum2{numCom,1} = sum([x{i,4},x{i,4},x{j,4}]);
        end
    end
end

for i = 1:numX
    for j = 1:numX
        for k = 1:numX
            if((i~=j)&&(j~=k)&&(k~=i))
                numCom = numCom + 1;
                com{numCom,1} = [x{i,1},x{j,1},x{k,1}];
```

```
            id{numCom,1} = sort([i j k]);
            sum1{numCom,1} = sum([x{i,3},x{j,3},x{k,3}]);
            sum2{numCom,1} = sum([x{i,4},x{j,4},x{k,4}]);
         end
      end
   end
end

totalNumComUse = factorial(numX)/factorial(numX-3)/factorial(3)+numX*numX;
idUse = cell(totalNumComUse,1);
comUse = cell(totalNumComUse,1);

numComUse = 1;
comUse{numComUse,1} = com{1,1};
idUse{numComUse,1} = id{1,1};
sum1Use{numComUse,1} = sum1{1,1};
sum2Use{numComUse,1} = sum2{1,1};

for i = 1:numCom
   disp(['please wait: ',num2str(i),'/',num2str(numCom)]);
   length_idUse = numComUse;
   comInl = 0; % have not included yet
   for j = 1:length_idUse
      errorVec = id{i,1} - idUse{j,1};
      if((max(errorVec)==0)&&(min(errorVec)==0))
         comInl = 1;
      else
```

```
            comInl = min(comInl,1);
        end
    end
    if(comInl==0)
        numComUse = numComUse + 1;
        comUse{numComUse,1} = com{i,1};
        idUse{numComUse,1} = id{i,1};
        sum1Use{numComUse,1} = sum1{i,1};
        sum2Use{numComUse,1} = sum2{i,1};
    end
end

% now start the calculation using comUse and idUse
sumCom = 0;
for i = 1:length(idUse)
    disp(['calculating the combination ',num2str(i),' of ',num2str(length(idUse)),' combinations']);
    temp = idUse{i,1};
    if(max(temp)==min(temp)) % first case
        comUse{i,3} = x{temp(1),2}*x{temp(1),2}*x{temp(1),2}/10000;
    else
        if(temp(1)==temp(2))
            comUse{i,3} = 3*x{temp(1),2}*x{temp(1),2}*x{temp(3),2}/10000;
        elseif(temp(1)==temp(3))
            comUse{i,3} = 3*x{temp(1),2}*x{temp(1),2}*x{temp(2),2}/10000;
        elseif(temp(2)==temp(3))
            comUse{i,3} = 3*x{temp(2),2}*x{temp(2),2}*x{temp(1),2}/10000;
        else
```

```
            comUse{i,3} = 6*x{temp(1),2}*x{temp(2),2}*x{temp(3),2}/10000;
        end
    end
    sumCom = sumCom + comUse{i,3};
end
for i = 1:length(idUse)
    comUse{i,2} = comUse{i,3}*100/sumCom;
end

% display only when > 0.01
sumLimit = 0;
numComUseLimit = 0;
for i = 1:length(idUse)
    if(comUse{i,3}>=threshold)
        numComUseLimit = numComUseLimit + 1;
        comUseLimit{numComUseLimit,1} = comUse{i,1};
        comUseLimit{numComUseLimit,3} = comUse{i,3};
        idUseLimit{numComUseLimit,1} = idUse{i,1};
        sum1UseLimit{numComUseLimit,1} = sum1Use{i,1};
        sum2UseLimit{numComUseLimit,1} = sum2Use{i,1};
        sumLimit = sumLimit + comUseLimit{numComUseLimit,3};
    end
end
for i = 1:length(comUseLimit)
    comUseLimit{i,2} = comUseLimit{i,3}*100/sumLimit;
end
% write to file 1
```

```
xlswrite(outFile1, comUseLimit);


use = zeros(length(sum1UseLimit),1);
numGroup = 0;
for i = 1:length(sum1UseLimit)
   if(use(i)==0)
      numGroup = numGroup + 1;
      sameSum = 0;
      for j = 1:length(sum1UseLimit)
         if(use(j)==0)

if((sum1UseLimit{i}==sum1UseLimit{j})&&(sum2UseLimit{i}==sum2UseLimit{j}))
               sameSum = sameSum + 1;
               group{numGroup}(sameSum,1) = j;
               groupSum1{numGroup,1} = sum1UseLimit{j};
               groupSum2{numGroup,1} = sum2UseLimit{j};
               use(j) = 1;
            end
         end
      end
      if(sameSum==0)
         group{numGroup}(1,1) = i;
         groupSum1{numGroup,1} = sum1UseLimit{i};
         groupSum2{numGroup,1} = sum2UseLimit{i};
         use(i) = 1;
      end
      idGroupRep{numGroup} = idUseLimit{i};
   end
```

```
end

for i = 1:numGroup
   for j = 1:length(group{i})
      groupPer{i}(j) = comUseLimit{group{i}(j),2};
   end
   [maxValue,index]= max(groupPer{i});
   sumGroup{i,1} = comUseLimit{group{i}(index),1};
   sumGroup{i,2} = sum(groupPer{i});
   sumGroup{i,3} = groupSum1{i};
   sumGroup{i,4} = groupSum2{i};
   sumPTK = 0;
   for k = 1:length(idGroupRep{i})
      sumPTK = sumPTK + x{idGroupRep{i}(k),5};
   end
   sumPTK = sumPTK + 38.0488;
   sumGroup{i,5} = sumPTK;
end
% write to file 2
xlswrite(outFile2, sumGroup);
```

C1.1.3 Code of the plotting program

```
function [] = tri_veg_plot(inFileName,outFileName)


% load file from inFileName
for i = 1:length(inFileName)
   [num{i},txt{i},a{i}] = xlsread(inFileName{i});
   c{i} = [cell2mat(a{i}(:,3)) cell2mat(a{i}(:,4)) cell2mat(a{i}(:,2))];
   [sort_c{i},index_c{i}] = sortrows(c{i},[1,2]);
end


% create the final list
numC = 1;
allC(1,1) = sort_c{1}(1,1);
allC(1,2) = sort_c{1}(1,2);
for i = 1:length(inFileName)
   for j = 1:length(index_c{i})
      include = 0;
      for k = 1:numC
         if((sort_c{i}(j,1)==allC(k,1))&&(sort_c{i}(j,2)==allC(k,2)))
            include = 1;
         else
            include = min(include,1);
         end
      end
      if(include==0)
         numC = numC + 1;
         allC(numC,1) = sort_c{i}(j,1);
```

```
            allC(numC,2) = sort_c{i}(j,2);
        end
    end
end
allC = sortrows(allC,[1,2]);
% add data from each inFile to the final list
c_table{1,1} = 'combination';
for i = 1:length(inFileName)
    c_table{1,i+1} = inFileName{i};
end
for i = 1:numC
    c_table{i+1,1} = ['C',num2str(allC(i,1)),':',num2str(allC(i,2))];
    for j = 1:length(inFileName)
        for k = 1:length(index_c{j})
            if((allC(i,1)==sort_c{j}(k,1))&&(allC(i,2)==sort_c{j}(k,2)))
                c_table{i+1,j+1} = sort_c{j}(k,3);
            end
        end
    end
end
for i = 1:numC+1
    for j = 1:length(inFileName)+1
        if(isempty(c_table{i,j}))
            c_table{i,j} = 0;
        end
    end
end
```

```
figureName = outFileName(1:length(outFileName)-4);
figure('Name',figureName)
for i = 1:length(inFileName)
   for j = 1:numC
      data(j,i) = c_table{j+1,i+1};
   end
end
for j = 1:numC
   xtick_loc(j,1) = j;
   xtick_label{j,1} = c_table{j+1,1};
end
bar(data,'group');
legend(inFileName);
set(gca,'XTickLabelMode','manual','XTick',xtick_loc,'XTickLabel',xtick_label);
xlswrite(outFileName, c_table);
```

C.2 Lower heating value (LHV) calculation for microemulsion fuels (Chapter 5)

This section represents the sample calculation for microemulsion fuel MF1. Table C.2.1 shows the properties of MF1:

Table C.2.1: MF1 fuel properties

	Molecular formula	**Molecular weight, MW_i (g/mole)**	**Density, ρ_i (g/mL)**	**Mole fraction, X_i**
Canola	$C_{56.8}H_{101}O_6$	879.99	0.94	0.050
OA[a]	$C_{18}H_{36}O$	268.48	0.81	0.029
EHL[a]	$C_8H_{18}O$	139.23	0.83	0.053
EGBE[a]	$C_6H_{14}O_2$	118.17	0.90	0.053
Ethanol	C_2H_6O	46.05	0.79	0.640
No 2 Diesel	$C_{16}H_{34}$	226.27	0.85	0.175

[a] For abbreviations, see Table 6.3

The LHV_i of each component in the fuel was calculated using Mendeleyev's formula as shown in Equation B.1:

$$LHV_i = 34.013c_i' + \ 125.6h_i' + \ -10.9o_i' - 2.512(9h_i' + w_i') \qquad \text{Equation C.2.1}$$

where c_i', h_i', o_i', w_i' are the amounts of separate elements in unit mass of the fuel component and can be calculated as below:

$$c_i' = \frac{12.01 \times \#C_i}{MW_i} \qquad \text{Equation C.2.2}$$

$$h_i' = \frac{1.01 \times \#H_i}{MW_i} \qquad \text{Equation C.2.3}$$

$$o_i' = \frac{16 \times \#O_i}{MW_i} \qquad \text{Equation C.2.4}$$

where MW$_i$ is the molecular weight of the component i and #C$_i$, #O$_i$, #H$_i$ are the number of carbon, oxygen and hydrogen atoms in the component i, respectively. Water content in all components in the fuel has no water; therefore, it is assumed that $w_i' = 0$

Amounts of separate elements in unit mass of canola can be calculated as below:

$$c'_{canola} = \frac{12.01 \times 56.8}{879.99} = 0.7752$$

$$h'_{canola} = \frac{1.02 \times 101.3}{879.99} = 0.1157$$

$$o'_{canola} = \frac{16 \times 6}{879.99} = 0.1091$$

Therefore, the lower heating value of canola (LHV$_{canola}$) is:

$$LHV_{canola} = 34.013 \times 0.7552 + \ 125.6 \times 0.1157 + \ -10.9 \times 0.091 - 2.512(9 \times 0.1157 + 0)$$

$$LHV_{canola} = 37.09 \text{ (MJ/kg)}$$

Table C.2.2 shows the c_i', h_i', o_i' and LHV$_i$ of the individual component in the microemulsion fuel MF1

Table C.2.2 Calculated values of c_i', h_i', o_i' and LHV$_i$ of the microemulsion fuel MF1

	c_i'	**h_i'**	**o_i'**	**LHV$_i$ (MJ/kg)**
Canola	0.7752	0.1157	0.1091	37.09
OA[a]	0.8052	0.1352	0.0596	40.66
EHL[a]	0.7378	0.1393	0.1229	38.10
EGBE[a]	0.6098	0.1194	0.2708	30.09
Ethanol	0.5216	0.1313	0.3476	27.48
No 2 Diesel	0.8492	0.1515	0	44.48

[a] See Table 6.3 for abbreviations

The lower heating value of the microemulsion fuel blend (LHV$_{MF}$) was calculated based on equation C.2.5:

$$LHV_{MF} = \frac{\sum X_i \rho_i LHV_i}{\sum X_i \rho_i} \qquad \text{Equation C.2.5}$$

Therefore, the lower heating value of MF1 (LHV$_{MF1}$) is:

$$LHV_{MF1} = (0.050 \times 0.94 \times 37.09 + 0.029 \times 0.81 \times 40.66 + 0.053 \times 0.83 \times 38.10 + 0.053 \times 0.90 \times 30.09 + 0.640 \times 0.789 \times 27.48 + 0.175 \times 0.85 \times 44.48) \times \frac{1}{0.050 \times 0.94 + 0.029 \times 0.81 + 0.053 \times 0.83 + 0.053 \times 0.90 + 0.640 \times 0.789 + 0.175 \times 0.85}$$

$LHV_{MF1} = 37.10$ MJ/kg

C. 3 Cost estimation of microemulsion fuels

Raw material cost for formulated microemulsion fuels was estimated based on the current price as of December 2010 and shown in Table C.3.1.

Table C.3.1: Raw material cost

Materials	**USD/ton**	**USD/kg**	**USD/gal**
Canola[a]	884	0.884	3.045
No 2 Diesel[b]	1102	1.102	3.197
OA[c]	890	0.890	2.860
EGBE[c]	900	0.900	3.073
EHL[c]	1090	1.090	7.630
Ethanol[c]	701	0.701	2.202

[a]Canola Council of Canada (http://www.canolacouncil.org/canolaprices.aspx); [b]Oklahoma local price; [c]Alibaba global trade market (http://www.alibaba.com).

Based on Table C.3.1, raw material cost for MF1 (see Table 5.3 for abbreviations) at 15.7 wt% of total surfactant and additives (OA/EHL/EGBE, mole ratio at 1:2:2; 5 mL of 50 vol% diesel and canola blend; 2 mL ethanol) would be \$2.875/gal. At equivalent energy content to No 2 diesel fuel, raw materials for MF1 would cost \$3.162/gal; whereas the current selling price of No 2 diesel fuel in Oklahoma is \$3.196/gal. Table C.3.2 shows the breakdown cost of MF1.

Table C.3.2: Cost estimation of MF1

	Composition in 1 kg (wt%)	Breakdown cost in 1 kg of MF (USD)
Canola	31.8	0.351
No 2 Diesel	29.4	0.259
Ethanol	22.0	0.155
OA	5.1	0.045
EGBE	5.6	0.056
EHL	5.1	0.050
	MF1 cost per kg (USD)	0.916
	MF1 cost per gallon (USD)	2.875

Production cost of microemulsion fuels is negligible compared to that of biodiesel because it only requires simple stirring. Therefore, total cost of raw materials and production of microemulsion fuels is less than that of soybean and canola biodiesel at equivalent energy content, which was approximately \$4.360/gal without incentive and \$3.015/gal with incentive (http://www.eia.doe.gov/oiaf/analysispaper/biodiesel/). The cost of B20 biodiesel (20 vol% canola and 80 vol% No 2 diesel fuel) is \$3.430 without incentives.

C.4 Confirmation of aggregate formation using dynamic light scattering equipment

Confirmation of aggregate formation for studied fuel blends was performed using particle sizer (PSS-NICOMP^{TM} ZLS 380, Santa Barbara, CA). Formulated fuel blends had particle size in the range of 1 – 20 nm, with 75% particle size distribution in the range of 5 – 6 nm. This result confirmed the presence of aggregates in the blends or possible reverse micellar microemulsion formation.