

12-2008

OPTIMIZATION OF BIODIESEL PRODUCTION FROM CRUDE COTTONSEED OIL AND WASTE VEGETABLE OIL: CONVENTIONAL AND ULTRASONIC IRRADIATION METHODS

Xiaohu Fan

Clemson University, xfan@clemson.edu

Follow this and additional works at: https://tigerprints.clemson.edu/all_dissertations

 Part of the [Food Science Commons](#)

Recommended Citation

Fan, Xiaohu, "OPTIMIZATION OF BIODIESEL PRODUCTION FROM CRUDE COTTONSEED OIL AND WASTE VEGETABLE OIL: CONVENTIONAL AND ULTRASONIC IRRADIATION METHODS" (2008). *All Dissertations*. 310.
https://tigerprints.clemson.edu/all_dissertations/310

This Dissertation is brought to you for free and open access by the Dissertations at TigerPrints. It has been accepted for inclusion in All Dissertations by an authorized administrator of TigerPrints. For more information, please contact kokeefe@clemson.edu.

OPTIMIZATION OF BIODIESEL PRODUCTION FROM CRUDE COTTONSEED
OIL AND WASTE VEGETABLE OIL: CONVENTIONAL AND ULTRASONIC
IRRADIATION METHODS

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Food Technology

by
Xiaohu Fan
December 2008

Accepted by:
Dr. Feng Chen, Committee Chair
Dr. Xi Wang
Dr. Terry H Walker
Dr. Joe E Toler

ABSTRACT

Biodiesel, derived from the transesterification of vegetable oils or animal fats with simple alcohols, has attracted more and more attention recently. As a cleaner burning diesel alternative, biodiesel has many attractive features including: biodegradability, non-toxicity, renewability and low emission profiles.

Although cottonseed oil was the first commercial cooking oil in the U.S, it has progressively lost its market share to some vegetable oils that have larger production and less cost. However, regarding the active researches on biodiesel production from vegetable oils, there is a promising prospective for the cottonseed oil as a feedstock for biodiesel production, which may enhance the viability of the cottonseed industry.

The focus of this research is to optimize the biodiesel production from crude cottonseed oil. The effect of variables including methanol/oil molar ratio, catalyst concentration, reaction time, reaction temperature, and rate of mixing on the biodiesel yield was examined and optimized by response surface methodology (RSM). Besides, a second-order model was deduced to predict the biodiesel yield. Confirmation experiment was further conducted, validating the efficacy of the model.

In addition to conventional transesterification method, low frequency ultrasonic irradiation was also investigated for biodiesel production. This study demonstrated that the ultrasound treatment was more efficient in biodiesel production than the conventional method. This was attributed to the ultrasound effect, which can make methanol to cavitate so as to disperse the oil phase into nano-droplets and form a fine emulsion of

methanol in oil. As a result, contact surface between the reagents is dramatically increased resulting in a significant increase of the reaction speed.

Moreover, engine performance test of the cottonseed oil biodiesel (cottonseed oil methyl esters, COME) was examined. The results showed that CO, CO₂ and NO_x emissions of the COME were lower than those of the No. 2 diesel fuel, although there was no significant difference at the statistical level of $p < 0.05$. The engine test also demonstrated a slightly higher amount of consumption and less tendency of coke formation from the COME than those from the No. 2 diesel fuel. In general, the cottonseed oil biodiesel exhibited friendly environmental benefits and acceptable stability, demonstrating its feasibility as an alternative fuel.

DEDICATION

I would like to dedicate this dissertation to my loving parents, Shiling Zhang and Chunheng Fan, my lovely sisters, Xiumei Fan and Xiuli Fan for their priceless support and endless encouragement. Particularly, to my beloved wife, Feiyan Tu, and my lovely daughter, Cathy, whose love and inspiration have enlightened me throughout the course of this work.

ACKNOWLEDGEMENTS

First of all, I wish to express my deepest gratitude to my advisor, Dr. Feng Chen, whose guidance, encouragement, wisdom, motivation, and expectations are indispensable to my achievements and will serve as a continuous inspiration for my future career.

My deepest thanks also go to Dr. Xi Wang, one of my Ph.D committee members, who gave me a lot of helpful ideas, suggestions, and discussions that contribute to the remarkable success achieved in this work. Dr. Wang deserves my greatest appreciation.

I would like to thank my other committee members, Dr. Terry Walker, for his permission for the use of his laboratory facilities, and Dr. Joe Toler, for his statistical discussion and guidance to my research.

I also would like to thank Dr. James C. Acton and Dr. Ronald D. Galyean for their technical help. I also appreciate Kim Collins' kindly help and all other faculties and staffs in the Department of Food Science and Human Nutrition for their directly and indirectly assistance.

Thanks go to all the members in my lab, Dr. Huaping Zhang, Mr. Mike Nigh, Mrs. Yongxiang Yu, Mrs. Juanjuan Yin, Miss Yenhui Chen, Miss Xiaowen Wang and Dr. Huarong Tong for their help in this research.

Finally, I would like to thank my family and friends in China. My success is directly related to their love and strong support.

TABLE OF CONTENTS

	Page
TITLE PAGE	i
ABSTRACT.....	ii
DEDICATION.....	iv
ACKNOWLEDGEMENTS.....	v
LIST OF TABLES.....	ix
LIST OF FIGURES	x
CHAPTER	
1. LITERATURE REVIEW	1
1.1 Introduction.....	1
1.2 Biodiesel Production Method-Transesterification	2
1.3 Variables Influencing the Transesterification Reaction	3
1.4 Biodiesel Production by Using Ultrasound.....	11
1.5 Lower-Cost Feedstocks for Biodiesel Production	12
1.6 From Glycerol to Value-Added Products	32
1.7 Significance of the Project.....	36
1.8 References.....	37
2. OPTIMIZATION OF BIODIESEL PRODUCTION FROM CRUDE COTTONSEED OIL BY USING CONVENTIONAL METHOD.....	50
Abstract	50
2.1 Introduction.....	51
2.2 Materials and Methods.....	52
2.3 Results and Discussion	55
2.3.1 Fractional Factorial Design and First-Degree Polynomial Model Analysis.....	56
2.3.2 The Central Composite Design and the Second-order Polynomial Model Analysis	58

Table of Contents (Continued)

	Page
2.3.3 The Response Surface and Ridge Max Analysis.....	58
2.4 Conclusions.....	60
2.5 Figures and Tables	62
2.6 References.....	73
3. ENGINE PERFORMANCE TEST OF COTTONSEED OIL BIODIESEL	75
Abstract.....	75
3.1 Introduction.....	76
3.2 Material and Methods	78
3.3 Results and Discussion	82
3.3.1 Effect of Feedstocks on Biodiesel Engine Emissions Compared with the No. 2 Diesel	82
3.3.2 Fuel Consumption and Coking	84
3.3.3 Effect of Color (pigments) in Biodiesel on Oxidative Stability	84
3.4 Conclusions.....	86
3.5 Figures and Tables	87
3.6 References.....	94
4. ULTRASONICALLY ASSISTED PRODUCTION OF BIODIESEL FROM CRUDE COTTONSEED OIL.....	96
Abstract.....	96
4.1 Introduction.....	97
4.2 Material and Methods	99
4.3 Results and Discussion	100
4.3.1 Effect of Methanol/oil Molar Ratio	100
4.3.2 Effect of Reaction Time.....	101
4.3.3 Effect of Catalyst Type and Concentration.....	102
4.3.4 Effect of Ultrasound Frequency.....	103
4.4 Conclusions.....	104
4.5 Figures and Tables	105
4.6 References.....	110

Table of Contents (Continued)

	Page
5. TRANSESTERIFICATION OF CRUDE COTTONSEED OIL TO PRODUCE BIODIESEL USING ULTRASONIC IRRADIATION: AN OPTIMIZED PROCESS APPLYING RESPONSE SURFACE METHODOLOGY	112
Abstract	112
5.1 Introduction.....	113
5.2 Material and Methods	116
5.3 Results and Discussion	118
5.3.1 RSM Analysis of Transesterification.....	118
5.3.2 Effect of Parameters.....	119
5.3.3 Attaining Optimum Conditions and Model Verification	121
5.3.4 The Advantages of Using Ultrasonic Irradiation to Produce Biodiesel	121
5.4 Conclusions.....	121
5.5 Figures and Tables	123
5.6 References.....	130
6. OTHER APPROACHES TO PRODUCE BIODIESELS	132
Abstract	132
6.1 Introduction.....	133
6.2 Materials and Methods.....	136
6.3 Results.....	138
6.4 Figures.....	140
6.5 References.....	145

LIST OF TABLES

Table	Page
2.1 3-Level-5-Factor Experimental Design	63
2.2 Experimental Matrix for the Factorial Design and Center Points.....	64
2.3 SAS Results of Statistical Analysis for the 2 ⁵ Factorial Design	66
2.4 Central Composite Design	69
3.1 Properties of Commercial Pacific Biodiesel Produced from Cottonseed Oil	87
3.2 Specifications of the No.2 Diesel.....	88
3.3 Comparison of Engine Emissions of COME Average, SOB and No.2 Diesel.....	89
3.4 Color Measurement of Biodiesels.....	91
3.5 Oxidative Stability Comparison of Biodiesels.....	92
3.6 The Effect of Gossypol Addition on COME A's Oxidative Stability	93
4.1 Effect of Ultrasound Frequency on the Biodiesel Yield.....	109
5.1 Independent Variable and Levels Used for CCRD in Methyl Ester Production.....	123
5.2 CCRD Arrangement and Responses for Methyl Ester Production.....	124
5.3 Regression Coefficients of Predicted Quadratic Polymial Model for Methyl Ester Production	125
5.4 Analysis of Variance (ANOVA) for the Quadratic Model.....	126

LIST OF FIGURES

Figure	Page
2.1	Chemical Reaction for Biodiesel Production..... 62
2.2	Biodiesel Yield vs. Temperature and Time 68
2.3	Response Surface and Contour Plot of the Effects of Methanol/oil Molar Ratio and Catalysts on the Yield of Biodiesel 70
2.4	HPLC Chromatogram of Crude Cottonseed Oil..... 71
2.5	HPLC Chromatogram of Biodiesel from Crude Cottonseed Oil 72
3.1	Fuel Consumption and Coking Index 90
4.1	The Phenomenon of Cavitation 105
4.2	Effect of Methanol/oil Molar Ratio on the Biodiesel Yield 106
4.3	Effect of Catalyst Type on the Biodiesel Yield 107
4.4	Effect of Catalyst Concentration on the Biodiesel Yield..... 108
5.1	Contour Plot of Methyl Ester Yield (wt%) in Terms of Coded Factors 127
6.1	GC Chromatogram of Supelco™ 37 Component FAME Mix Standard..... 140
6.2	GC Chromatogram of WCO Biodiesel..... 141
6.3	GC Chromatogram of COME A..... 142
6.4	HPLC Chromatogram of Biodiesel from WCO..... 143
6.5	TLC Results for <i>in situ</i> Transesterification of Crude Cottonseed Oil 144

CHAPTER 1

LITERATURE REVIEW

1.1 Introduction

Nowadays, the world energy demand has increased significantly due to the global industrialization and increase of population. As a result, the current limited reservoirs will soon be depleted at the current rate of consumption. The Oil and Gas Journal (O&GJ) estimates that at the beginning of 2004, the worldwide reserves still had 1.27 trillion barrels of oil and 6,100 trillion cubic feet of natural gas left. However, at today's consumption level of about 85 million barrels of oil per day and 260 billion cubic feet of natural gas per day, the current reserves can only be used for another 40 years for the oil and 64 years for the natural gas (Vasudevan & Briggs, 2008). Moreover, increase of pollutant emissions from the use of petroleum fuel will affect human health, such as respiratory system, nervous system and skin diseases etc. Both the increased energy needs and environmental consciousness have stimulated the research of searching an alternative fuel. Biodiesel may be the best answer due to its following advantages:

- (i) Reduces the country's dependence on imported petroleum.
- (ii) Be renewable and contributes less to global warming than petroleum fuel due to its closed carbon cycle. The primary feedstocks are sustainable and most of the carbon in the fuel can be removed from the air by the plant.
- (iii) Provides good engine performance and can be used without engine modification.
- (iv) Provides the market with biodiesels from sufficient production of vegetable

oils and animal fats, thus enhancing the rural economies.

(v) Biodegradable and nontoxic.

(vi) Exhibits lower combustion profile, especially SO_x.

1.2 Biodiesel Production Method-Transesterification

Direct use of vegetable oil as fuel for diesel engine can cause particle agglomeration, injector fouling due to its low volatility and high viscosity, which is about 10 to 20 times greater than petroleum diesel. There are four techniques applied to reduce the high viscosity of vegetable oils: dilution, micro-emulsification, pyrolysis, and transesterification. Among these methods, the transesterification seems to be the best option since this process can significantly reduce the high viscosity of vegetable oils. Furthermore, the physical properties of biodiesel produced by this simple process are very close to the petroleum diesel fuel.

Transesterification is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that alcohol is employed instead of water (Srivastava & Prasad, 2000). The transesterification process consists of a sequence of three consecutive reversible reactions, which include conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides. The glycerides are converted into glycerol and yield one ester molecule in each step.

Since this reaction is reversible, excess amount of alcohol is often used to help drive the equilibrium towards the right. In the presence of excess alcohol, the forward reaction is a pseudo-first order reaction and the reverse reaction is a second-order reaction.

1.3 Variables Influencing the Transesterification Reaction

1.3.1 Effect of Alcohol/oil Molar Ratio and Alcohol Type

The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, more alcohol is preferred to shift the equilibrium to form esters. Zhou *et al.* (Zhou, Konar & Boocock, 2003) studied the effect of alcohol/oil molar ratio on the single-phase base-catalyzed ethanolyse of sunflower oils. In that study, four molar ratios of ethanol to sunflower oil (6:1, 20:1, 25:1, and 30:1) were examined. The authors found that at ethanol/oil molar ratios of 20, 25, and 30:1, equilibrium was reached in 6 to 10 min at 23°C when 1.4% of potassium hydroxide was used; While at the molar ratio of 6:1, equilibrium could not be reached even after 30 min. Increasing the molar ratio did favor the formation of esters, but the difference for the range of molar ratios from 25:1 to 20:1 was small. Meher *et al.* (Meher, Dharmagadda & Naik, 2006) concluded that the reaction was faster with higher molar ratio of methanol to oil whereas longer time was required for lower molar ratio (6:1) to get the same conversion. In their research, the molar ratio of methanol to oil, i.e., 6:1, 9:1, 12:1, and 24:1, were investigated for optimizing biodiesel production from Karanja oil. Canakci *et al.* (Canakci & Gerpen, 1999) investigated the effect of different alcohol types on transesterification. Methanol, ethanol, 2-propanol, and 1-butanol were tested for a 48-h test period, with sulfuric acid catalyst concentration equal to 3% and the molar ratio of alcohol to oil at 6:1. The conversion was 87.8%, 95.8%, 92.9%, and 92.1% for methyl ester, ethyl ester, 2-propyl ester, and 1-butyl ester, respectively. Higher conversion rate was observed for the longer chain alcohols

compared with methanol. The authors attributed this to the fact that higher reaction temperatures were chosen due to the higher boiling point of the long chain alcohols. Also, long chain alcohols can increase the solubility between the oil and alcohol since they are more non-polar than shorter chain alcohols.

1.3.2 Effect of Catalyst Type and Concentration

Triglycerides in vegetable oils and animal fats are immiscible with methanol, so the catalyst is required to be added to enhance the transesterification. Both homogeneous and heterogeneous catalysts can be used in this process.

1.3.2.1 Homogeneous catalysts

Biodiesel production using homogeneous alkaline catalysts has been comprehensively studied since it has several advantages over acid catalysts.

- (1) The transesterification reaction is faster and the reaction conditions are mild.
- (2) The consumption of methanol is significantly less.
- (3) The catalyst is less corrosive.
- (4) The acid-catalyzed process requires a high methanol to oil molar ratio and high acid catalyst concentration.

Commonly used alkaline catalysts include sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide (NaOCH₃), and potassium methoxide (KOCH₃). While the acid numbers for ultimate product using NaOCH₃ were significantly lower than those using NaOH, NaOH is widely used in industrial biodiesel production due to its cheapness and effectiveness. Meka *et al.* (Meka, Tripathi & Singh, 2007) studied the effect of catalyst (NaOH) concentration on reaction time at two temperatures 50 and 60

°C for safflower oil, when the methanol/oil molar ratio was kept at 6:1. The authors found that in both cases, reaction time decreased proportionally with increase in catalyst concentration from 1% to 2%, but soap was formed when catalyst concentration was above 2%. Ataya *et al.* (Ataya, Dubé & Ternan, 2006) performed canola oil transesterification experiments and found triglyceride conversion increased when the catalyst (NaOH) concentration increased from 1% to 3%. Rashid *et al.* (Rashid & Anwar, 2008) evaluated the effect of catalyst type and concentration on the rapeseed oil ester yields, and observed that the hydroxides gave rise to higher yield than the counterpart methoxides. The results showed that 1% KOH was the optimal value when the concentration varied between 0.25% and 1.5%. This was in accordance with the result obtained by Tomasevic *et al.* (Tomasevic & Siler-Marinkovic, 2003) and Meher *et al.* (Meher, Dharmagadda & Naik, 2006). The same trends were observed for varying the concentration of NaOH from 0% to 1.5%. The best ester yield was achieved for NaOH concentration of 1%, which was also recommended by Freedman *et al.* (Freedman, Pryde & Mounts, 1984). In contrast, Vicente *et al.* (Vicente, Martínez & Aracil, 2004) drew a conclusion that biodiesel yields after separation and purification steps were higher for methoxide catalysts (NaOCH₃, KOCH₃) than for hydroxide catalysts (NaOH, KOH) when methanolysis of sunflower oil was conducted. This phenomenon of the yield loss was ascribed to the fact that hydroxide catalysts could cause more triglyceride saponification and methyl ester dissolution in glycerol. Moreover, among these catalyzed transesterifications, the reactions using NaOH were fastest.

Though alkaline catalysts have many advantages as mentioned earlier, they are more sensitive to free fatty acid and water. Their application in vegetable oil transesterification can cause soap formation by neutralizing the free fatty acid in the oil, which can partially consume the catalyst, thus decreasing the biodiesel yield. Usually in basic conditions, the acceptable total FFA and water content are 0.5% and 0.1%-0.3%, respectively (Williams, Mulcahy, Ford, Oliphant, Caldwell & Soriano, 2007). Acid catalysts were preferred for biodiesel production when the FFA is high. The acids could be sulfuric acid (H_2SO_4), phosphoric acid, hydrochloric acid (HCl) or organic sulfonic acid. H_2SO_4 and HCl are commonly preferred. Goff *et al.* (Goff, Bauer, Lopes, Sutterlin & Suppes, 2004) studied a single step acid-catalyzed alcoholysis of soybean oil using sulfuric, hydrochloric, formic, acetic, and nitric acids at 0.1 and 1 wt.% loadings and temperatures of 100 and 120°C in sealed ampules, only sulfuric acid was found effective. Further kinetic studies demonstrated that at 100°C, 0.5 wt.% sulfuric acid catalyst, and nine times methanol stoichiometry, >99 wt.% conversion of TG was achieved in 8 h. The same conversion could be obtained at less than 4 h if FFA concentrations are less than 0.8 wt.%. Reaction conditions near 100°C at 0.1 to 0.5 wt.% were identified as providing the necessary conversions in a 24-h batch cycle. Zullaikah *et al.* (Zullaikah, Lai, Vali & Ju, 2005) undertook a two-step acid-catalyzed process for the production of biodiesel from rice bran oil. The first step was carried out at 60°C and the second step at 100°C. In their work, the organic phase of the first step reaction product was used as the substrate for a second acid-catalyzed methanolysis. By this two-step sulfuric acid catalyzed reaction, the yield could be more than 98% in less than 8h. Williams *et al.* (Williams, Mulcahy, Ford,

Oliphant, Caldwell & Soriano, 2007) successfully prepared biodiesel from waste vegetable oil by 1% sulfuric acid catalyzed reaction at 117°C in which butanol was selected as alcohol. Al-Widyan *et al.* (Al-Widyan & Al-Shyoukh, 2002) evaluated the effect of different concentrations of HCl, H₂SO₄, and excess ethanol on the transesterification of waste palm oil. The authors reported that higher catalyst concentrations (1.5-2.25 M) produced biodiesel with lower specific gravity in a much shorter reaction time than lower concentrations. The specific gravity served as an indicator for the effectiveness and completeness of the conversion process. Lower values meant more complete reaction since more of the heavy glycerol was removed. At 2.25 M, the H₂SO₄ performed better than HCl.

1.3.2.2 Heterogeneous catalysts

Although homogeneous catalyzed process gives a high conversion level, the reaction is energy intensive and the catalyst needs to be removed. In addition, the by-product, glycerol, is difficult to recover. In contrast, the application of heterogeneous catalysts can simplify the post-treatment, and eliminate the cost associated with the homogeneous catalysts.

Kiss *et al.* (Kiss, Dimian & Rothenberg, 2006) reported the results of screening catalyst candidates such as zeolites, ion-exchange resins, and mixed metal oxides. Sulphated zirconia was found to be a good candidate due to its better activity, selectivity and stability. Furuta *et al.* (Furuta, Matsushashi & Arata, 2004) prepared sulfated tin and zirconium oxides and tungstated zirconia. These superacid catalysts were evaluated in the transesterification of soybean oil with methanol at 200-300°C. The conversion of over

90% was obtained using tungstated zirconia-alumina, which exhibited good performance because of its activity. Serio *et al.* (Serio, Tesser, Dimiccoli, Cammarota, Nastasi & Santacesaria, 2005) studied the use of carboxylic salts (such as Cd, Mn, Pb, Zn carboxylic salts) as a possible alternative catalyst since they are active even in the presence of high FFA concentrations. A correlation of the activities with the cation acidity was further established.

Solid base catalysts include simple metal oxides such as MgO and CaO in supported or unsupported form, Zn-Al mixed oxides, cesium-exchanged zeolite, anion exchange resins, polymer-supported guanidines, Na/NaOH/Al₂O₃, and K- and Li-promoted oxides.

NaX faujasite zeolite such as occluded sodium oxide (NaO_x/NaX) and occluded sodium azide (NaO_x/NaX), and Titanosilicate structure-10 (ETS-10) were preferred to transesterify soybean oil. The basicity of zeolites NaX and ETS-10 were enhanced by ion exchange with higher electropositive metals like K and Cs using conventional techniques. At temperatures of 150°C and 120°C, the conversion to methyl esters could reach above 90% in 24h. Compared with homogeneous reaction, the increased conversion of one to over two orders of magnitude was observed when metal and zeolite catalysts were used (Suppes, Dasari, Doskocil, Mankidy & Goff, 2004). Kim *et al.* (Kim, Kang, Kim, Park, Kim & Lee *et al.*, 2004) developed the Na/NaOH/γ-Al₂O₃ heterogeneous base catalyst, which offered almost the same activity under the optimized reaction conditions compared with conventional homogeneous NaOH catalyst. Li *et al.* (Li & Xie, 2006) studied Zn/I₂ as an alternative catalyst for biodiesel production from soybean oil. The highest

conversion of 96% was obtained under the optimum condition (methanol oil molar ratio, 42:1; catalyst amount of Zn 5 wt.% and I₂ 5 wt.%; reaction temperature, 65°C). Xie *et al.* (Xie, Peng & Chen, 2006) used alumina loaded with potassium as a solid base catalyst for soybean oil transesterification. The optimal catalyst was obtained with 35% wt.% KNO₃ loaded on Al₂O₃ and calcined at 773 K for 5h. The highest conversion could reach 87% with a molar ratio of methanol to soybean oil at 15:1, reaction time 7h, and 6.5% amount of catalyst amount. The authors emphasized that the existence of the active basic sites were probably due to the formation of either K₂O species or Al-O-K group in the composite. They also selected Ba-ZnO as a solid catalyst to transesterify soybean oil. In that study, the Ba-ZnO with loading of 2.5 mmol/g Ba on ZnO was calcined at 873 K for 5h. 95.8% conversion of soybean oil was achieved using this optimal catalyst with a 12:1 molar ratio of methanol to oil and a catalyst concentration of 6 wt.% (Xie & Yang, 2007). Dossin *et al.* (Dossin, Reyniers, Berger & Marin, 2006) performed simulations of the industrial scale biodiesel production from rapeseed oil by transesterification of triolein with methanol using MgO catalyst. The reaction occurred between methanol adsorbed on a magnesium oxide free basic site and the glyceride from liquid phase. The simulations indicated that a continuous production of 100,000 tonnes of biodiesel per year can be achieved at 323 K in a continuous stirred reactor of 25m³ containing 5700 kg of MgO catalyst. CaO could also be used as the catalyst for biodiesel production according to reference (Granados, Poves, Alonso, Mariscal, Galisteo & Moreno-Tost *et al.*, 2007). In their research, the activity of activated CaO was studied and found they were able to be reused for several runs without significant deactivation. Meher *et al.* (Meher, Kulkarni,

Dalai & Naik, 2006) optimized reaction conditions for methanolysis of karanja oil using solid basic Li/CaO catalyst. 94.9% conversion could be reached at 2 wt.% of catalyst concentration, 65°C, 12:1 molar ratio of methanol to oil, and 8h reaction time. Serio *et al.* (Serio, Cozzolino, Tesser, Patrono, Pinzari & Bonelli *et al.*, 2007) investigated the possibility of using vanadyl phosphate-based catalysts in biodiesel production. It was reported that the reaction yield was about 80% in the temperature range 150-180°C in less than 1h. Second transesterification stage after glycerol and catalyst separation was recommended to achieve higher conversions required by industrial plants. Shumaker *et al.* (Shumaker, Crofcheck, Tackett, Santillan-Jimenez & Crocker, 2007) utilized calcined Li-Al layered double hydroxide catalysts to produce biodiesel from soybean oil. This catalyst exhibited high activity. At low catalyst loadings (2-3 wt.%) and short reaction time (less than 2h), near quantitative conversion was achieved.

1.3.3 Effect of Reaction Time and Temperature

Freedman *et al.* (Freedman, Pryde & Mounts, 1984) investigated the transesterification of peanut, cottonseed, sunflower and soybean oil under the condition of 6/1 methanol/oil molar ratio, 0.5% sodium methoxide catalyst concentration and 60°C temperature. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1h, the conversion was almost the same for all four oils (93–98%). Ma *et al.* (Ma, Clements & Hanna, 1999) evaluated the effect of reaction time on transesterification of beef tallow with methanol. Due to the difficulty of mixing and dispersion of methanol into beef tallow, the reaction was very slow during the first

minute. From 1 to 5 min, the reaction proceeds very fast. At about 15 min, the production of beef tallow methyl esters reached the maximum value.

The boiling point of methanol is 337.8 K. Reaction temperature higher than this will burn the alcohol and will cause reduced yield. Leung *et al.* (Leung & Guo, 2006) indicated that reaction temperature higher than 323 K had a negative impact on the product for neat oil.

1.4 Biodiesel Production by Using Ultrasound

In recent years, ultrasound received increasing interest in producing biodiesel due to its high mixing efficiency. Many studies were conducted in this area. Hanh *et al.* evaluated the methanolysis and ethanolysis of triolein under ultrasonic irradiation. The effects of molar ratio, catalyst concentration and temperature on transesterification of triolein were examined and the optimum condition was obtained (Hanh, Dong, Okitsu, Maeda & Nishimura, 2007; Hanh, Dong, Starvarache, Okitsu, Maeda & Nishimura, 2008). The ultrasonic irradiation method was proved to be efficient, time saving and economically functional to produce biodiesel fuel. Colucci *et al.* (Colucci, Borrero & Alape, 2005) investigated the feasibility of using ultrasonic mixing to produce biodiesel from soybean oil. The authors found the reaction rate constants were three to five times higher than those reported in the literature for mechanical agitation. This was explained by the fact that the interfacial area and activity of the microscopic and macroscopic bubbles increased when ultrasonic waves of 20 kHz were applied to a two-phase reaction system. This explanation was further confirmed by Wu *et al.* (Wu, Yang, Colucci & Grulke, 2007), who investigated the effect of ultrasonification on droplet size in biodiesel

mixtures. Their results showed ultrasonic mixing produced dispersions with average droplet sizes 42% smaller than those generated using standard impellers, leading to larger interfacial area for the transesterification to occur. Armenta *et al.* (Armenta, Vinatoru, Burja, Kralovec & Barrow, 2007) used ultrasonic energy to produce fatty acid ethyl esters from fish oil as the feedstock. The study showed that ultrasonic energy not only could be used to efficiently transesterify fish oil, but applicable for the production of EPA and DHA. Stavarache *et al.* (Stavarache, Vinatoru, Nishimura & Maeda, 2005; Stavarache, Vinatoru & Maeda, 2006; Stavarache, Vinatoru & Maeda, 2007; Stavarache, Vinatoru, Maeda & Bandow, 2007) also conducted an extensive study concerning the application of ultrasonic energy on the transesterification of commercial edible oil. The researchers concluded that by using ultrasound, the reaction time was much shorter than by mechanical stirring. It was also found that under ultrasonic activation the rate-determining reaction switches from DG→MG (classical mechanical agitation) to MG + ROH→Gly + ME (ultrasonically driven transesterification).

In summary, using ultrasonic irradiation to transesterify vegetable oil will make biodiesel production more efficient than using conventional method.

1.5 Lower-cost Feedstocks for Biodiesel Production

Biodiesel can be produced from triglycerides present in naturally occurring fats and oils by transesterification with alcohol, usually methanol, in the presence of catalyst. Transesterification is a reversible process and glycerol is as the by-product. The feedstocks used for biodiesel production currently are mainly high quality food-grade vegetable oils, such as soybean oil in United States, rapeseed oil in European, palm oil in

Malaysia (Azam, Waris & Nahar, 2005). However, in order to compete with diesel fuel and survive in the market, lower-cost feedstocks are preferred, including waste cooking oil (WCO), grease, soapstocks, since feedstocks costs are more than 85% of the total cost of biodiesel production (Haas, McAloon, Yee & Foglia, 2006; Zhang, Dubé, McLean & Kates, 2003). The non-edible oils, like *Jatropha*, can also be used to produce biodiesel (Tiwari, Kumar & Raheman, 2007; Berchmans & Hirata, 2008; Tapanes, Aranda, Carneiro & Antunes, 2008; Kachhwaha, Maji, Faran, Gupta, Ramchandran & Kumar, 2006; Shah & Gupta, 2007; Rathore & Madras, 2007). In addition, growing interest arises concerning algae-based biodiesel (Aresta, Dibenedetto, Carone, Colonna & Fragale, 2005).

Though biodiesel has many advantages compared with petroleum diesel, its high production cost has become the primary barrier to its commercialization. Currently, biodiesel unit price is 1.5-3.0 times higher than that of petroleum derived diesel fuel depending on feedstock (Zhang, Dubé, McLean & Kates, 2003; Zhang, Dubé, McLean & Kates, 2003; Demirbas, 2007). Therefore, many studies have focused on the utilization of lower-cost feedstocks, such as WCO, grease, soapstock, *Jatropha*, and algae to produce biodiesel.

1.5.1 Biodiesel Production from Waste Cooking Oil

Waste vegetable oils are generally low in cost. They usually can be collected from large food processing and service facilities. However, due to very high temperature during food frying process, chemical reactions such as hydrolysis, polymerization and oxidation will occur, which can lead to the increase of free fatty acid (FFA) level. Hence,

acid catalysis is preferred since it is insensitive to FFA (Freedman, Pryde & Mounts, 1984). Zheng *et al.* (Zheng, Kates, Dubé & McLean, 2006) studied the reaction kinetics of acid-catalyzed transesterification of waste frying oil. The authors found that at the methanol/oil molar ratio of 250:1 at 70°C or in the range 74:1-250:1 at 80°C, the reaction was a pseudo-first-order reaction. High yield of 99±1% could be achieved at both 70°C and 80°C and a stirring rate of 400 rpm, using a feed molar ratio oil:methanol:acid of 1:245:3.8. In contrast, Wang *et al.* (Wang, Ou, Liu, Xue & Tang, 2006) investigated a two-step catalyzed processes for synthesis of biodiesel by using WCO from Chinese restaurants. In the first step, ferric sulfate-catalyzed methanolysis was carried out, while potassium hydroxide catalysis was performed in the second step. The authors made a conclusion that compared with one-step sulfur acid catalysis the two-step catalyzed process provided a more simple and economic method to produce biodiesel from WCO. Moreover, the by-products of glycerol and soapstock in this process could be easily handled. Similarly, Issariyakul *et al.* (Issariyakul, Kulkarni, Dalai & Bakhshi, 2007) also used the two-step process to transesterify WCO, except that sulfuric acid was selected as acid catalyst and mixtures of methanol and ethanol were used for transesterification in order to use the better solvent property of ethanol and rapid equilibrium using methanol. More than 90% ester was obtained by using the two-stage method compared with yield of ~50% ester by using the single stage alkaline catalyst. In the above mentioned two-step process that was developed by Canakci *et al.* (Canakci & Gerpen, 2001), acid catalyst (usually sulfuric acid) was first chosen to reduce the FFA to less than 1%, then the pretreated feedstock was transesterified under alkaline catalysis. The advantage of this

two-step process relies on the fact that it can increase the reaction rate by using alkaline catalyst and avoid soap formation by applying acid catalyst.

In addition to homogeneous acid and base catalysts, enzyme catalyst was also investigated to transesterify WCO. Chen *et al.* (Chen, Ying & Li, 2006) used immobilized lipase from *Rhizopus oryzae*. Their study focused on optimization of several parameters, including the molar ratio of methanol to waste oils, biocatalyst load, adding method, reaction temperature, and water content. Their results indicated that methanol/oil ratio of 4/1, immobilized lipase/oil of 30 wt.% and 40°C were suitable for waste oils under 1 atm. The irreversible inactivation of the lipase was presumed and a stepwise addition of methanol to reduce inactivation of immobilized lipases was proposed. Under the optimum conditions the yield of methyl esters was around 88–90%.

Heterogeneous catalysts, such as acidic ion-exchange resins, could also be applied on esterification of FFA in WCO. It possessed several advantages over homogeneous catalysts, for example, corrosion prevention (Silva & Rodrigues, 2006), easy separation, and high FFA conversions (Loterio, Liu, Lopez, Suwannakarn, Bruce & Goodwin, 2005). Özbay *et al.* (Özbay, Oktar & Tapan, 2008) examined activities of resins in direct FFA esterification in the temperature range of 50-60°C and found all resin catalysts were active. The authors attributed this to the superiority of physical properties of resins. The differences of catalytic activities between resins were concluded to be related to the size of average pore diameters and magnitude of BET surface area. The experimental results also indicated that FFA conversion increased with increasing reaction temperature and catalyst amount.

The performances of biodiesel obtained from WCO in terms of engine performance and emissions were also studied by many researchers. Çetinkaya *et al.* (Çetinkaya, Ulusoy, Tekin & Karaosmanoğ, 2005) investigated the engine performance of biodiesel fuel originated from used cooking oil in a Renault Mégane automobile and four stroke, four cylinder, F9Q732 code and 75 kW Renault Mégane Diesel engine in winter conditions for 7500 km road tests in urban and long distance traffic. The results showed that the torque and brake power output obtained from the used cooking oil biodiesel were 3-5% less than those of No. 2 diesel fuel. The engine exhaust gas temperature at each engine speed of biodiesel was less than that of No. 2 diesel fuel. Higher values of exhaust pressures were found for No. 2 diesel fuel at each engine speed. The injection pressures of both fuels were similar. Based on the experimental results, the authors concluded that used cooking oil biodiesel could be recommended as a No. 2 diesel fuel alternative for winter conditions. Lin *et al.* (Lin, Wu & Chang, 2007) also used WCO to prepare biodiesel and then conducted a study in which the exhaust tail gas of biodiesels were compared when the engine was operated by using the different fuel types, including neat biodiesel, biodiesel/diesel blends, and normal diesel fuels. Among the collected data, the authors found that B20 and B50 were the optimum fuel blends. Al-Widyan *et al.* (Al-Widyan, Tashtoush & Abu-Qudais, 2002) utilized ethyl ester of waste vegetable oils as fuel in diesel engines and initiated a study to investigate its potential to substitute oil-based diesel fuel. The fuels evaluated included 100% ester, several ester/diesel blends and diesel fuel as the baseline fuel. The tests were run on a standard test rig of a single-cylinder, direct-injection diesel engine. The results indicated that the

blends burned more efficiently with less specific fuel consumption, resulting in higher thermal efficiency. Moreover, less carbon monoxide (CO) and unburned hydrocarbons (HC) than diesel fuel were produced for the blends. The blends and 100% ester surpassed the diesel fuel in essentially all aspects of engine performance considered. Overall, 100% ester and 75:25 ester/diesel gave the best results regarding performance, while as for emissions concerned, the 50:50 blends exhibited the best results. The ester fuel demonstrated a high potential as fuel for diesel engines. Similar trend for emission results was observed by Dorado *et al.* (Dorado, Ballesteros, Arnal, Gómez & López, 2003), who characterized exhaust emissions from a diesel engine fueled with transesterified waste olive oil and found lower emissions of CO, carbon dioxide (CO₂), nitrogen oxide (NO), and SO₂. The particulate emissions from used cooking oil biodiesel were also evaluated by the other research group (Lapuerta, Rodríguez-Fernández & Agudelo, 2008). The biodiesel fuels were tested in a DI diesel commercial engine either pure or in 30% and 70% v/v blends with a reference diesel fuel. A sharp decrease was observed in both smoke and particulate matter emissions as the biodiesel concentration increased. This was attributed to the fact that the oxygen content of the biodiesel improved the oxygen availability in rich-zone flames in the combustion chamber. Recently, an environmental approach was suggested by Nas *et al.* (Nas & Berkay, 2007), who presented an overview of energy potential of biodiesel generated from WCO. The authors finally drew a conclusion that biodiesel could reduce nearly all forms of air pollution, especially air toxics and cancer-causing compounds.

1.5.2 Biodiesel Production from Grease

Greases also are one of the less-expensive feedstocks for biodiesel production. Greases mainly contain triglycerides (TG), diglycerides (DG), monoglycerides (MG), and FFA (8-40%). A grease containing 8-12 wt.% FFA is categorized as a yellow grease, and a grease containing >35 wt.% FFA is categorized as a brown grease (Kulkarni & Dalai, 2006). Canakci *et al.* (Canakci & Gerpen, 2001) extended their two-step process to yellow and brown grease, and was successfully scaled up the process to pilot plant. The biodiesel produced from yellow grease was further tested in a four-cylinder turbocharged diesel engine. Significant reductions in particulates, CO, and HC were observed compared with those of the No. 2 diesel (Canakci & Gerpen, 2003). Although the pretreatment step could reduce the FFA content in the greases to <1 wt.%, a large amount of base catalyst was required to neutralize the acid catalyst remaining in the pretreated greases, thus increased the overall biodiesel production cost. As a solution, Ngo *et al.* (Ngo, Zafiropoulos, Foglia, Samulski & Lin, 2008) developed an efficient procedure for the biodiesel production from greases, in which a series of diarylammonium catalysts were used that are highly effective in catalyzing the esterification of the FFA present in greases (12-40 wt.% FFA). At a catalyst loading of 2-3 mol%, high conversions of FFA to esters (95-99%) were achieved by treating the greases with 5-20 equiv of methanol at 95 °C for 2h. The treated greases had a final FFA content of 0.5-1 wt.%. The authors also incorporated these diarylammonium catalysts into insoluble porous polymers via free radical-initiated polymerization. The polymer-immobilized catalysts were found to be equally effective as their homogeneous counterparts in esterifying FFA to esters. More

importantly, the heterogeneous catalysts could be readily removed from the treated greases and reused for esterification reactions upon reactivation with triflic acid.

Other novel approaches were also reported. Cao *et al.* (Cao, Dubé & Tremblay, 2008) used a continuous membrane reactor to produce biodiesel from different feedstocks, including yellow and brown grease. The high purity biodiesel produced could meet and exceed the ASTM D6751 standard.

1.5.3 Biodiesel Production from Soapstock

Soapstock, known as the by-product of the refining of vegetable oils, is another low value feedstock for biodiesel production. Soapstock contains a substantial amount of water, which can be emulsified with the lipid constituents and is difficult to remove. In addition, the presence of both FFA and acylglycerols makes the transesterification reaction more complicated. Alkaline catalysis cannot be utilized due to the high FFA level (Canakci & Gerpen, 2001). Haas *et al.* (Haas, Bloomer & Scott, 2000) developed a simple, high-efficiency method for synthesis of biodiesel from soybean oil soapstock. The process involved two steps: the first step, alkaline hydrolysis of all lipid-linked fatty acid ester bonds and the second step, acid-catalyzed esterification of the resulting fatty acid sodium salts. In the first step, all glycerides and phosphoglycerides in the soapstock could be completely saponified. After water removal, the resulting FFA sodium salts were rapidly and quantitatively converted into fatty acid methyl ester (FAME) by incubation with methanol and sulfuric acid at 35°C and ambient pressure in the second step. The specifications of the FAME produced could meet the current specifications for biodiesel. This bench-scale method was further developed to the small pilot scale,

producing about 2.5 L of material per run (Haas, Scott, Alleman & McCormick, 2001). All variables examined for the ester product, including flash point, water and sediment, carbon residue, sulfated ash, density, kinematic viscosity, sulfur, cetane number, cloud point, copper corrosion, acid number, free glycerin, and total glycerin were within the provisional biodiesel specifications of the ASTM. Density and iodine values were comparable to those of commercial soy-based biodiesel. The emission profile was quite similar to that of biodiesel produced from refined soy oil, showing the reductions of total hydrocarbons, particulates and CO, compared with petroleum diesel fuel. However, Haas *et al.* (Haas, Michalski, Runyon, Nunez & Scott, 2003) found that though this method could achieve the efficient production of high-purity biodiesel, substantial amounts of solid sodium sulfate were generated as a by-product. The cost related to the disposal of this waste material could be high. Therefore, they only used acid catalyzed esterification to produce biodiesel from soapstock. The optimal conditions for the maximum esterification were found to be at 65°C, 26h, a molar ratio of total FA/methanol/sulfuric acid of 1:1.5:1.5. Further economic analysis by Haas (Haas, 2005) suggested that the production cost of soapstock biodiesel would be approximately US\$ 0.41/l, a 25% reduction relative to the estimated cost of biodiesel produced from soy oil.

Jin *et al.* (Jin, Zhu, Fan & Yu, 2008) developed a three-step process for producing biodiesel from the mixture of oil sediments (OS) and soapstocks (SS), at the same time, phosphatides were obtained. In the first step, the OS-SS mixture was extracted with ethyl ether and the mixture was divided into three phases. Cooled acetone was chosen to extract the organic top phase, including triglycerides and phosphatides. Phosphatides

were separated from triglycerides since they were insoluble in the acetone. In the second step, soap phase was acidified with sulfuric acid to yield fatty acid. Then the so called “high acid” oil was efficiently converted into methyl esters by acid-catalyzed esterification. The esterification reaction was carried out with 5:1 methanol/oil (mol/mol) in the presence of 3% sulfuric acid as an acid catalyst at 85°C for 5h. Biodiesel recovery under these conditions was 92.1% of theoretical. Alkaline catalyzed transesterification process was performed in the third step to convert the triglycerides into biodiesel and glycerol. The maximum ester yield of 94% was obtained under the optimal variables: 6/1 methanol/oil (mol/mol), 1% NaOH (wt.%), 65°C, and 1h. Five important fuel properties of biodiesel from the OS-SS mixture, including density (at 15°C), kinematic viscosity (at 40°C), flash point, calorific value, and acid value, were found to be comparable to those of the No. 2 diesel fuel and conforming to both the American and German standards for biodiesel.

Recently, Wang *et al.* (Wang, Lee, Park, Wu & Yuan, 2007) pointed out three major disadvantages of the process developed by Haas: (1) High temperature steam is required since conventional acidulation method is taken to recover acid oil from soapstock; (2) Additional process, saponification of the glycerides, is needed to convert them to free fatty acid salts; (3) The esterification reaction time is too long, leading to low productivity. The authors developed an attractive method to produce biodiesel from soybean soapstock. Separation of extracted acid oil from soapstock was performed with only sulfuric acid solution under the ambient temperature ($25\pm 2^\circ\text{C}$). The maximum acid oil recovery yield of 97% could be achieved based on the total fatty acids of the

soapstock. The acid oil could be directly converted into biodiesel at 95°C in a pressurized reactor within 5h and the yield of purified biodiesel was 94% based on the total fatty acids of the soapstock. The optimal esterification conditions were determined to be a weight ratio of 1:1.5:0.1 of acid oil/methanol/sulfuric acid. After distillation, the biodiesel produced by using this method could meet the Biodiesel Specification of Korea.

Besides soybean oil soapstock, other soapstocks are also of interest to be utilized to produce biodiesel, thus increasing the potential supply of this fuel as well. Usta *et al.* (Usta, Öztürk, Can, Conkur, Nas & Çon *et al.*, 2005) first used hazelnut soapstock/waste sunflower oil mixture to produce biodiesel. The process involved two steps, including acid (sulfuric acid) and base (sodium hydroxide) catalysis. The hazelnut soapstock/waste sunflower oil mixture was first heated to 100°C to remove the water. Then, the mixture was cooled down to 35°C before the 2nd-step catalysis. The effects of the biodiesel addition to the diesel fuel on the performance and emissions of a four cycles, four cylinder, turbocharged indirect injection diesel engine were investigated at both full and partial loads. Experimental results indicated that the hazelnut soapstock/waste sunflower oil methyl ester could be partially substituted for diesel fuel at most operating conditions without any engine modification and preheating of the blends. Keskin *et al.* (Keskin, Gürü, Altıparmak & Aydın, 2008) used cottonseed oil soapstock to produce biodiesel, then the cottonseed oil soapstock biodiesel was blended with diesel fuel. The blends were tested in a single cylinder direct injection diesel engine. It was reported that high calorific value and cetane number, low sulfur and aromatic content, and similar characteristics were observed for the blends. The power output and torque of engine with blends were

decreased by 6.2% and 5.8%, respectively. Particulate material emission of the engine with blends at maximum torque speed was decreased by 46.6%. It was concluded that blends of cottonseed oil soapstock biodiesel and diesel fuel could be used as alternative fuels in conventional diesel engines without any major changes. However, since biodiesel has a solvent effect that may release deposits accumulated on tank walls and pipes from previous diesel fuel usage, the release of deposits may end up in fuel filters, which needs to be checked more frequently.

In summary, WCO, grease, and soapstock are potential feedstocks for biodiesel production, which can lower the cost of biodiesel since they are inexpensive. However, since all these feedstocks contain high FFA, it will cause soap and water formation when using alkaline catalyst, which could decrease the ester yield and make the separation of ester, glycerol, and wash water more difficult. Acid catalysts can convert FFAs into esters, but the reaction rate is too slow. Moreover, this process requires more alcohol and large reactors and it is corrosive (Canakci & Sanli, 2008). The two-step process, of which the first step serves as a pretreatment, is usually preferred. However, this will increase the additional unit cost. Supercritical transesterification process can be an alternative method due to the following advantage: Pretreatment step, soap and catalyst removal are not necessary since catalyst is not required (He, Wang & Zhu, 2007; Demirbaş, 2002; Kasteren & Nisworo, 2007; Han, Cao & Zhang, 2005); The reaction duration is significantly shorter than traditional transesterification reaction (Saka & Kusdiana, 2001); The reaction is not sensitive to both FFA and water (Kasteren & Nisworo, 2007; Kusdiana & Saka, 2004). However, this method requires high molar ratio of alcohol to

feedstock (He, Wang & Zhu, 2007; Demirbaş, 2002; Saka & Kusdiana, 2001) and high reaction pressure and temperature, which will cause high operating cost.

1.5.4 Biodiesel Production from *Jatropha* Oil

There is growing interest for biodiesel production from non-edible oil source, like *Jatropha curcas L.* (JCL). JCL is a plant belonging to Euphorbiaceae family, which is a non-edible oil-bearing plant widespread in arid, semi-arid and tropical regions of the world (Chhetri, Tango, Budge, Watts & Islam, 2008). JCL has an estimated annual production potential of 200 thousand metric tones in India and can grow in waste land (Srivastava & Prasad, 2000). Singh *et al.* (Singh, Vyas, Srivastava & Narra, 2008) gave detailed information on the use of different components of JCL fruit for energy purposes. It was found that the shell could be for combustion, hull/husk for gasification, cake for production of biogas, spent slurry as manure, oil and biodiesel (made from *Jatropha* oil) for running CI engines.

The kernels of JCL have about 50% oil. The oil recovery in mechanical expeller was about 85%, while more than 95% recovery of oil could be achieved when extracted by solvent method. The biodiesel from JCL oil has a great potential due to its comparable properties to diesel, such as calorific value and cetane number (Sirisomboon, Kitchaiya, Pholpho & Mahuttanyavanitch, 2007). Therefore, many researchers have shown great interest in using *Jatropha* oil to produce biodiesel. Azam *et al.* (Azam, Waris & Nahar, 2005) found FAME of *Jatropha curcas* were most suitable for use as biodiesel and it met the major specification of biodiesel standards of USA, Germany and European Standard Organization. Sarin *et al.* (Sarin, Sharma, Sinharay & Malhotra, 2007) made an

appropriate blends of *Jatropha* and palm biodiesel to improve oxidation stability and low temperature property based on the fact that *Jatropha* biodiesel has good low temperature property and palm biodiesel has good oxidative stability. It was found that antioxidant dosage could be reduced by 80-90% when palm oil biodiesel is blended with *Jatropha* biodiesel at about 20-40%. This techno-economic combination could be an optimum mix for Asian Energy Security. Tiwari *et al.* (Tiwari, Kumar & Raheman, 2007) used response surface methodology to optimize three important reaction variables, including methanol quantity, acid concentration, and reaction time. The optimum combination for reducing the FFA of *Jatropha* oil from 14% to less than 1% was found to be 1.43% v/v sulfuric acid catalyst, 0.28 v/v methanol-to-oil ratio and 88 min reaction time at 60°C for producing biodiesel. The properties of *Jatropha* oil biodiesel conformed to the American and European standards. As comparison, Berchmans *et al.* (Berchmans & Hirata, 2008) developed a two-step pretreatment process in which the high FFA (15%) of *Jatropha curcas* seed oil was reduced to less than 1%. In the first step, the reaction was carried out with 0.60 w/w methanol-to-oil ratio in the presence of 1 wt.% sulfuric acid as an acid catalyst in 1h at 50°C. In the second step, the transesterification reaction was performed using 0.24 w/w methanol-to-oil ratio and 1.4 wt.% sodium hydroxide as alkaline catalyst to produce biodiesel at 65°C. The final biodiesel yield of 90% in 2h was reported. As well as experimental study, theoretical studies of reaction mechanism were also conducted regarding to base-catalyzed transesterification of the glycerides of the *Jatropha* oil (Tapanes, Aranda, Carneiro & Antunes, 2008). In that study, semi-empirical AM1 molecular orbital calculations were used to investigate the reaction pathways of base-

catalyzed transesterification of glycerides of palmitic, oleic and linoleic acid. The researchers concluded that the reaction mechanism included three steps: Step 1- Nucleophilic attack of the alkoxide anion on the carbonyl group of the glyceride to form a tetrahedral intermediate. Step 2-Breaking of the tetrahedral intermediate to form the alkyl ester and the glyceride anion. Step 3-Regeneration of the active catalyst, which may start another catalytic cycle. This study suggested that the Step 2, decomposition of the tetrahedral intermediate, determined the rate of base-catalyzed transesterification of glycerides.

A lot of different approaches were taken when producing biodiesel from *Jatropha* oil. In addition to conventional methods, preparation of biodiesel from *Jatropha* oil using ultrasonic energy was investigated (Kachhwaha , Maji , Faran , Gupta , Ramchandran & Kumar, 2006). Low frequency ultrasound (33 kHz) was applied to transesterify *Jatropha* oil with methanol in the presence of base catalyst at 6:1 methanol/oil molar ratio. The reaction time (about 15-30 min) was much shorter than conventional mechanical stirring method. This method was proved to be efficient and economically functional. Moreover, enzyme catalysts were also utilized for biodiesel production from *Jatropha* oil. Shah *et al.* (Shah & Gupta, 2007) evaluated the lipase from *P. cepacia* for conversion of *Jatropha* oil into biodiesel. The best yield of 98% was obtained by using *Pseudomonas cepacia* lipase immobilized on celite at 50°C in the presence of 4-5% (w/w) water in 8h. With respect to economic factor, this enzyme-based process could use commercial grade ethanol instead of expensive grade ethanol. Moreover, the biocatalyst could be used four times without loss of any activity. Rathore

et al. (Rathore & Madras, 2007) used Novozym-435 lipase to synthesize biodiesel from *Jatropha* oil in presence of supercritical carbon dioxide. The optimum conditions were found to be 8h, 45°C, 5:1 molar ratio of alcohol to oil and an enzyme loading of 30% based on the weight of oil. However, conversions of only 60-70% were obtained even after 8h. The authors attributed this to the fact that the enzymatic reaction encountered both substrate and product inhibition. In contrast, when synthesis of biodiesel in supercritical alcohols, high conversions (>80%) were obtained within 10 min and nearly complete conversions were obtained within 40 min. Despite of expected high operating cost due to high temperature and pressure associated with supercritical alcohol, it was still considered to be economically feasible since the reaction time was very short (Kasteren & Nisworo, 2007). Furthermore, the absence of pre-treatment step, soap removal, and catalyst removal can significantly reduce the capital cost of a biodiesel plant.

Meanwhile, many researches were conducted aiming at evaluating the performance, emission, and combustion characteristics in a diesel engine for *Jatropha* oil and *Jatropha* oil biodiesel (Singh, Vyas, Srivastava & Narra, 2008; Sivaprakasam & Saravanan, 2007; Halдар, Ghosh & Nag, 2008; Kumar, Ramesh & Nagalingam, 2003). Halдар *et al.* (Halдар, Ghosh & Nag, 2008) found that *Jatropha* oil gave the best results related to the performance and emissions, such as CO, CO₂, HC, smoke and particulates, at high loads and 45° before Top Dead Center (bTDC) injection timing when compared with non-edible straight vegetable oils of *Putranjiva*, *Jatropha* and *Karanja*. Kumar *et al.* (Kumar, Ramesh & Nagalingam, 2003) used *Jatropha* oil and methanol in various methods, such as blending, transesterification and dual fuel operation (methanol/*Jatropha*

oil=3:7, v/v) to compare with performance, emission and combustion parameters. Experimental results indicated that *Jatropha* oil and methyl ester showed higher diffusion combustion compared to standard diesel operation. *Jatropha* oil could be used as fuel in diesel engines directly and by blending it with methanol. Use of methyl ester of *Jatropha* oil and dual fuel operation with methanol induction could give better performance and reduced smoke emissions than the blend. Similar observation was obtained from other researchers (Singh, Vyas, Srivastava & Narra, 2008), who found that biodiesel from *Jatropha* oil offered higher brake thermal efficiency than blended de-waxed de-gummed *Jatropha* oil or even diesel. *Jatropha* oil biodiesel could be blended with diesel in any proportion or could be used as pure biodiesel successfully in CI engine without any problem. In spite of above-mentioned advantages related to engine emissions, higher NO_x level in the *Jatropha* based biodiesel exhaust was reported by several researchers (Sharma, 2003; Chairman, 2003). To solve this, Pradeep *et al.* (Pradeep & Sharma, 2007) effectively employed a low cost technique, hot exhaust gas recirculation (HOT EGR). Compared with COOLED EGR, this method was cost-effective and easy to implement. The optimal EGR level was 15%, based on adequate reduction in nitric oxide emissions, minimum possible smoke, CO, HC emissions and reasonable brake thermal efficiency.

Though received a booming interest due to its general characteristics and potential, it was recommended by some researchers that better data are urgently needed to guide investment since uncertainty do exist, based on the fact that *Jatropha curcas* is still a wild plant which exhibits a lot of variability in yield, oil content and oil quality (Achten, Mathijs, Verchot, Singh, Aerts & Muys, 2007). These researchers conducted an extensive

study on *Jatropha* biodiesel fueling sustainability, including three inseparable dimensions: environmental, economic and social. They emphasized the situation-specific interactions between different sustainability dimensions and the consideration of the political and ethical side of bioenergy production. Achten *et al.* (Achten, Verchot, Franken, Mathijs, Singh & Aerts *et al.*, 2008) pointed out in their review article that based on the available information it is still difficult to conclude if JCL biodiesel will meet the two essential minimum requirements for bio-fuels to be a more sustainable alternative for fossil fuels (i.e. (i) produced from renewable raw material and (ii) their use has a lower negative environmental impact).

1.5.5 Biodiesel Production from Microalgae

Replacing all the transport fuel consumed in the United States with biodiesel will require 0.53 billion m³ of biodiesel annually at the current rate of consumption (Chisti, 2007). Therefore, oil crops, waste cooking oil, soapstock, *Jatropha* oil cannot satisfy this demand. However, this situation may be changed dramatically when microalgae are used to produce biodiesel. Microalgae are grown in such a well-designed system with better access to water, CO₂, and nutrients provided by the aquatic environment. This contributes to its higher average photosynthetic efficiency compared with land crops. Any biofuel is ultimately a means of collecting solar energy and storing it in an energy dense chemical (Vasudevan & Briggs, 2008). Feedstocks possessing greater net efficiency for utilizing solar energy through photosynthesis will be highly desired. Moreover, microalgae grow extremely rapidly and commonly double their biomass within 34h. During exponential growth, this time can be shortened as low as 3.5h. It is estimated that the biomass

productivity of microalgae could be 50 times more than that of switchgrass, which is the fastest growing terrestrial plant (Demirbaş). The oil content in microalgae is rich, commonly 20-50% (Chisti, 2007). Some microalgae exceeds 80% oil content by weight of dry biomass (Metting, 1996; Spolaore, Joannis-Cassan, Duran, Isambert, 2006).

Currently the practical methods of large-scale production of microalgae are open ponds, most commonly raceway ponds (Terry & Raymond, 1985), and tubular photobioreactors (Grima, Fernáñeda, Camacho & Chisti, 1999; Mirón, Gómez, Camacho, Grima & Chisti, 1999). The United States Department of Energy sponsored extensive studies concerning production of microalgae biomass for making biodiesel (Sheehan, Dunahay, Benemann & Roessler, 1998). Although raceways are low-cost, the biomass productivity was lower than photobioreactors. The main disadvantage of open systems is that they lose water by evaporation at a rate similar to land crops and are also susceptible to contamination by unwanted species, being open to the atmosphere (Schenk, Thomas-hall, Stephens, Marx, Mussnug & Posten *et al.*, 2008). Unlike open raceways, photobioreactors save water, energy and chemicals. It can provide a controlled environment that can be tailored to the specific demands of highly productive microalgae to attain a consistently good annual yield of oil (Chisti, 2007). Therefore, the choice of cultivation systems is the key point which can significantly affect the efficiency and cost-effectiveness of microalgal biofuel production process (Li, Horsman, Wu, Lan & Dubois-Calero, 2008). This topic was discussed extensively by many researchers (Chisti, 2007; Lee, 2001; Pulz, 2001; Carvalho, Meireles & Malcata, 2006; Chaumont, 1993; Janssen, Tramper, Mur & Wijffels, 2003).

Microalgae possess the following attractive characteristics that are ideal for biodiesel production (Miyamoto, 1997):

1. Costs associated with the harvesting and transportation of microalgae are relatively low, compared with those of other biomass materials such as conventional crops.
2. Microalgae can be chemically treated.
3. Algae can grow under conditions that are unsuitable for conventional crops.
4. Microalgae are capable of fixing CO₂ in the atmosphere, thereby assisting the reduction of atmospheric CO₂ levels, which are now considered a global problem.

Many projects were funded for microalgae biodiesel production, such as the one at the University of Utah. A number of other projects to manufacture biodiesel from algae are under way around the world. For example, International Power Hazelwood (Morwell, VIC, Australia) and the Victor Smorgon Group (VSG; Melbourne, VIC, Australia) are running a six-month pilot test of a process from GreenFuel Technologies Corp. (Cambridge, MA) that uses microalgae in a photobioreactor to sequester carbon dioxide from furnace gases (IB 11/24/06). VSG will convert the oil from the algal biomass into biodiesel at its existing large plant for manufacturing biodiesel from canola oil. In another project, Solazyme Inc. (Menlo Park, CA) is working to genetically engineer *Dunaliella*, a green eukaryotic microalga to improve its performance (IB 7/7/06). It is already used to produce beta-carotene and also can accumulate significant quantities of lipids suitable for making biodiesel (Seefeldt, 2007). Aresta *et al.* (Aresta, Dibenedetto, Carone, Colonna &

Fragale, 2005) conducted a research to compare with two different techniques, the thermochemical liquefaction and the supercritical carbon dioxide (sc-CO₂) extraction, for the extraction of oil from microalgae to produce biodiesel. It was found that thermochemical liquefaction was more efficient than the sc-CO₂ method from the quantitative point of view but decomposition of the fatty acid might occur under the operative conditions. Also, it required temperature around 350 and 395°C to obtain the optimal amount of extracted oil.

Despite the seemingly bright future of using microalgae to produce biodiesel, this is still years away from being ready for actual commercial implementation. Vasudevan *et al.* (Vasudevan & Briggs, 2008) pointed out in their review paper that the biggest challenge is the capital cost of photobioreactors, which will present a barrier to commercialization. On the other hand, Chisti was optimistic with the improvement level which could be achieved for economical microalgae biodiesel production. The author stated in the review article that through genetic and metabolic engineering, algal biology could be improved for producing lower-cost microalgae biodiesel. Furthermore, by incorporation of biorefinery concept and utilizing the advances in photobioreactor engineering, the production cost could be further reduced (Chisti, 2007).

1.6 From Glycerol to Value-Added Products

The cost of biodiesel includes two aspects. One is the raw material (feedstocks) cost. The other is the production cost, of which the recovery of by-product (glycerol) is one of the important parts. Due to the large surplus of glycerol formed as a by-product during the production of biodiesel, new opportunities for the conversion of glycerol into

value-added chemicals have emerged in recent years, which will definitely promote biodiesel commercialization and further development.

As a nontoxic, edible, biosustainable and biodegradable compound (Wang, ZhuGe, Fang & Prior, 2001; Chiu, Goff & Suppes, 2005; Bournay, Casanave, Delfort, Hillion & Chodorge, 2005), glycerol can be converted into promising commodity chemicals and fuels through chemoselectively catalysis, such as selective oxidation, selective hydrogenolysis, catalytic dehydration, pyrolysis and gasification, selective glycerol transesterification and esterification, selective etherification and carboxylation.

Selective oxidation includes: (1) oxidation of primary hydroxyl groups, which yields glyceric acid and further tartronic acid; (2) oxidation of the secondary hydroxyl group, which yields the important fine chemical dihydroxyacetone (DHA); and (3) oxidation of all three hydroxyl groups, which yields the highly functionalized molecule mesoxalic acid. Extensive researches concerning selective catalysis of glycerol to produce glyceric acid (Abadi & Bekkum, 1995; Kimura, 2001; Kimura, 1996; Kimura, 1996; Kimura, 1998; Besson & Gallezot, 2000; Carretin, McMorn, Johnston, Griffin, Kiely & Hutchings, 2003), DHA (Garcia, Besson & Gallezot, 1995; Gallezot, 1997; Fordham, Besson & Gallezot, 1995; Ciriminna, Palmisano, Pina, Rossi & Pagliaro, 2006; Pyle, Garcia & Wen, 2008), and mesoxalic acid were conducted. All the functional derivatives obtained have commercial values. For instance, DHA is the main active ingredient in all sunless tanning skincare preparations and can be as building block of new degradable polymers if in a lower market price situation (Davis, Tomsho, Nikam, Cook, Somand & Peliska, 2000; Kimura & Tsuto, 1993). Mesoxalic acid is potentially

valuable chelating agents that can be used as intermediate compounds for the synthesis of fine chemicals and novel polymers.

Selective hydrogenolysis of glycerol in the presence of metallic catalysts and hydrogen can produce 1,2-propanediol (1,2-PD), 1,3-propanediol (1,3-PD), or ethylene glycol (EG). 1,2-PD is used for polyester resins, liquid detergents, pharmaceuticals, cosmetics, tobacco humectants, flavors and fragrances, personal care, paints, animal feed, antifreeze, etc. 1,3-PD is used in specialty polyester fibers, films, and coatings. EG is a raw material for synthetic fibers and explosives (Kim, Park, Shin, Lee, Lee & Moon, 2003).

Dehydration of glycerol can produce acrolein, which is a versatile intermediate largely employed by the chemical industry for the production of acrylic acid esters, superabsorber polymers, and detergents.

Pyrolysis and gasification of glycerol were also investigated by many researchers (Bühler, Dinjus, Ederer, Kruse & Mas, 2002; Hirai, Ikenaga, Miyake & Suzuki, 2005; Soares, Simonetti & Dumesic, 2006) to generate CO, H₂, etc. Similar promising is the conversion of glycerol into syngas by steam reforming.

Selective glycerol transesterification and esterification can yield monoglycerides (MG) and polyglycerol esters (PEG). MG can be applied as emulsifiers in food, pharmaceutical, and cosmetic industries (Baumann, Bühler, Fochem, Hirsinger, Zobelein & Falbe, 1988). Melero *et al.* (Melero, Grieken, Morales & Paniagua, 2007) reported the esterification of glycerol with acetic acid to produce glycerine acetates, such as diacetylglycerol (DAG) and triacetylglycerol (TAG), which have been shown to be

valuable petrol fuel additives leading to either enhanced cold and viscosity properties when blended with diesel fuel or antiknocking properties when added to gasoline.

Selective etherification of glycerol can yield more valuable fuel additives or solvents with suitable properties. Among these, *tert*-butyl ethers exhibit potential to be used as diesel fuel additives in gasoline and offer an alternative to oxygenates such as methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE). However, there have been restrictions on the use of MTBE in USA. The use of MTBE in the USA has resulted in growing detections of MTBE in drinking water. The major source of groundwater contamination appears to be releases from underground petrol storage systems. Legislation that would ban or restrict the use of MTBE in gasoline has already been passed in 16 States: California, Colorado, Connecticut, Illinois, Indiana, Iowa, Kansas, Kentucky, Michigan, Minnesota, Missouri, Nebraska, New York, Ohio, South Dakota, and Washington. Selective etherification can also convert glycerol into polyglycerol (PG) and PEG, which have been recommended to be used as biodegradable surfactants, lubricants, cosmetics, food additives (Clacens, Pouilloux & Barrault, 2002; Kunieda, Akahane, Feng & Ishitobi, 2002; Oudhoff, VanDamme, Mes, Schoenmakers & Kok, 2004).

Carboxylation of glycerol can produce glycerol carbonate. A lot of attentions have been received for this new and interesting material in the chemical industry (Vieville, Yoo, Pelet & Mouloungui, 1998; Dibenedetto, Pastore & Aresta, 2006; Aresta, Dibenedetto, Nocito & Pastore, 2006). Inexpensive glycerol carbonate can be utilized as

a source of new polymeric materials for the production of polycarbonates and polyurethanes (Plasman, Caulier & Boulos, 2005).

Glycerol can also be used to prepare dichloropropanol (DCP) (Lee, Park, Kim, Lee, Jung & Woo *et al.*, 2008) and as substrate to produce organic solvent tolerant lipase (Volpato, Rodrigues, Heck & Ayub, 2008).

To sum up, glycerol can be converted into many value-added products through catalytic process. However, new challenges appear since the glycerol obtained as a by-product from the biodiesel industry is crude and impure. Zhou *et al.* (Zhou, Beltramini, Fan & Lu, 2008) stated the following four challenges we need face in their review article: (1) new application and products based for directly using crude glycerol need to be found; (2) cost-effective purification process needs to be developed to purify raw glycerol from biodiesel processes; (3) a combination of separation of crude glycerol with catalytic conversion; and (4) direct biocatalytic conversion using crude glycerol should be investigated and developed to make it economically practical.

1.7 Significance of the Project

The main objective of this research was to optimize biodiesel production from crude cottonseed oil by using both conventional and ultrasonic irradiation methods. The engine performance test of cottonseed oil biodiesel was further evaluated. The use of crude cottonseed oil as raw material for biodiesel production will enhance the viability of the cottonseed industry, making cottonseed oil preferred renewable biobased ingredients for existing or new industrial applications.

1.8 References

- Abbadi, A., & Bekkum, H.V. (1995). Highly Selective Oxidation of Aldonic Acids over Pt-Bi and Pt-Pb Catalysts. *Appl Catal*, 124(2), 409-417.
- Achten, W.M.J., Mathijs, E., Verchot, L., Singh, V.P., Aerts, R., & Muys, B. *Jatropha* Biodiesel Fueling Sustainability. *Biofuels, Bioproducts & Biorefining*, 1, 283-291.
- Al-Widyan, M.I., & Al-Shyoukh, A.O. (2002). Experimental Evaluation of the Transesterification of Waste Palm Oil into Biodiesel. *Bioresour Technol*, 85(3), 253-256.
- Al-Widyan, M.I., Tashtoush, G., Abu-Qudais, M. (2002). Utilization of Ethyl Ester of Waste Vegetable Oils as Fuel in Diesel Engine. *Fuel Process Technol*, 76, 91-103.
- Aresta, M., Dibenedetto, A., Carone, M., Colonna, T., & Fragale, C. (2005). Production of Biodiesel from Macroalgae by Supercritical CO₂ Extraction and Thermochemical Liquefaction. *Environ Chem Lett*, 3, 136-139.
- Aresta, M., Dibenedetto, A., Nocito, F., & Pastore, C. (2006). A Study on the Carboxylation of Glycerol to Glycerol Carbonate with Carbon Dioxide: the Role of the Catalyst, Solvent and Reaction Conditions. *J Mol Catal A-Chem*, 257, 149-153.
- Armenta, R.E., Vinatoru, M., Burja, A.M., Kralovec, J.A., & Barrow, C.J. (2007). Transesterification of Fish Oil to Produce Fatty Acid Ethyl Esters Using Ultrasonic Energy. *J Am Oil Chem Soc*, 84, 1045-1052.
- Ataya, F., Dubé, M.A., & Ternan, M. (2006). Single-Phase and Two-Phase Base-Catalyzed Transesterification of Canola Oil to Fatty Acid Methyl Esters at Ambient Conditions. *Ind Eng Chem Res*, 45, 5411-5417.
- Azam, M.M., Waris, A., & Nahar, N.M. (2005). Prospects and Potential of Fatty Acid Methyl Esters of Some Non-Traditional Seed Oils for Use as Biodiesel in India. *Biomass Bioenerg*, 29, 293-302.
- Baumann, H., Bühler, M., Fochem, H., Hirsinger, F., Zoebelein, H., & Falbe, J. (1988). Natural Fats and Oils - Renewable Raw Materials for the Chemical Industry. *Angew Chem Int Ed Engl*, 27(1), 41-62.

- Berchmans, H.J., & Hirata, S. (2008). Biodiesel Production from Crude *Jatropha* Curcas L. Seed Oil with a High Content of Free Fatty Acids. *Bioresour Technol*, 99, 1716-1721.
- Besson, M., & Gallezot, P. (2000). Selective Oxidation of Alcohols and Aldehydes on Metal Catalysts. *Catal Today*, 57, 127-141.
- Bournay, L., Casanave, D., Delfort, B., Hillion, G., & Chodorge, J.A. (2005). New Heterogeneous Process for Biodiesel Production: A Way to Improve the Quality and the Value of the Crude Glycerin Produced by Biodiesel Plants. *Catal Today*, 106, 190-192.
- Bühler, W., Dinjus, E., Ederer, H.J., Kruse, A., & Mas, C. (2002). Ionic Reactions and Pyrolysis of Glycerol as Competing Reaction Pathways in Near- and Supercritical Water. *J Supercrit Fluid*, 22, 37-53.
- Canakci, M., & Gerpen, J.V. (1999). Biodiesel Production via Acid Catalysis. *Trans ASAE*, 42(5), 1203-1210.
- Canakci, M., & Gerpen, J.V. (2001). Biodiesel Production from Oils and Fats with High Free Fatty Acids. *Trans ASAE*, 44(6), 1429-1436.
- Canakci, M., & Gerpen, J.V. (2003). A Pilot Plant to Produce Biodiesel from High Free Fatty Acid Feedstocks. *Trans ASAE*, 46(4), 945-954.
- Canakci, M., & Gerpen, J.H.V. (2003). Comparison of Engine Performance and Emissions for Petroleum Diesel Fuel, Yellow Grease Biodiesel, and Soybean Oil Biodiesel. *Trans ASAE*, 46(4), 937-944.
- Canakci, M., & Sanli, H. (2008). Biodiesel Production from Various Feedstocks and Their Effects on the Fuel Properties. *J Ind Microbiol Biotechnol*, 35, 431-441.
- Cao, P.G., Dubé, M.A., & Tremblay, A.Y. (2008). High-Purity Fatty Acid Methyl Ester Production from Canola, Soybean, Palm, and Yellow Grease Lipids by Means of a Membrane Reactor. *Biomass Bioenerg*, doi:10.1016/j.biombioe.2008.01.020.
- Carrettin, S., McMorn, P., Johnston, P., Griffin, K., Kiely, C.J., & Hutchings, G.J. (2003). Oxidation of Glycerol Using Supported Pt, Pd and Au Catalysts. *Phys Chem Chem Phys*, 5, 1329-1336.

- Carvalho, A.P., Meireles, L.A., & Malcata, F.X. (2006). Microalgal Reactor: A Review of Enclosed System Design and Performances. *Biotechnol Prog*, 22, 1490-1506.
- Chairman. (2003). Report of Committee on Development of Bio-fuels.
- Chaumont, D. (1993). Biotechnology of Algal Biomass Production: A Review of Systems for Outdoor Mass Culture. *J Appl Phycol*, 5(6), 593-604.
- Chen, G., Ying, M., & Li, W.Z. (2006). Enzymatic Conversion of Waste Cooking Oils into Alternative Fuel-Biodiesel. *Appl Biochem Biotechnol*, 129-132, 911-921.
- Chhetri, A.B., Tango, M.S., Budge, S.M., Watts, K.C., & Islam, M.R. (2008). Non-Edible Plant Oils as New Sources for Biodiesel Productin. *Int J Mol Sci*, 9, 169-180.
- Chisti, Y. (2007). Biodiesel from Microalgae. *Biotechnol Adv*, 25, 294-306.
- Chiu, C.W., Goff, M.J., & Suppes, G.J. (2005). Distribution of Methanol and Catalysts between Biodiesel and Glycerin Phases. *AIChE J*, 51(4), 1274-1278.
- Ciriminna, R., Palmisano, G., Pina, C.D., Rossi, M., & Pagliaro, M. (2006). One-Pot Electrocatalytic Oxidation of Glycerol to DHA. *Tetrahedron Lett*, 47, 6993-6995.
- Clacens, J.M., Pouilloux, Y., & Barrault, J. (2002). Selective Etherification of Glycerol to Polyglycerols over Impregnated Basic MCM-41 Type Mesoporous Catalysts. *Appl Catal A-Gen*, 227, 181-190.
- Colucci, J.A., Borrero, E.E., & Alape, F. (2005). Biodiesel from an Alkaline Transesterification Reaction of Soybean Oil Using Ultrasonic Mixing. *J Am Oil Chem Soc*, 82(7), 525-530.
- Çetinkaya, M., Ulusoy, Y., Tekin, Y., & Karaosmanoğlu, F. (2005). Engine and Winter Road Test Performances of Used Cooking Oil Originated Biodiesel. *Energy Convers Manage*, 46, 1279-1291.
- Davis, W.R., Tomsho, J., Nikam, S., Cook, E.M., Somand, D., & Peliska, J.A. (2000). Inhibition of HIV-1 Reverse Transcriptase-Catalyzed DNA Strand Transfer Reactions by 4-Chlorophenylhydrazone of Mesoxalic Acid. *Biochemistry*, 39, 14279-14291.

- Demirbaşı, A. (2002). Biodiesel from Vegetable Oils via Transesterification in Supercritical Methanol. *Energy Convers Manage*, 43, 2349-2356.
- Demirbaşı, A. (2006). Oily Products from Mosses and Algae via Pyrolysis. *Energy Sources, Part A*, 28, 933-940.
- Demirbaşı, A. (2007). Importance of Biodiesel as Transportation Fuel. *Energy Policy*, 35, 4661-4670.
- Dibenedetto, A., Pastore, C., & Aresta, M. (2006). Direct Carboxylation of Alcohols to Organic Carbonates: Comparison of the Group 5 Element Alkoxides Catalytic Activity an Insight into Reaction Mechanism and its Key Steps. *Catal Today*, 115, 88-94.
- Dorado, M.P., Ballesteros, E., Arnal, J.M., Gómez, J., & López, F.J. (2003). Exhaust Emissions from a Diesel Engine Fueled with Transesterified Waste Olive Oil. *Fuel*, 82, 1311-1315.
- Dossin, T.F., Reyniers, M.F., Berger, R.J., & Marin, G.B. (2006). Simulation of Heterogeneously Mgo-Catalyzed Transesterification for Fine Chemical and Biodiesel Industrial Production. *Appl Catal B-Environ*, 67, 136-148.
- Fordham, P., Besson, M., & Gallezot, P. (1995). Selective Catalytic Oxidation of Glyceric Acid to Tartronic and Hydroxypyruvic Acids. *Appl Catal A-Gen*, 133, L179-L184.
- Freedaman, B., & Mounts, T.L. (1984). Variables Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils. *J Am Oil Chem Soc*, 61(10), 1639-1643.
- Furuta, S., Matsushashi, H., & Arata, K. (2004). Biodiesel Fuel Production with Solid Superacid Catalysis in Fixed Bed Reactor under Atmospheric Pressure. *Catalysis Communications*, 5, 721-723.
- Gallezot, P. (1997). Selective Oxidation with Air on Metal Catalysts. *Catal Today*, 37, 405-418.
- Garcia, R., Besson, M., & Gallezot, P. (1995). Chemoselective Catalytic Oxidation of Glycerol with Air on Platinum Metals. *Appl Catal A-Gen*, 127, 165-176.
- Goff, M.J., Bauer, N.S., Lopes, S., Sutterlin, W.R., & Suppes, G.J. (2004). Acid-Catalyzed Alcoholysis of Soybean Oil. *J Am Oil Chem Soc*, 81(4), 415-420.

- Granados, M.L., Poves, M.D.Z., Alonso, D.M., Mariscal, R., Galisteo, F.C., & Moreno-Tost, R. *et al.* (2007). Biodiesel from Sunflower Oil by Using Activated Calcium Oxide. *Appl Catal B-Environ*, 73, 317-326.
- Grima, E.M., Fernández, F.G.A., Camacho, F.G., & Chisti, Y. (1999). Photobioreactors: Light Regimes, Mass Transfer, and Scaleup. *J Biotechnol*, 70, 231-247.
- Haas, M.J. (2005). Improving the Economics of Biodiesel Production through the Use of Low Value Lipids as Feedstocks: Vegetable Oil Soapstock. *Fuel Process Technol*, 86, 1087-1096.
- Haas, M.J., Bloomer, S., & Scott, K. (2000). Simple, High-Efficiency Synthesis of Fatty Acid Methyl Esters from Soapstock. *J Am Oil Chem Soc*, 77(4), 373-379.
- Haas, M.J., McAloon, A.J., Yee, W.C., & Foglia, T.A. (2006). A Process Model to Estimate Biodiesel Production Costs. *Bioresour Technol*, 97(4), 671-678.
- Haas, M.J., Michalski, P.J., Runyon, S., Nunez, A., & Scott, K.M. (2003). Production of FAME from Acid Oil, a By-Product of Vegetable Oil Refining. *J Am Oil Chem Soc*, 80(1), 97-102.
- Haas, M.J., Scott, K.M., Alleman, T.L., & McCormick, R.L. (2001). Engine Performance of Biodiesel Fuel Prepared from Soybean Soapstock: A High Quality Renewable Fuel Produced from a Waste Feedstock. *Energ Fuel*, 15, 1207-1212.
- Haldar, S.K., Ghosh, B.B., & Nag, A. (2008). Studies on the Comparison of Performance and Emission Characteristics of a Diesel Engine Using Three Degummed Non-Edible Vegetable Oils. *Biomass Bioenerg*, doi:10.1016/j.biombioe.2008.01.021.
- Han, H.W., Cao, W.L., & Zhang, J.C. (2005). Preparation of Biodiesel from Soybean Oil Using Supercritical Methanol and CO₂ as Co-Solvent. *Fuel*, 84, 3148-3151.
- Hanh, H.D., Dong, N.T., Okitsu, K., Maeda, Y., & Nishimura, R. (2007). Effects of Molar Ratio, Catalyst Concentration and Temperature on Transesterification of Triolein with Ethanol under Ultrasonic Irradiation. *Journal of the Japan Petroleum Institute*, 50(4), 195-199.

- Hanh, H.D., Dong, N.T., Starvarache, C., Okitsu, K., Maeda, Y., & Nishimura, R. (2008). Methanolysis of Triolein by Low Frequency Ultrasonic Irradiation. *Energy Convers Manage*, 49, 276-280.
- He, H.Y., Wang, T., & Zhu, S.L. (2007). Continuous Production of Biodiesel Fuel from Vegetable Oil Using Supercritical Methanol Process. *Fuel*, 86, 442-447.
- Hirai, T., Ikenaga, N.O., Miyake, T., & Suzuki, T. (2005). Production of Hydrogen by Steam Reforming of Glycerin on Ruthenium Catalyst. *Energy Fuel*, 19, 1761-1762.
- Issariyakul, T., Kulkarni, M.G., Dalai, A.K., & Bakhshi, N.N. (2007). Production of Biodiesel from Waste Fryer Grease Using Mixed Methanol/Ethanol System. *Fuel Process Technol*, 88, 429-436.
- Janssen, M., Tramper, J., Mur, L.R., & Wijffels, R.H. (2003). Enclosed Outdoor Photobioreactors: Light Regime, Photosynthetic Efficiency, Scale-Up, and Future Prospects. *Biotechnol Bioeng*, 81(2), 193-210.
- Jin, B., Zhu, M., Fan, P., & Yu, L.J. (2008). Comprehensive Utilization of the Mixture of Oil Sediments and Soapstocks for Producing FAME and Phosphatides. *Fuel Process Technol*, 89, 77-82.
- Kachhwaha, S.S., Maji, S., Faran, M., Gupta, A., Ramchandran, J., & Kumar, D. (2006). Preparation of Biodiesel from *Jatropha* Oil Using Ultrasonic Energy. 1-5.
- Kasteren, J.M.N.V., & Nisworo, A.P. (2007). A Process Model to Estimate the Cost of Industrial Scale Biodiesel Production from Waste Cooking Oil by Supercritical Transesterification. *Resour Conserv Recy*, 50, 442-458.
- Keskin, A., Gürü, M., Altıparmak, D., & Aydın, K. (2008). Using of Cotton Oil Soapstock Biodiesel-Diesel Fuel Blends as an Alternative Diesel Fuel. *Renew Energ*, 33, 553-557.
- Kim, H.J., Kang, B.S., Kim, M.J., Park, Y.M., Kim, D.K., & Lee, J.S. *et al.* (2004). Transesterification of Vegetable Oil to Biodiesel using Heterogeneous Base Catalyst. *Catal Today*, 93-95, 315-320.
- Kim, Y.C., Park, N.C., Shin, J.S., Lee, S.R., Lee, Y.J., & Moon, D.J. (2003). Partial Oxidation of Ethylene to Ethylene Oxide over Nanosized Ag/ α -Al₂O₃ Catalysts. *Catal Today*, 87, 153-162.

- Kimura, H. (1996). Polyketomalones by Catalytic Oxidation of Glycerol. I. J Polym Sci, Part A: Polym Chem, 34, 3595-3605.
- Kimura, H. (1996). Polyketomalone by Catalytic Oxidation of Glycerol over a CeBiPt Catalyst. II. J Polym Sci, Part A: Polym Chem, 34, 3607-3614.
- Kimura, H. (1998). Poly (Ketomalone) by Catalytic Oxidation of Glycerol (4) Anionic Polymerization. J Polym Sci Part A: Polym Chem, 36, 195-205.
- Kimura, H. (2001). Oxidation Assisted New Reaction of Glycerol. Polym Adv Technol, 12, 697-710.
- Kimura, H., & Tsuto, K. (1993). Catalytic Synthesis of DL-Serine Glycine from Glycerol. J Am Oil Chem Soc, 70(10), 1027-1030.
- Kiss, A.A., Dimian, A.C., & Rothenberg, G. (2006). Solid Acid Catalysts for Biodiesel Production-Towards Sustainable Energy. Adv Synth Catal, 348, 75-81.
- Kulkarni, M.G., & Dalai, A.K. (2006). Waste Cooking Oils-An Economical Source for Biodiesel: A Review. Ind Eng Chem Res, 45, 2901-2913.
- Kumar, M.S., Ramesh, A., & Nagalingam, B. (2003). An Experimental Comparison of Methods to Use Methanol and *Jatropha* Oil in a Compression Ignition Engine. Biomass Bioenerg, 25, 309-318.
- Kunieda, H., Akahane, A., Feng, J., & Ishitobi, M. (2002). Phase Behavior of Polyglycerol Didodecanoates in Water. J Coll Interfac Sci, 245(2), 365-370.
- Kusdiana, D., & Saka, S. (2004). Effects of Water on Biodiesel Fuel Production by Supercritical Methanol Treatment. Bioresour Technol, 91(3), 289-295.
- Lapuerta, M., Rodríguez-Fernández, J., & Agudelo, J.R. (2008). Diesel Particulate Emissions from Used Cooking Oil Biodiesel. Bioresour Technol, 99, 731-740.
- Lee, S.H., Park, D.R., Kim, H., Lee, J., Jung, J.C., & Woo, S.Y. *et al.* (2008). Direct Preparation of Dichloropropanol (DCP) from Glycerol Using Heteropolyacid (HPA) Catalysts: A Catalyst Screen Study. Catalysis Communications, 9, 1920-1923.

- Leung, D.Y.C., & Guo, Y. (2006). Transesterification of Neat and Used Frying Oil: Optimization for Biodiesel Production. *Fuel Process Technol*, 87, 883-890.
- Li, H.T., & Xie, W.L. (2006). Transesterification of Soybean Oil to Biodiesel with Zn/I₂ Catalyst. *Catal Lett*, 107(1-2), 25-30.
- Li, Y.K. (2001). Microalgal Mass Culture Systems and Methods: Their Limitation and Potential. *J Appl Phycol*, 13, 307-315.
- Li, Y.Q., Horsman, M., Wu, N., Lan, C.Q., & Dubois-Calero, N. (2008). Biofuels from Microalgae. *Biotechnol Prog*, doi: 10.1021/bp070371k.
- Lin, Y.F., Wu, Y.P.G., & Chang, C.T. (2007). Combustion Characteristics of Waste-Oil Produced Biodiesel/Diesel Fuel Blends. *Fuel*, 86, 1772-1780.
- Lotero, E., Liu, Y.J., Lopez, D.E., Suwannakarn, K., Bruce, D.A., & Goodwin, J.G. (2005). Synthesis of Biodiesel via Acid Catalysis. *Ind Eng Chem Res*, 44, 5353-5363.
- Ma, F.R., Clements, L.D., & Hanna, M.A. (1999). The Effect of Mixing on Transesterification of Beef Tallow. *Bioresour Technol*, 69, 289-293.
- Meher, L.C., Dharmagadda, V.S., & Naik, S.N. (2006). Optimization of Alkaline-Catalyzed Transesterification of Pongamia Pinnata Oil for Production of Biodiesel. *Bioresour Technol*, 97(12), 1392-1397.
- Meher, L.C., Kulkarni, M.G., Dalai, A.K., & Naik, S.N. (2006). Transesterification of Karanja (Pongamia Pinnata) Oil by Solid Basic Catalysts. *Eur J Lipid Sci Technol*, 108,389-397.
- Meka, P.K., Tripathi, V., & Singh, R.P. (2007). Synthesis of Biodiesel Fuel from Safflower Oil Using Various Reaction Parameters. *J Oleo Sci*, 56(1), 9-12.
- Melero, J.A., Grieken, R.V., Morales, G., & Paniagua, M. (2007). Acidic Mesoporous Silica for the Acetylation of Glycerol: Synthesis of Bioadditives to Petrol Fuel. *Energ Fuel*, 21, 1782-1791.
- Metting, F.B. (1996). Biodiversity and Application of Microalgae. *J Ind Microbiol Biot*, 17(5-6), 477-489.
- Mirón, A.S., Gómez, A.C., Camacho, F.G., Grima, E.M., & Chisti, Y. (1999). Comparative Evaluation of Compact Photobioreactors for Large-Scale Monoculture of Microalgae. *J Biotechnol*, 70, 249-270.

- Miyamoto, K. (1997). Renewable Biological Systems for Alternative Sustainable Energy Production. FAO-Food and Agriculture Organization of the United Nations: Osaka, Japan.
- Nas, B., & Berkday, A. (2007). Energy Potential of Biodiesel Generated from Waste Cooking Oil: An Environmental Approach. *Energy Sources, Part B*, 2, 63-71.
- Ngo, H.L., Zafiropoulos, N.A., Foglia, T.A., Samulski, E.T., & Lin, W.B. (2008). Efficient Two-Step Synthesis of Biodiesel from Grease. *Energy Fuel*, 22, 626-634.
- Oudhoff, K.A., VanDamme, F.A., Mes, E.P.C., Schoenmakers, P.J., & Kok, W.T. (2004). Characterization of Glycerin-Based Polyols by Capillary Electrophoresis. *J Chromatogr A*, 1046, 263-269.
- Özbay, N., Oktar, N., & Tapan, N.A. (2008). Esterification of Free Fatty Acids in Waste Cooking Oils (WCO): Role of Ion-exchange Resins. *Fuel*, 87, 1789-1798.
- Plasman, V., Caulier, T., & Boulos, N. (2005). Polyglycerol Esters Demonstrate Superior Antifogging Properties for Films. *Plastics, Additives and Compounding*, 7(2), 30-33.
- Pradeep, V., & Sharma, R.P. (2007). Use of HOT EGR for NO_x Control in a Compression Ignition Engine Fueled with Bio-diesel from *Jatropha* Oil. *Renew Energ*, 32, 1136-1154.
- Pulz, O. (2001). Photobioreactors: Production Systems for Phototrophic Microorganisms. *Appl Microbiol Biotechnol*, 57, 287-293.
- Pyle, D.J., Garcia, R.A., & Wen, Z.Y. (2008). Producing Docosahexaenoic Acid (DHA)-Rich Algae from Biodiesel-Derived Crude Glycerol: Effects of Impurities on DHA Production and Algal Biomass Composition. *J Agric Food Chem*, 56, 3933-3939.
- Rashid, U., & Anwar, F. (2008). Production of Biodiesel through Base-Catalyzed Transesterification of Safflower Oil Using an Optimized Protocol. *Energy Fuel*, 22, 1306-1312.
- Rathore, V., & Madras, G. (2007). Synthesis of Biodiesel from Edible and Non-Edible Oils in Supercritical Alcohols and Enzymatic Synthesis in Supercritical Carbon Dioxide. *Fuel*, 86, 2650-2659.

- Saka, S., & Kusdiana, D. (2001). Biodiesel Fuel from Rapeseed Oil as Prepared in Supercritical Methanol. *Fuel*, 80, 225-231.
- Sarin, R., Sharma, M., Sinharay, S., & Malhotra, R.K. (2007). *Jatropha*-Palm Biodiesel Blends: An Optimum Mix for Asia. *Fuel*, 86, 1365-1371.
- Schenk, P.M., Thomas-Hall, S.R., Stephens, E., Marx, U.C., Mussnug, J.H., & Posten, C. *et al.* (2008). Second Generation Biofuels: High-Efficiency Microalgae for Biodiesel Production. *Bioenerg Res*, 1, 20-43.
- Seefeldt, L.C. (2007). Utah Group Plans to Make Biodiesel from Algae. *Ind Bioprocess*, 5-6.
- Serio, M.D., Cozzolino, M., Tesser, R., Patrono, P., Pinzari, F., & Bonelli, B. *et al.* (2007). Vanadyl Phosphate Catalysts in Biodiesel Production. *Appl Catal A-Gen*, 320, 1-7.
- Serio, M.D., Tesser, R., Dimiccoli, M., Cammarota, F., Nastasi, M., & Santacesaria, E. (2005). Síntesis of Biodiesel via Homogeneous Lewis Acid Catalyst. *J Mol Catal A-Chem*, 239, 111-115.
- Shah, S., & Gupta, M.N. (2007). Lipase Catalyzed Preparation of Biodiesel from *Jatropha* Oil in a Solvent Free System. *Process Biochem*, 42, 409-414.
- Sharma, R.P. (2003). Bio-diesel and E-diesel in Transportation-An OEM Perspective. 539-550.
- Sheehan, J., Dunahay, T., Benemann, J., & Roessler, P. (1998). A Look Back at the U.S. Department of Energy's Aquatic Species Program-Biodiesel from Algae.
- Shumaker, J.L., Crofcheck, C., Tackett, S.A., Santillan-Jimenez, E., & Crocker, M. (2007). Biodiesel Production from Soybean Oil Using Calcinated Li-Al Layered Double Hydroxide Catalysts. *Catal Lett*, 115(1-2), 56-61.
- Silva, V.M.T.M., & Rodrigues, A.E. (2006). Kinetic Studies in a Batch Reactor Using Ion Exchange Resin Catalysts for Oxygenates Production: Role of Mass Transfer Mechanisms. *Chem Eng Sci*, 61, 316-331.
- Singh, R.N., Vyas, D.K., Srivastava, N.S.L., & Narra, M. (2008). SPRERI Experience on Holistic Approach to Utilize All Parts of *Jatropha Curcas* Fruit for Energy. *Renew Energ*, 33, 1868-1873.

- Sirisomboon, P., Kitchaiya, P., Pholpho, T., & Mahuttanyavanitch, W. (2007). Physical and Mechanical Properties of *Jatropha Curcas* L. Fruits, Nuts and Kernels. *Biosyst Eng*, 97, 201-207.
- Sivaprakasam, S., & Saravanan, C.G. (2007). Optimization of the Transesterification Process for Biodiesel Production and Use of Biodiesel in a Compression Ignition Engine. *Energ Fuel*, 21, 2998-3003.
- Soares, R.R., Simonetti, D.A., & Dumesic, J.A. (2006). Glycerol as a Source for Fuels and Chemicals by Low-Temperature Catalytic Processing. *Angew Chem Int Ed*, 45, 3982-3985.
- Spolaore, P., Joannis-Cassan, C., Duran, E., & Isambert, A. (2006). Commercial Application of Microalgae. *J Biosci Bioeng*, 101(2), 87-96.
- Srivastava, A., & Prasad, R. (2000). Triglycerides-based Diesel Fuels. *Renew Sust Energ Rev*, 4, 111-133.
- Stavarache, C., Vinatoru, M., & Maeda, Y. (2006). Ultrasonic versus Silent Methylation of Vegetable Oils. *Ultrason Sonochem*, 13, 401-407.
- Stavarache, C., Vinatoru, M., & Maeda, Y. (2007). Aspects of Ultrasonically Assisted Transesterification of Various Vegetable Oils with Methanol. *Ultrason Sonochem*, 14, 380-386.
- Stavarache, C., Vinatoru, M., Maeda, Y., & Bandow, H. (2007). Ultrasonically Driven Continuous Process for Vegetable Oil Transesterification. *Ultrason Sonochem*, 14, 413-417.
- Stavarache, C., Vinatoru, M., Nishimura, R., & Maeda, Y. (2005). Fatty Acids Methyl Ester from Vegetable Oil by Means of Ultrasonic Energy. *Ultrason Sonochem*, 12, 367-372.
- Suples, G.J., Dasari, M.A., Daskocil, E.J., Mankidy, P.J., & Goff, M.J. (2004). Transesterification of Soybean Oil with Zeolite and Metal Catalysts. *Appl Catal A-Gen*, 257, 213-223.
- Tapanes, N.C.O., Aranda, D.A.G., Carneiro, J.W.D.M., & Antunes, O.A.C. (2008). Transesterification of *Jatropha Curcas* Oil Glycerides: Theoretical and Experimental Studies of Biodiesel Reaction. *Fuel*, 87, 2286-2295.
- Terry, K.L., & Raymond, L.P. (1985). System Design for the Autotrophic Production of Microalgae. *Enzyme Microb Technol*, 7, 474-487.

- Tiwari, A.K., Kumar, A., & Raheman, H. (2007). Biodiesel Production from *Jatropha* Oil (*Jatropha Curcas*) with High Free Fatty Acids: An Optimized Process. *Biomass Bioenerg*, 31, 569-575.
- Tomasevic, A.V., & Siler-Marinkovic, S.S. (2003). Methanolysis of Used Frying Oil. *Fuel Process Technol*, 81, 1-6.
- Usta, N., Öztürk, E., Can, Ö., Conkur, E.S., Nas, S., & Çon, A.H. *et al.* (2005). Combustion of Biodiesel Fuel Produced from Hazelnut Soapstock/Waste Sunflower Oil Mixture in a Diesel Engine. *Energy Convers Manage*, 46, 741-755.
- Vasudevan, P.T., & Briggs, M. (2008). Biodiesel Production-Current State of the Art and Challenges. *J Ind Microbiol Biotechnol*, 35, 421-430.
- Vicente, G., Martínez, M., & Aracil, J. (2004). Integrated Biodiesel Production: a Comparison of Different Homogeneous Catalysts Systems. *Bioresour Technol*, 92(3), 297-305.
- Vieville, C., Yoo, J.W., Pelet, S., & Mouloungui, Z. (1998). Synthesis of Glycerol Carbonate by Direct Carbonatation of Glycerol in Supercritical CO₂ in the Presence of Zeolites and Ion Exchange Resins. *Catal Lett*, 56, 245-247.
- Volpato, G., Rodrigues, R.C., Heck, J.X., & Ayub, M.A.Z. (2008). Production of Organic Solvent Tolerant Lipase by *Staphylococcus Caseolyticus* EX17 Using Raw Glycerol as Substrates. *J Chem Technol Biotechnol*, 83, 821-828.
- Wang, Y., Ou, S., Liu, P., Xue, F., & Tang, S. (2006). Comparison of Two Different Processes to Synthesize Biodiesel by Waste Cooking Oil. *J Mol Catal A-Chem*, 252, 107-112.
- Wang, Z.M., Lee, J.S., Park, J.Y., Wu, C.Z., & Yuan, Z.H. (2007). Novel Biodiesel Production Technology from Soybean Soapstock. *Korean J Chem Eng*, 24(6), 1027-1030.
- Wang, Z.X., ZhuGe, J., Fang, H.Y., & Prior, B.A. (2001). Glycerol Production by Microbial Fermentation: A Review. *Biotechnol Adv*, 19(3), 201-223.
- Williams, P., Mulcahy, F., Ford, J.T., Oliphant, J., Caldwell, J., & Soriano, D. (2007). Biodiesel Preparation via Acid Catalysis and Characterization. *Journal of Undergraduate Chemistry Research*, 6(2), 87-96.

- Wu, P., Yang, Y., Colucci, J.A., & Grulke, E.A. (2007). Effect of Ultrasonication on Droplet Size in Biodiesel Mixtures. *J Am Oil Chem Soc*, 84, 877-884.
- Xie, W.L., Peng, H., & Chen, L.G. (2006). Transesterification of Soybean Oil Catalyzed by Potassium Loaded on Alumina as a Solid-Base Catalyst. *Appl Catal A-Gen*, 300, 67-74.
- Xie, W.L., & Yang, Z.Q. (2007). Ba-ZnO Catalysts for Soybean Oil Transesterification. *Catal Lett*, 117(3-4), 159-165.
- Zhang, Y., Dubé, M.A., McLean, D.D., & Kates, M. (2003). Biodiesel Production from Waste Cooking Oil: 1. Process Design and Technological Assessment. *Bioresour Technol*, 89, 1-16.
- Zhang, Y., Dubé, M.A., McLean, D.D., & Kates, M. (2003). Biodiesel Production from Waste Cooking Oil: 2. Economic Assessment and Sensitivity Analysis. *Bioresour Technol*, 90(3), 229-240.
- Zheng, S., Kates, M., Dubé, M.A., & McLean, D.D. (2006). Acid-Catalyzed Production of Biodiesel from Waste Frying Oil. *Biomass Bioenerg*, 30, 267-272.
- Zhou, C.H., Beltramini, J.N., Fan, Y.X., Lu, G.Q. (2008). Chemoselective Catalytic Conversion of Glycerol as a Biorenewable Source to Valuable Commodity Chemicals. *Chem Soc Rev*, 37, 527-549.
- Zhou, W.Y., Konar, S.K., & Boocock, D.G.B. (2003). Ethyl Esters from the Single-Phase Base-Catalyzed Ethanolysis of Vegetable Oils. *J Am Oil Chem Soc*, 80(4), 367-371.
- Zullaikah, S., Lai, C.C., Vali, S.R., & Ji, Y.H. (2005). A Two-Step Acid-Catalyzed Process for the Production of Biodiesel from Rice Bran Oil. *Bioresour Technol*, 96(17), 1889-1896.

CHAPTER 2

**OPTIMIZATION OF BIODIESEL PRODUCTION FROM CRUDE
COTTONSEED OIL BY USING CONVENTIONAL METHOD**

Abstract

Biodiesel, known as fatty acid methyl ester (FAME), was produced from crude cottonseed oil (triglycerides) by transesterification with methanol in the presence of sodium hydroxide. This process was optimized by applying factorial design and response surface methodology (RSM) with SAS and PSIPLOT programs. A second-order mathematical model was obtained to predict the yield as a function of methanol/oil molar ratio, catalyst concentration, reaction temperature, and rate of mixing. Based on ridge max analysis and RSM, as well as economic cost consideration, the practical optimal condition for the production of biodiesel was found to be: methanol/oil molar ratio, 6.0; temperature, 53°C; time, 45 min; catalyst concentration, 1.0 %; and rate of mixing, 268 rpm. The optimized condition was validated with the actual biodiesel yield of 95%. Furthermore, the biodiesel was confirmed by HPLC analyses that triglycerides of cottonseed oil were almost completely converted to FAME.

2.1 Introduction

Biodiesel, the most promising alternative diesel fuel, has received considerable attention in recent years due to its following merits: biodegradable, renewable, non-toxic, less emission of gaseous and particulate pollutants with higher cetane number than normal diesel. In addition, it meets the currently increasing demands of world energy that, in a large degree, is dependent on petroleum based fuel resources, which will be depleted in the foreseeable future if the present pattern of energy consumption continues.

Biodiesel is derived from vegetable oils or animal fats through transesterification (Fukuda, Kondo & Noda, 2001). Transesterification is also called alcoholysis, which uses alcohols in the presence of catalyst (e.g., base, acid or enzyme depending on the free fatty acid content of the raw material) that chemically breaks the molecules of triglycerides into alkyl esters as biodiesel fuels and glycerol as a by-product. The commonly used alcohols for the transesterification include methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are adopted most frequently, particularly the former due to its low cost.

Commonly used feedstocks (vegetable oil) for transesterification include soybean oil, rapeseed oil, etc. In recent years, there exist active researches on biodiesel production from cottonseed oil (Demirbas, 2008; Cui, Xiao, Xu & Teng, 2007; Plentz, Meneghetti, Wolf, Silva, Lima & Coimbra *et al.*, 2006; Yücesu & İlkiliç, 2006; Karabektas, Ergen & Hosoz, 2008; Köse, Tüter & Aksoy, 2002), of which the conversion between 72% and 94% was obtained by enzyme catalyzed transesterification when the refined cottonseed oil reacted with short-chain primary and secondary alcohols. The application of solid acid

catalysts on cottonseed oil transesterification was investigated by Chen *et al.* (Chen, Peng, Wang & Wang, 2007). Their results showed that the yield of methyl ester was above 90% after 8h of reaction. In contrast, transesterifying cottonseed oil by microwave irradiation could produce a biodiesel yield in the range of 89.5-92.7% (Azcan & Danisman, 2007). No matter what kind of catalysts or approaches were applied, all those studies aimed to produce high yield of biodiesel by optimized reaction conditions based on optimized parameters in terms of alcohol/oil molar ratio, catalyst concentration, reaction temperature, and time. However, nearly in all studied cases, there existed complex interactions among the variables that remarkably affected the biodiesel yield. Moreover, it seems unrealistic to optimize the process by the traditional 1-factor-at-a-time approach, which is time-consuming and nearly impossible to achieve the true optimal condition. Alternatively, response surface methodology (RSM), an experimental strategy described first by Box and Wilson for seeking an optimal condition for a multivariable system, is an efficient technique for processing optimization (Kong, He, Chen & Chen, 2004). In this study, RSM was applied to optimize the transesterification of crude cottonseed oil with methanol in the presence of sodium hydroxide to produce biodiesel with the highest yield.

2.2 Materials and Methods

2.2.1 Materials

Methanol and sodium hydroxide were purchased from Fisher Scientific (Suwanee, GA, USA). Crude cottonseed oil derived from expeller (i.e., screw pressed cottonseed) was obtained from the Elgin Cotton Oil Mill, Inc. (Elgin, TX, USA). The Gyrotory water bath shaker was purchased from New Brunswick Scientific Co. Inc. (NJ, USA).

2.2.2 Fatty Acid Profile of Crude Cottonseed Oil

An aliquot of about 10 mg of oil was weighed and mixed with 2 ml of hexane, then 0.2 ml of 2 M methanolic KOH was added for transesterification. The mixture was vortexed for 2 min at room temperature, and centrifuged, then an aliquot (2 microliters) of the hexane layer was collected for GC analysis. Shimadzu's GC-FID system, used for the qualitative and quantitative analyses of fatty acids of the crude cottonseed oil and biodiesel, consists of a GC-17A, a flame ionization detector, and a DB-WAX capillary column (60 m×0.25 mm, thickness=0.25 µm; J&W Scientific). The initial temperature for oven was set at 180°C and held for 2 min. Then the temperature increased from 180 °C to 250°C at the ramp of 5°C/min and held at 250°C for 30 min. The injector and detector were maintained at 200°C and 220°C, respectively. Helium was used as a carrier gas, and its flow rate was kept at 1.5 ml/min.

2.2.3 Free Fatty Acid Analysis

Free fatty acid content of the cottonseed oil was measured according to the A.O.C.S. Official Method Ca 5a-40 (AOCS, 1997).

2.2.4 Transesterification of Crude Cottonseed Oil

The crude cottonseed oil reacted with methanol in the presence of sodium hydroxide to produce methyl esters of fatty acids (biodiesel) and glycerol (**Figure 2.1**). To optimize the above transesterification process, a three-level-five-factor (2^5) fractional factorial experimental design was employed (**Table 2.1**). The crude cottonseed oil was precisely quantitatively transferred into an Erlenmeyer flask immersed in the Gyrotory water bath shaker. Then specific amount of sodium hydroxide (by weight of crude

cottonseed oil) dissolved in the required amount of methanol was added. The reaction flask was kept in the water bath under constant temperature with defined agitation throughout the reaction. At the defined time, sample was taken out, cooled, and the biodiesel (i.e. the methyl ester in the upper layer) was separated from the by-product (i.e., the glycerol in the lower layer) by settlement overnight under ambient condition. The percentage of the biodiesel yield was determined by comparing the weight of up layer biodiesel with the weight of crude cottonseed oil added.

2.2.5 Purification of Methyl Ester Phase

Since the remaining unreacted methanol in the biodiesel has safety risks and can corrode engine components, the residual catalyst (sodium hydroxide) can damage engine components, and soap in the biodiesel can reduce fuel lubricity and cause injector coking and other deposits (Ryan, 2004), the methyl ester layer (biodiesel) was washed by mist washing with 1:1 volume of hot distilled water (about 60°C) using a misting nozzle to make a fine, gentle mist, which was allowed to float over the surface of the biodiesel. After removing the unreacted methanol, the remaining catalyst, and soap, the washed biodiesel was placed into an oven at 55°C to evaporate the water residue and then dried with sodium sulphate so as to minimize the undesired biological growth.

2.2.6 HPLC Methods

Reverse phase HPLC was used to qualitatively and quantitatively analyze the conversion of triglyceride into biodiesel. The Shimadzu HPLC system consisted of an evaporative light scattering detector (ELSD) with a Phenomenex Gemini C18 column (250×4.6mm, 5µm). HPLC grade acetonitrile (A) and dichloromethane (B) were selected

as the mobile phase. The gradient program was as follows: Time: (0, 5, 30, 32, 35 min) for solvent B: (0, 15, 70, 70, 0%). The flow rate of the mobile phase was 1.0 ml/min. Twenty microliters of the diluted biodiesel sample was injected via autosampler.

2.3 Results and Discussion

Usually crude cottonseed oil contains palmitic acid (22-26%), oleic acid (15-20%), linoleic acid (49-58%) and approximately 10% mixture of arachidic acid, behenic acid and lignoceric acid, as well as about 1% sterculic and malvalic acids (Cottonseed oil from Wikipedia, 2008). In this study, the used crude cottonseed oil contained 23.67% of palmitic acid, 17.09% of oleic acid, and 50.33% of linoleic acid.

Since higher amount of free fatty acids (FFA) (>1% w/w) in the feedstock can directly react with the alkaline catalyst to form soaps, which are subject to form stable emulsions and thus prevent separation of the biodiesel from the glycerol fraction and decrease the yield (Demirbaş, 2003), it is better to select reactant oils with low FFA content or to remove FFA from the oil to an acceptable level before the reaction. Nevertheless, the FFA (calculated as oleic acid) content of the crude cottonseed oil used in this experiment was only 0.8%, which was in an allowed level for being directly used for reaction with the alkaline catalyst to produce biodiesel.

The remaining main factors affecting the transesterification include reaction time, temperature, alcohol/oil molar ratio, rate of mixing, and catalyst concentration. In order to optimize the reaction condition to produce a high yield of biodiesel with high purity, response surface method was adopted to design the experiment. This methodology is a sequential process that usually starts at one reasonable operating condition, and then

requires three stages to achieve a set of “better” conditions as rapidly and efficiently as possible. The first stage is to conduct several experiments to determine the direction so as to take the next move towards the optimal value. The second stage is to perform several runs along the direction as indicated by the first stage until an optimal value was approached. The last step is to deduce a mathematical model (equation) and profile the response surface to determine the optimal condition, which should be validated by the actual process.

2.3.1 Fractional Factorial Design and First-Degree Polynomial Model Analysis

Based on our experience and previous literature (Fillières, Benjelloun-Mlayah & Delmas, 1995), the following factor (variable) levels were selected. The central point of the methanol/oil molar ratio was set at 6:1. The upper level of temperature was 65°C, equal to the boiling point of methanol. Since high catalyst concentration can facilitate the soap formation, catalyst amount (catalyst/oil) of 1.5 wt.% was chosen as the upper level of catalyst concentration. In addition, the central points for the reaction time and rate of mixing were 55 min and 350 rpm, respectively.

Table 2.2 shows the experimental matrix for the 2ⁿ factorial design, of which n was the number of factors. Herein, n equals to 5 that represented A, B, C, D and E, which corresponded to the uncoded values of the methanol/oil molar ratio, catalyst concentration (%), temperature (°C), time (min), and rate of mixing (rpm), respectively. X₁, X₂, X₃, X₄ and X₅ are coded values corresponding to the uncoded values of A to E, respectively. The data in the last column of **Table 2.2** indicates the response Y (%) (yield

of biodiesel) obtained from each experimental run. Eight additional center-point runs coded by 0 were performed to check the curvature in the response surface.

A complete statistical analysis of the first-degree polynomial model was performed using a single model in PROC REG of SAS program for Windows, Version 9.1, (Cary, NC, USA). The following expression for yield (Y) was obtained:

$$Y=77.95+7.67X_1-15.54X_2+2.70X_3-1.92X_4-5.26X_5 \text{ (Eq. 1)}$$

Yet, from the observed results shown in the **Table 2.3**, it is evident that there are interactions existing between the factors, and the response surface is more likely curved. Also, at 95% confidence level, all the factors, i.e., time, methanol/oil molar ratio, catalyst concentration, temperature, and rate of mixing, had significant influence on the reaction. Among them, methanol/oil molar ratio and temperature showed positive effects, while catalyst concentration, reaction time and rate of mixing had negative effects on the transesterification reaction. The negative effects of the catalyst concentration and rate of mixing (rpm) might be associated with the side reaction-soap formation, which was even more significant at higher levels of these variables.

The three-dimensional surface profiles (**Figure 2.2**) plotted by the PSI-Plot (Poly Software International, Inc., Pearl River, NY, USA) shows that a higher yield could be obtained when the reaction time was kept at about 45 min, so this factor was fixed at 45 min. Other four factors, including methanol/oil molar ratio, catalyst concentration, temperature, and rate of mixing, fit into a second-order model to simplify the procedure. Thus, a new higher degree polynomial equation (**Eq. 2**) was used to express the processing:

$$Y = \beta_0 + \sum_{i=1}^4 \beta_i X_i + \sum_{i=1}^4 \beta_{ii} X_i^2 + \sum_{i=1}^4 \sum_{j=1}^{i-1} \beta_{ij} X_i X_j \quad (\text{Eq. 2})$$

2.3.2 The Central Composite Design and the Second-order Polynomial Model

Analysis

Eight additional experiments (**Table 2.4**) were carried out with a coded distance equaled to 2.0 when the reaction time was fixed at 45 min. Then eight axial points were obtained. The matrix corresponding to the central composite design is shown in **Table 2.4**.

Using the RSREG program of SAS, a second-order polynomial equation (**Eq. 3**) for the experimental data was deduced as follows:

$$Y = 92.53 + 7.71X_1 - 10.36X_2 + 1.21X_3 - 3.79X_4 - 3.08X_1^2 + 9.07X_1X_2 - 21.09X_2^2 - 3.02X_1X_3 - 0.67X_2X_3 + 0.30X_3^2 - 0.14X_1X_4 - 0.84X_2X_4 + 0.59X_3X_4 + 1.66X_4^2 \quad (\text{Eq.3})$$

The analysis of variance revealed that this model was adequate to express the actual relationship between the response and significant variables, with a satisfactory coefficient of determination ($R^2=0.84$), which indicated 84% of the variability in the response could be explained by the 2nd-order polynomial predictive equation given above. Also, the *P*-value of the lack of fit in 0.061 confirmed that the new polynomial model fit the processing.

2.3.3 The Response Surface and Ridge Max Analysis

The 3D response surface profile and its contour of the optimal production of biodiesel is shown in **Figure 2.3** based on **Eq. 3**, from which the variables of temperature

and rate of mixing are fixed at central coded levels (i.e., temperature=55°C, rate of mixing=300 rpm). The values in the picture have been transformed back to the uncoded (real) values. **Figure 2.3** clearly shows that the catalyst concentration around 1.0% (or within the range of 0.9~1.2%) could most likely yield the maximal production of the biodiesel. The yield decreased when the catalyst concentration was beyond the above range. Since the methanol and triglyceride in the crude cottonseed oil are immiscible, addition of catalyst can facilitate the transesterification reaction, and rapidly increase the yield. However, when the catalyst concentration was too high, soap could be quickly formed which made the separation of glycerol from biodiesel more difficult, thus reduced the yield. In contrast, inadequate usage of catalyst could result in an incomplete reaction and a lower yield. The RSM shown in **Figure 2.3** exhibits the optimal value of the methanol/oil molar ratio for the yield, in which too high or too low values of the methanol/oil ratio have negative effects. This can be explained by the fact that the transesterification is an equilibrium reaction in which excessive amount of alcohol will, on one hand, drive the reaction to the right for more products; on the other hand, excess alcohol will help increase the solubility of glycerol resulting in the reaction driven to the left, thus decreasing the yield. Too low methanol/oil molar ratio also led to an incomplete reaction. Therefore, both catalyst concentration and methanol/oil molar ratio exhibited respective optimal values. The RSM demonstrated that the optimal conditions for catalyst concentration and methanol/oil molar ratio were about 1% and 7.5, respectively, very close to the SAS ridge max analysis results that will be discussed in the following section.

The ridge max method, which computes the estimated ridge of optimum response when increasing radii from the center of the original design, was performed to attain an optimal condition for maximum biodiesel production. The ridge max analysis showed that the maximum yield could be theoretically approachable to 100% at 53°C, 7.9 methanol/oil molar ratio, 1.0% catalyst concentration, and 268 rpm. Further biodiesel production using the above suggested optimal condition validated the yield in 97% that was very close to the theoretical value. Moreover, when we decreased the methanol/oil ratio to 6.0 while keeping all other parameters the same as those mentioned above, we found that the biodiesel yield could reach 95%. Although the yield decreased from 97% to 95%, from the cost-efficiency and processing safety point of view, we suggest using the molar ratio of methanol to oil at 6.0:1 for the biodiesel production. To ensure the conversion reaction, HPLC was used for product quality control. The results confirmed a nearly complete conversion based on the disappearance of triglyceride peaks (**Figure 2.4**) and the appearance of FAME peaks (**Figure 2.5**).

2.4 Conclusions

In summary, RSM was successfully applied to assess the effects of multiple variables, including the alcohol/oil molar ratio, catalyst concentration, temperature, rate of mixing, and reaction time, for the production of biodiesel from the crude cottonseed oil. The experimental results suggested the optimal condition as the follows: methanol/oil molar ratio, 7.9; temperature, 53°C; time, 45 min; catalyst concentration, 1.0 %; and rate of mixing, 268 rpm. This optimized condition was validated with the actual biodiesel yield in 97%. Moreover, the decrease of the methanol/oil molar ratio from 7.9/1 to 6.0/1

while keeping other variable parameters in their respective optimal conditions could produce biodiesel with yield of 95%. Since increasing the biodiesel yield by 2% with the cost of significantly increasing the molar ratio of methanol versus oil (6.0 to 7.9) does not appear to be cost-effective, we suggest using the methanol/oil molar ratio at 6.0 for the optimal production of biodiesel from crude cottonseed oil.

2.5 Figures and Tables

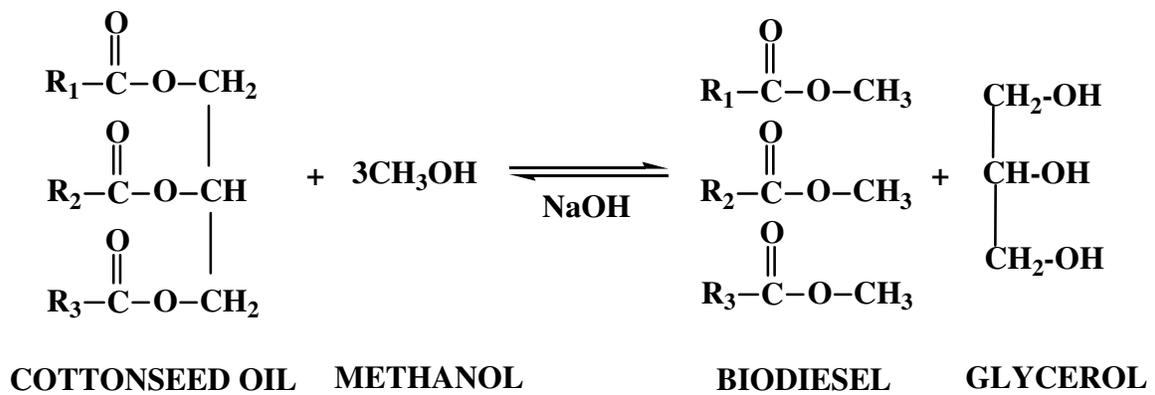


Figure 2.1 Chemical Reaction for Biodiesel Production

Table 2.1 3-Level-5-Factor Experimental Design

Level	Methanol/oil molar ratio	Catalyst/oil (wt.%)	Temperature (°C)	Time (min)	Rpm
1	4	0.5	45	30	250
2	6	1	55	45	300
3	8	1.5	65	60	350

Table 2.2 Experimental Matrix for the Factorial Design and Center Points

Run	Original Factors and Levels					Coded Factors and Levels					Yield
	A	B	C	D	E	X ₁	X ₂	X ₃	X ₄	X ₅	Y (%)
1	4/1	0.5	45	30	250	-1	-1	-1	-1	-1	92.97
2	8/1	0.5	45	30	250	+1	-1	-1	-1	-1	95.52
3	4/1	1.5	45	30	250	-1	+1	-1	-1	-1	43.45
4	8/1	1.5	45	30	250	+1	+1	-1	-1	-1	83.52
5	4/1	0.5	65	30	250	-1	-1	+1	-1	-1	94.55
6	8/1	0.5	65	30	250	+1	-1	+1	-1	-1	94.99
7	4/1	1.5	65	30	250	-1	+1	+1	-1	-1	60.33
8	8/1	1.5	65	30	250	+1	+1	+1	-1	-1	89.30
9	4/1	0.5	45	60	250	-1	-1	-1	+1	-1	96.83
10	8/1	0.5	45	60	250	+1	-1	-1	+1	-1	87.85
11	4/1	1.5	45	60	250	-1	+1	-1	+1	-1	39.30
12	8/1	1.5	45	60	250	+1	+1	-1	+1	-1	80.87
13	4/1	0.5	65	60	250	-1	-1	+1	+1	-1	94.81
14	8/1	0.5	65	60	250	+1	-1	+1	+1	-1	97.26
15	4/1	1.5	65	60	250	-1	+1	+1	+1	-1	52.48
16	8/1	1.5	65	60	250	+1	+1	+1	+1	-1	70.39
17	4/1	0.5	45	30	350	-1	-1	-1	-1	+1	93.52
18	8/1	0.5	45	30	350	+1	-1	-1	-1	+1	63.85
19	4/1	1.5	45	30	350	-1	+1	-1	-1	+1	22.58
20	8/1	1.5	45	30	350	+1	+1	-1	-1	+1	80.76
21	4/1	0.5	65	30	350	-1	-1	+1	-1	+1	90.93
22	8/1	0.5	65	30	350	+1	-1	+1	-1	+1	95.93
23	4/1	1.5	65	30	350	-1	+1	+1	-1	+1	51.83
24	8/1	1.5	65	30	350	+1	+1	+1	-1	+1	67.08
25	4/1	0.5	45	60	350	-1	-1	-1	+1	+1	82.51

26	8/1	0.5	45	60	350	+1	-1	-1	+1	+1	79.47
27	4/1	1.5	45	60	350	-1	+1	-1	+1	+1	16.92
28	8/1	1.5	45	60	350	+1	+1	-1	+1	+1	87.26
29	4/1	0.5	65	60	350	-1	-1	+1	+1	+1	84.53
30	8/1	0.5	65	60	350	+1	-1	+1	+1	+1	93.43
31	4/1	1.5	65	60	350	-1	+1	+1	+1	+1	50.06
32	8/1	1.5	65	60	350	+1	+1	+1	+1	+1	45.60
33	6/1	1.0	55	45	300	0	0	0	0	0	92.85
34	6/1	1.0	55	45	300	0	0	0	0	0	90.80
35	6/1	1.0	55	45	300	0	0	0	0	0	94.88
36	6/1	1.0	55	45	300	0	0	0	0	0	88.52
37	6/1	1.0	55	45	300	0	0	0	0	0	93.75
38	6/1	1.0	55	45	300	0	0	0	0	0	89.31
39	6/1	1.0	55	45	300	0	0	0	0	0	91.89
40	6/1	1.0	55	45	300	0	0	0	0	0	95.17

Herein: A (X_1)=methanol/oil molar ratio, B (X_2)=catalyst/oil (wt.%), C (X_3)=temperature (°C), D (X_4)=time (min), and E (X_5)=rate of mixing (rpm)

Table 2.3 SAS Results of Statistical Analysis for the 2⁵ Factorial Design

Variable	Parameter Estimate	t Value	Pr> t
Intercept	77.95	196.25	<0.0001
X ₁	7.67	17.28	<0.0001
X ₂	-15.54	-34.99	<0.0001
X ₃	2.70	6.07	0.0003
X ₄	-1.92	-4.33	0.0025
X ₅	-5.26	-11.83	<0.0001
X ₁ *X ₂	9.07	20.42	<0.0001
X ₁ *X ₃	-3.02	-6.80	0.0001
X ₁ *X ₄	0.12	0.28	0.7883
X ₁ *X ₅	-0.14	-0.32	0.7580
X ₂ *X ₃	-0.67	-1.54	0.1680
X ₂ *X ₄	-1.58	-3.55	0.0075
X ₂ *X ₅	-0.84	-1.93	0.0953
X ₃ *X ₄	-1.60	-3.60	0.0069
X ₃ *X ₅	0.59	1.34	0.2224
X ₄ *X ₅	0.25	0.58	0.5787
X ₁ *X ₂ *X ₃	-6.51	-14.67	<0.0001
X ₁ *X ₂ *X ₄	-1.19	-2.68	0.0278
X ₁ *X ₂ *X ₅	0.81	1.86	0.1046
X ₁ *X ₃ *X ₄	-1.68	-3.77	0.0054
X ₁ *X ₃ *X ₅	-1.43	-3.21	0.0123
X ₁ *X ₄ *X ₅	1.31	2.96	0.0181
X ₂ *X ₃ *X ₄	-1.15	-2.60	0.0318
X ₂ *X ₃ *X ₅	-1.73	-3.89	0.0046
X ₂ *X ₄ *X ₅	0.44	1.01	0.3449
X ₃ *X ₄ *X ₅	-0.75	-1.72	0.1300
X ₁ *X ₂ *X ₃ *X ₄	-1.10	-2.48	0.0381

$X_1 * X_2 * X_3 * X_5$	-3.75	-8.46	<0.0001
$X_1 * X_2 * X_4 * X_5$	-1.19	-2.68	0.0281
$X_1 * X_3 * X_4 * X_5$	-1.74	-3.91	0.0045
$X_2 * X_3 * X_4 * X_5$	0.49	1.12	0.2979
$X_1 * X_2 * X_3 * X_4 * X_5$	0.53	1.21	0.2644
Curve	-113.60	-17.88	<0.0001

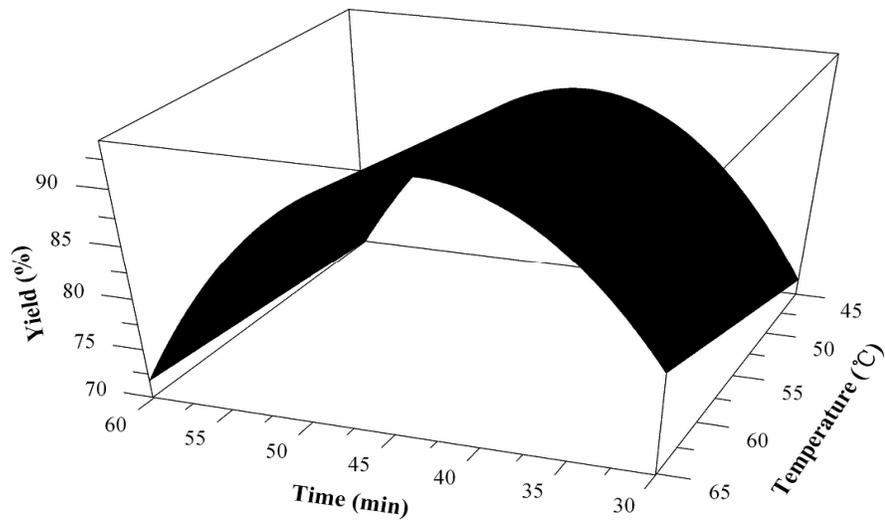


Figure 2.2 Biodiesel Yield vs. Temperature and Time

Table 2.4 Central Composite Design

Run	Original factors and levels				Coded factors and levels				Yield (%)
	A	B (wt.%)	C (°C)	D	X ₁	X ₂	X ₃	X ₄	
1	2	1	55	300	-2	0	0	0	56.48
2	10	1	55	300	2	0	0	0	87.61
3	6	0	55	300	0	-2	0	0	0
4	6	2	55	300	0	2	0	0	10
5	6	1	35	300	0	0	-2	0	89.13
6	6	1	75	300	0	0	2	0	82.04
7	6	1	55	200	0	0	0	-2	92.72
8	6	1	55	400	0	0	0	2	89.36

A: Methanol/oil molar ratio; B: Catalyst/oil (wt.%); C: Temperature (°C); D: Rate of mixing

$$Y = 27.387 + 5.873 * A + 98.532 * B - 0.924 * A * A - 86.827 * B * B + 9.067 * A * B$$

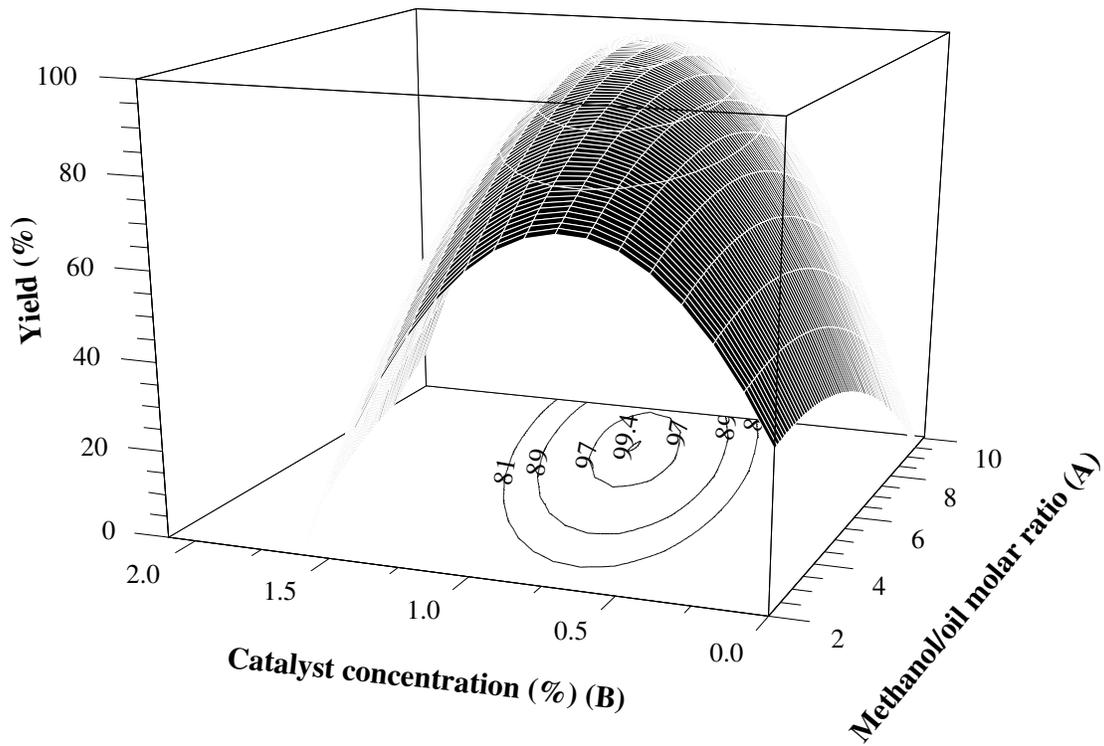


Figure 2.3 Response Surface and Contour Plot of the Effects of Methanol/oil Molar Ratio and Catalyst on the Yield of Biodiesel

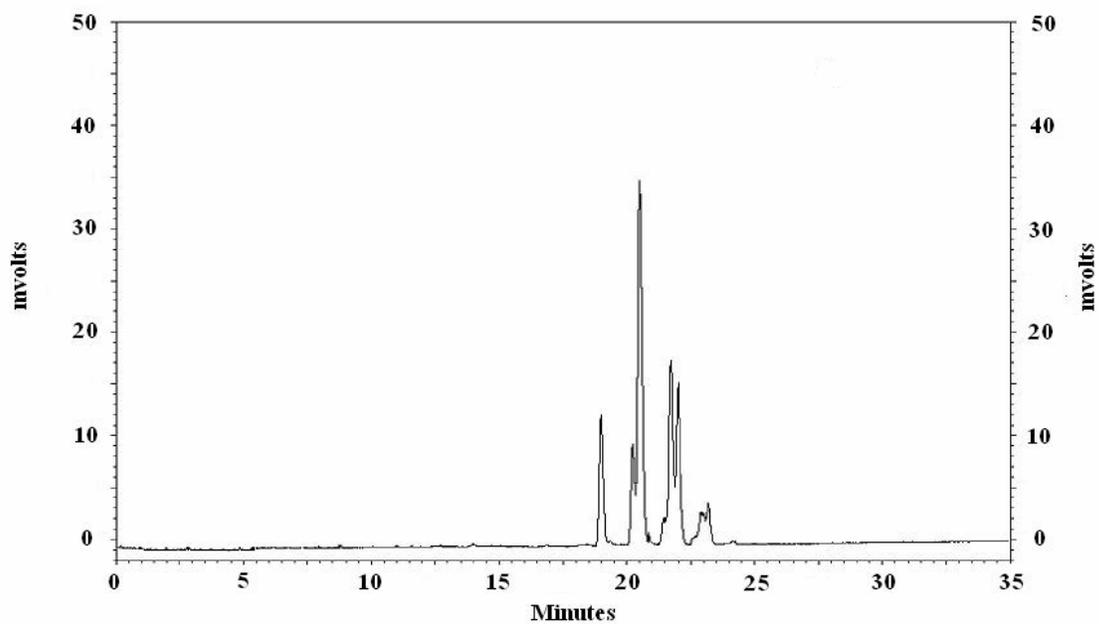


Figure 2.4 HPLC Chromatogram of Crude Cottonseed Oil

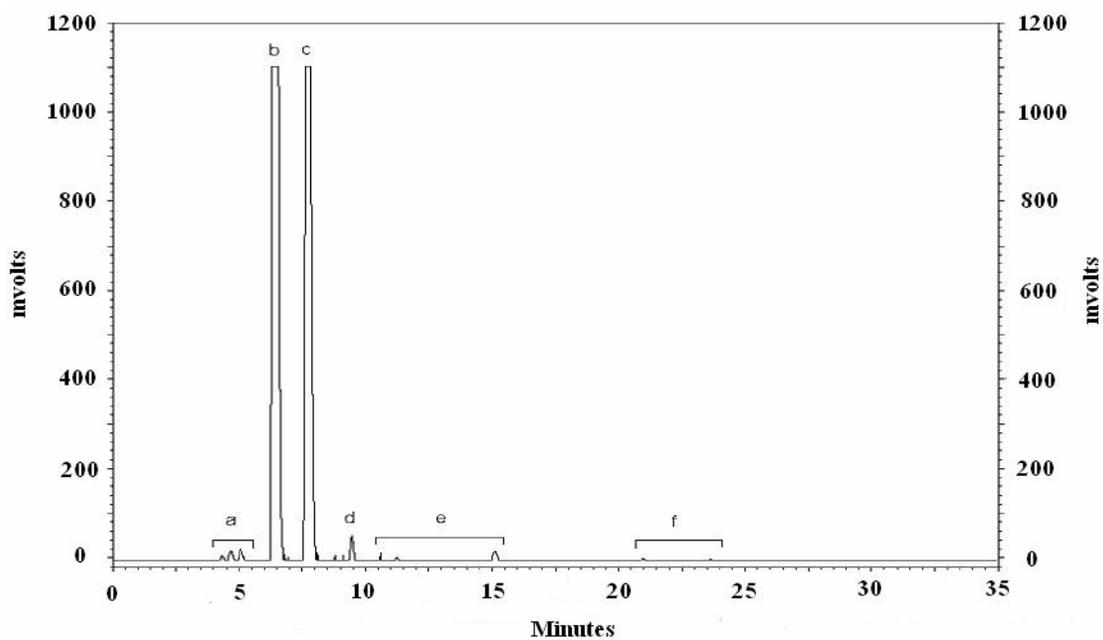


Figure 2.5 HPLC Chromatogram of Biodiesel from Crude Cottonseed Oil

a monoglycerides, **b** C18:2 (linoleic acid methyl ester), **c** C18:1 (oleic acid methyl ester), **d** C16:0 (palmitic acid methyl ester), **e** diglycerides, **f** unreacted triglycerides present in the biodiesel

2.6 References

- AOCS official method Ca 5a-40. (1997).
- Azcan, N., & Danisman, A. (2007). Alkali Catalyzed Transesterification of Cottonseed oil by microwave irradiation. *Fuel*, 86, 2639-2644.
- Chen, H., Peng, B.X., Wang, D.Z., & Wang, J.F. (2007). Biodiesel Production by the Transesterification of Cottonseed Oil by Solid Acid Catalysts. *Front Chem Eng China*, 1(1), 11-15.
- Cottonseed oil from Wikipedia. (2008). http://www.wikipedia.org/wiki/cotton-seed_oil.
- Cui, L.F., Xiao, G.M., Xu, B., & Teng, G.Y. (2007). Transesterification of Cottonseed oil to Biodiesel by Using Heterogeneous Solid basic Catalysts. *Energy Fuel*, 21, 3740-3743.
- Demirbaş, A. (2003). Biodiesel Fuels from Vegetable Oils via Catalytic and Non-Catalytic Supercritical Alcohol Transesterifications and Other Methods: A Survey. *Energy Convers Manage*, 44, 2093-2109.
- Demirbaş, A. (2008). Studies on Cottonseed Oil Biodiesel Prepared in Non-Catalytic SCF Conditions. *Bioresour Technol*, 99, 1125-1130.
- Fillières, R., Benjelloun-Mlayah, B., & Delmas, M. (1995). Ethanolysis of Rapeseed Oil: Quantitation of Ethyl Esters, Mono-, Di-, and Triglycerides and Glycerol by High Performance Size-Exclusion Chromatography. *J Am Oil Chem Soc*, 72(4), 427-432.
- Fukuda, H., Kondo, A., & Noda, H. (2001). Biodiesel Fuel Production by Transesterification of Oils. *J Biosci Bioeng*, 92(5), 405-416.
- Karabektas, M., Ergen, G., & Hosoz, M. (2008). The Effects of Preheated Cottonseed Oil Methyl Ester on the Performance and Exhaust Emissions of a Diesel Engine. *Appl Therm Eng*, 28, 2136–2143.
- Kong, Q., He, G.Q., Chen, Q.H., & Chen, F. (2004). Optimization of Medium Composition for Cultivating *Clostridium Butyricum* with Response Surface Methodology. *J Food Sci*, 69(7), M163-M168.
- Köse, Ö., Tüter, M., & Aksoy, H.A. (2002). Immobilized *Candida Antarctica* Lipase-Catalyzed Alcoholysis of Cotton Seed Oil in a Solvent-Free Medium. *Bioresour Technol*, 83, 125-129.

Plentz, M.S.M., Meneghetti, M.R., Wolf, C.R., Silva, E.C., Lima, G.E.S., & Coimbra, M.A. *et al.* (2006). Ethanolysis of Castor and Cottonseed Oil: A Systematic Study Using Classical Catalysts. *J Am Oil Chem Soc*, 83(9), 819-822.

Ryan, D.P.E. (2004). Biodiesel-A Primer. *Farm Energy Technical Note*, 1-14.

Yücesu, H.S., & İlkiliç, C. (2006). Effect of Cotton Seed Oil Methyl Ester on the Performance and Exhaust Emission of a Diesel Engine. *Energy Source, Part A*, 28, 389-398.

CHAPTER 3

ENGINE PERFORMANCE TEST OF COTTONSEED OIL BIODIESEL

Abstract

Two cottonseed oil biodiesel samples (cottonseed oil methyl esters, COME) produced in Clemson lab, together with other two commercial cottonseed oil biodiesels were evaluated on their engine performance with the No. 2 diesel fuel as a reference. The results revealed that CO, CO₂ and NO_x emissions of the cottonseed oil biodiesels were lower than those of the No. 2 diesel fuel. CO decreased by 13.8%, CO₂ by 11.1% and NO_x by 10%, though there was no significantly statistical difference at $p < 0.05$. The engine test also showed a slightly higher amount of consumption and less tendency of coke formation from COME than the No. 2 diesel fuel. The oxidative stability study showed COME with acceptable stability. COME exhibited friendly environmental benefits and acceptable stability, demonstrating its feasibility as an alternative fuel.

3.1 Introduction

As an alternative and renewable energy source, biodiesel received increasing interest in recent years because it can reduce global dependence on non-renewable petroleum. Moreover, increased environmental awareness prompts the development of biodiesels with less emission in an effort to reduce the environmental pollution.

In general, biodiesels contain 10% to 11% oxygen by weight, have a higher cetane number than petroleum diesel, have no aromatics, and have some attractive environmental benefits, such as lower emissions of CO, CO₂, and unburned hydrocarbons (HC) (Chang, Gerpen, Lee, Johnson, Hammond & Marley, 1996; Labeckas & Slavinskas, 2006). Biodiesel is commonly produced through chemical transesterification, a process in which triglycerides in vegetable oils or animal fats react with an alcohol in the presence of a catalyst. The transesterification process results in desirable biodiesel properties such as low viscosity, low molecular weight and high volatility, which overcome common problems such as an incomplete combustion, poor atomization, ring sticking, severe engine deposits, and injector coking that are encountered when natural oils and fats are used (Muniyappa, Brammer & Nouredini, 1996).

Engine performance test of biodiesels and their blends is indispensable for evaluating biodiesel properties. Several research groups (Chang, Gerpen, Lee, Johnson, Hammond & Marley, 1996; Graboski & McCormick, 1998) investigated the properties of a biodiesel blend with soybean oil methyl esters in diesel engines and found that particulate matter (PM), CO, and soot mass emissions decreased, while NO_x increased. Labeckas *et al.* (Labeckas & Slavinskas, 2006) examined the performance and exhaust

emissions of rapeseed oil methyl esters in direct injection diesel engines, and found that there were lower emissions of CO, carbon dioxide (CO₂) and HC. Similar results were reported (Kalligeros, Zannikos, Stournas, Lois, Anastopoulos & Teas *et al.*, 2003) for methyl esters of sunflower oil and olive oil when they were blended with marine diesel and tested in a stationary diesel engine. Raheman *et al.* (Raheman & Phadataré, 2004) studied the fuel properties of karanja methyl esters blended with diesel from 20% to 80% by volume. It was found that B20 (a blend of 20% biodiesel and 80% petroleum diesel) and B40 (a blend of 40% biodiesel and 60% petroleum diesel) could be used as appropriate alternative fuels of diesels because they had apparently less CO, NO_x emissions, and smoke density. Lin *et al.* (Lin, Lee & Hou, 2006) confirmed that emission of polycyclic aromatic hydrocarbons (PAH) decreased when the ratio of palm biodiesel increased in a blend with petroleum diesel. In general, biodiesel demonstrated improved emissions by reducing CO, CO₂, HC, PM, and PAH emissions though, in some cases, NO_x increased.

The source of biodiesel usually depends on the crops amenable to the regional climate. In the United States, soybean oil is the most commonly biodiesel feedstock, whereas in Europe, and in tropical countries the rapeseed (canola) oil and palm oil are the most common source for biodiesel, respectively. Cottonseed is a relatively small crop and its oil production volume has been reduced due to the direct feed of whole seed to dairy cattle. Cottonseed oil demonstrated superior lubricity property. Moreover, its unique minor components, such as natural anti-oxidants gossypol (O'Brien, 2004) and carotene (Caglayan, Kafa & Yigit, 2005) in the oil may play important role in retarding the oil

oxidation. Cottonseed oil itself could be a cost-effective component in the formulation to achieve a significant improvement in combustion efficiency, in increasing cetane number and reduction in exhaust in terms of CO, NO_x and PM (unpublished data from Oryxe). Since the properties of biodiesel are in large part correlated with the parent oil, biodiesel produced from cottonseed oil may exhibit appreciable oxidative stability and engine performance.

In this study, two biodiesel products produced from crude cottonseed oil in the Clemson University lab and other two commercial cottonseed oil biodiesels were tested on two identical diesel engines located in the Biofuels Engine Testing Laboratory at the University of Georgia in Athens, GA. Their engine performance and emissions were evaluated and compared with the No. 2 diesel fuel. In addition, the effect of pigments on oxidative stability of COME was also examined.

3.2 Material and Methods

3.2.1 Fuel Preparation

Cottonseed oil biodiesel COME A and COME B were produced from the same crude cottonseed oil through two different reaction conditions to prepare COME A with the highest conversion and COME B with the lightest color. Based on the response surface methodology, an optimized transesterification reaction (*i.e.*, temperature at 53°C, catalyst of NaOH at 1.0% based on weight of crude cottonseed oil, methanol/oil molar ratio at 6, and reaction time of 45 min) with conversion of 97% was used to prepare COME A in a temperature-controlled water bath shaker, while COME B was obtained from a non-optimized condition (*i.e.*, temperature at 65°C, catalyst of NaOH at 1.5%

based on weight of crude cottonseed oil, methanol/oil molar ratio at 8 and reaction time of 45 min). Briefly, a certain amount of crude cottonseed oil was weighed and added to a fixed Erlenmeyer flask, then a calculated amount of catalyst (sodium hydroxide) dissolved in the required amount of methanol was added. The reaction flask was immersed in the water bath to keep the temperature constant throughout the reaction with defined agitation. The produced COMEs were washed twice at 55°C with 1:1 volume of water. The conversion of the biodiesel from the cottonseed oil was quantified by a Shimadzu reverse-phase HPLC connected to an evaporative light scattering detector (ELSD).

All biodiesels, including the COME A and COME B, the commercial Pacific Biodiesel cottonseed oil biodiesel (TX), the PBSY cottonseed oil biodiesel from Safe Renewable (Conroe, TX), the soybean oil biodiesel (SOB) from a Houston-based company, and the No. 2 diesel, were evaluated on engine performance and emissions. Fuel properties and the No. 2 diesel specifications are shown in **Table 3.1** and **Table 3.2**, respectively.

3.2.2 Engine Experiments

The protocol used in this study was based on the method of Geller *et al.* with minor modifications (Geller, Goodrum & Campbell, 1999). The fuel temperature was maintained at room temperature (20-25°C). The test period was 2h. Each fuel was tested by two, 6-kW single cylinder, direct injection, water cooled test engines (Kubota model E750). At the end of test, the injectors were carefully removed and transported to the computer vision system. Carbon deposits on injector tips were scanned, while the coke

deposits were quantified by using an ImagingSource DMK 21AU04 monochrome digital camera and Image J software (Goodrum, Patel & McClendon, 1996). All values were referenced and calibrated to the same clean fuel injector. No. 2 ultra-low sulfur diesel (ULSD) fuel was selected as the baseline reference fuel. A coking index (CI) was assigned to each fuel and was determined using **Eq. 1**. In this system a coking index <1 indicates less coking than the No.2 diesel and an index >1 indicates more coking than the No.2 diesel.

$$\text{Coking Index (CI)} = \Delta p_{\text{fuel}} / \Delta p_{\text{D2}}, \quad (1)$$

where Δp_i = difference in pixels between image of dirty injector and image of clean injector.

A fuel consumption index was determined using a similar method shown in **Eq. 2** using the total amount of fuel consumed in the Peterson torque test described above.

$$\text{Fuel Consumption Index (FI)} = \frac{\text{Fuel of Interest Consumed}}{\text{ULSD consumed}} \quad (2)$$

With this system an index >1 indicates more consumption than the No.2 diesel and an index <1 indicates less consumption than the No.2 diesel. The ULSD has an index of 1 for both coking and fuel consumption. An ideal fuel has a both coking and fuel consumption indices < 1.

Stack emissions were measured using an ENERAC 3000E. The team recorded both average and instantaneous measurements of exhaust gas concentrations of CO, CO₂, NO_x, and sulfur dioxide. The analyzer software program enabled the recording of emission data directly to a spreadsheet file on the hard drive of a laptop computer. The ENERAC 3000 portable emissions analyzer is a self-contained, extractive emission

monitoring system utilizing electrochemical sensors with an internal sample pump designed for 600-900 cc/minute. A separate vacuum pump extracted emissions gas from a breaching port and discharged it to the ENERAC. Teflon tubing interconnected a filter probe in the breaching through two moisture condensers to the vacuum pump and then to the analyzer. The ENERAC sensors used an electronically controlled circuit to minimize zero drift and reject cross interference from other compounds, in compliance with EPA Conditional Test Methods (CTM) -022, -030 and -034. Performance specifications of the CTM-022 method are equivalent to US EPA Method 7E requirements. Accuracy of the sensors is +/-2%, and they are capable of operating at 1.5 orders of magnitude of gas concentrations. The tests were done in five replicates for each biodiesel or diesel fuel sample.

3.2.3 Color Measurement and Analyses of Pigments

Color measurement was conducted by using the Minolta Chroma Meter CR-300. Hunter lab color system was selected to record the color difference. In the color L^*a^*b system, L measures the luminous transmission and varies from 100 for perfect transmission to zero for opaque. The a and b values have no specific numerical limits. Positive a value represents redness, while negative a for greenness. Similarly, positive b is yellowness, while negative b for blueness. Pigment, i.e. carotene, was analyzed by RP-HPLC. The Shimadzu HPLC system consisted of photo diode array (PDA) detector with a Phenomenex C18 column (250×4.6 mm, 5 μ m). Mobile phase in an isocratic mode used HPLC grade solvents in a combination of acetonitrile/methanol/dichloromethane in a ratio of 90/8/2 (v/v). The flow rate of the mobile phase was 1.2 ml/min. Twenty

microliters of an appropriate diluted sample was injected into the column via an autosampler and monitored by PDA at the wavelength of 450nm during the whole running time of 40 min.

3.2.4 Oxidative Stability Measurement

The oxidative stability index was measured according to the AOCS official method Cd 12b-92 at 110°C (AOCS, 1997). The oxidative stability of biodiesel with gossypol addition was evaluated at the gossypol concentrations of 400, 600, 800, and 1000 ppm.

3.2.5 Data Analyses

Statistical analyses were performed by using the SAS program for Windows, Version 9.1, (Cary, NC) to examine the least significant difference (LSD) between the emissions results at the 95% confidence level.

3.3 Results and Discussion

3.3.1 Effect of Feedstocks on Biodiesel Engine Emissions Compared with the No. 2 Diesel

Emission data from the COME (average value for COME A, COME B, commercial Pacific Biodiesel cottonseed oil biodiesel and PBSY cottonseed oil biodiesel), SOB and No. 2 diesel are listed in **Table 3.3**.

Compared with the No. 2 diesel, COME and SOB had reduced CO emission by 13.8% and 2.6% though there was no significant difference at $p < 0.05$. This reduction might be related to the presence of oxygen in the biodiesel fuel, which enhanced the combustion process (Puhan, Vedaraman, Ram, Sankarnarayanan & Jeychandran, 2005).

Regarding the CO₂ emission, COME and SOB had 11.1% and 12.3% emission reduction compared with that of the No. 2 diesel. In addition, no SO_x emission was observed in all the vegetable oil biodiesels because neither the COME nor the SOB contained sulfur. Some researches reported that biodiesels had an increased NO_x emission (Graboski & McCormick, 1998; Jeong, Oh & Park, 2006; Almeida, Belchior, Nascimento, Vieira & Fleury, 2002), which was hypothesized that excessive NO_x might be formed in the cylinder where excessive oxygen content in biodiesels facilitated the oxidization of nitrogen in lean combustion areas. However, in our test the NO_x emission of the COME and SOB, compared with that of the No. 2 diesel, exhibited decreased values by 10% and 21%, respectively. These findings agree with the result reported by Yücesu *et al.* (Yücesu & İlkiliç, 2006) and Rakopoulos *et al.* (Rakopoulos, Antonopoulos, Rakopoulos, Hountalas & Giakoumis, 2006), who also found that the NO_x emission of biodiesel blends (including COME and SOB) decreased when the percentage of the biodiesel in the blend increased. It was proposed that higher cetane number and the absence of aromatics could, in a large part, offset the possible increase of the NO_x emission caused by the presence of the fuel bound oxygen, and result in a less NO_x production. Lower NO_x emission was also observed on mahua oil methyl ester (Puhan, Vedaraman, Ram, Sankarnarayanan & Jeychandran, 2005), which was ascribed to the ignition delay that might cause the reduction of peak pressure rise and the decrease of flame temperature because the low pressure and low temperature in the second stage of combustion process could cause the reduction in NO_x emission. In fact, it is generally accepted that the NO_x formation from atmospheric nitrogen is highly dependent upon temperature because high

activation energy is needed for the reaction involved. NO_x formation has also been linked to specific engine design. Therefore, the NO_x emission in the biodiesel combustion is dependent not only on the bound oxygen concentration, but also by combustion temperature and time, among which the former may be the most significant factor. Another possibility is that different fuel system designs and engine calibrations may also result in a measurable difference of the NO_x emission from biodiesels. Nevertheless, in our test, the cottonseed oil biodiesel, like the commercial product (i.e., SOB), showed lower emissions of CO, CO_2 and NO_x than those of the No. 2 diesel, which demonstrated the practical and feasible environmental benefits.

3.3.2 Fuel Consumption and Coking

The brake specific fuel consumption (BSFC) is defined as the fuel flow rate divided by the engine's output power. It has been shown that biodiesels and petrodiesels had the same efficiency in converting the energy in the fuel to power (Monyem & Gerpen, 2001). Therefore, it was reasonable in our observation that the BSFC values of the tested biodiesels (i.e., COME and SOB) were about 12.5% higher than that of the No. 2 diesel (see **Figure 3.1**) because the biodiesels had lower energy content, 12.5% less than that of the No. 2 diesel on a weight basis. The **Figure 3.1** also shows another benefit that both the COME and the SOB demonstrated less engine coking than the No. 2 diesel.

3.3.3 Effect of Color (pigments) in Biodiesel on Oxidative Stability

Biodiesel has many advantages over fossil fuels, but its stability is a big concern, especially when the fuel is produced from fats or oils with high levels of unsaturated fatty acids. Crude cottonseed oil contains approximately 49~58% linoleic acid, which is highly

susceptible to oxidation. The antioxidant pigments which cause the color differences in the biodiesels can affect the oxidative stability. **Table 3.4** lists the color difference of all four cottonseed oil biodiesel samples. From appearance, Pacific Biodiesel cottonseed oil biodiesel had the darkest color, followed by PBSY cottonseed oil biodiesel, COME A, while the COME B had the lightest color.

Table 3.5 lists the OSI values. All cottonseed oil biodiesels demonstrated acceptable stability according to the ASTM D 6751 specifications that required minimum 3h. In our test, the Pacific Biodiesel possessed the highest OSI value, followed by PBSY, COME A, and COME B. In coincidence, the oxidative stability of biodiesels is correlated to the color appearance of the biodiesels. The darker the biodiesel is, the more stable the biodiesel would be. Therefore, it was hypothesized that some strong antioxidant pigments, such as gossypol and carotene, might have played important roles in stabilizing the biodiesels. Our HPLC analyses confirmed that 2 ppm of carotene and a trace amount of gossypol were present in the COME A, and only a trace amount of carotene and gossypol present in the COME B. This may explain why the COME A was more stable than the COME B. In addition, the Pacific Biodiesel showed the best oxidative stability with the highest carotene content of 8 ppm.

Furthermore, considering the fact that gossypol is a strong antioxidant in cottonseed oil, biodiesel was fortified with gossypol to assess its effect on the OSI value. The added amount of gossypol in biodiesel was correlated to the oxidative stability of the biodiesel (**Table 3.6**). Gossypol exhibited a significant and positive effect on biodiesel stability. For example, an OSI value of 17.2h was achieved for the COME A after 0.1%

gossypol was added. Thus, retaining pigments in the biodiesel during production might have positive impact on biodiesel stability.

3.4 Conclusions

Biodiesel produced from crude cottonseed oil exhibited improved engine performance. Engine test demonstrated that the CO, CO₂, and NO_x emissions decreased by 13.8%, 11.1%, and 10%, respectively, compared with those of No. 2 ULSD. In addition, the oxidative stability of the cottonseed oil biodiesel was correlated to the content of pigments (such as antioxidants, gossypol, carotene etc.), the darker the color and the more stable the biodiesel, and all the sampled cottonseed oil biodiesel showed acceptable stability according to the ASTM D 6751 requirement.

3.5 Figures and Tables

Table 3.1 Properties of Commercial Pacific Biodiesel Produced from Cottonseed Oil

Property	Units	ASTM		ASTM D-6751 Specification
		Test Method	Test Results	
Flash point	°C	D-93	218	130 min.
Water and sediment	% volume	D-2079	<0.05	0.05 max.
Carbon residue	% mass	D-4530	0.04	0.05 max.
Sulfated ash	% mass	D-874	0.005	0.02 max.
Kinematic viscosity, 40 °C	mm ² /s (CST)	D-445	4.88	1.9-6.0
Cetane number		D-613	49.2	47 min.
Cloud point	°C	D-2500	11	Report value
Copper corrosion		D-130	1A	No. 3 max.
Acid number	mgKOH/g	D-664	0.25	0.80 max.
Free glycerin	% mass	D-6584	<0.01	0.02 max.
Total glycerin	% mass	D-6584	0.09	0.24 max.
Phosphorous content	ppm	D-4951	2.4	10 max.
Sodium	ppm	D-4951	1.3	5 max.
Potassium	ppm	D-4951	0.6	5 max.
Distillation, 90% recovered	°C	D-1160	356	360 max.

Table 3.2 Specifications of the No. 2 Diesel

Property	Units	ASTM Test Method	ASTM D-975 Specification
Flash point	°C	D-93	52min.
Water and sediment	% volume	D-2079	0.05 max.
Carbon residue	% mass	D-524	0.35 max.
Kinematic viscosity, 40 °C	mm ² /s	D-445	1.9-4.1
Sulfur	% mass	D-2622	0.05 max
Cetane number		D-613	40 min.
Copper corrosion		D-130	No. 3 max.

Table 3.3 Comparison of Engine Emissions of COME Average, SOB and No. 2 Diesel

	CO (ppm)	CO ₂ (%)	SO _x (ppm)	NO _x (ppm)
COME Average	8978 ^a	9.4581 ^a	0 ^a	509.68 ^{a,b}
SOB	10144 ^a	9.328 ^a	0 ^a	448.24 ^b
No.2 Diesel	10417 ^a	10.64 ^a	10.5 ^a	567.2 ^a
LSD _{0.05}	4849.8	1.7332	18.273	112.05

Mean values with different superscripts in the same column are significantly different ($P < 0.05$).

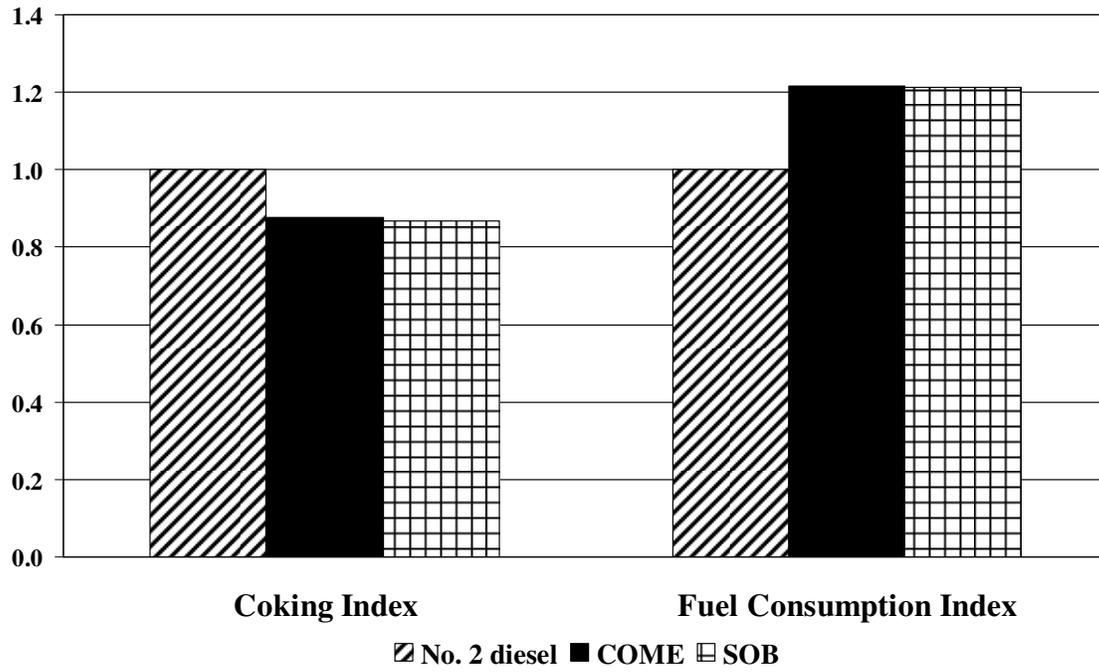


Figure 3.1 Fuel Consumption and Coking Index

Table 3.4 Color Measurement of Biodiesels

	L	a	b
COME A	49.49	-4.90	22.75
COME B	51.86	-2.16	5.04
Pacific Biodiesel	37.14	8.23	14.08
PBSY	50.49	-2.91	8.93
SOB	52.13	-1.40	4.91

Table 3.5 Oxidative Stability Comparison of Biodiesels

Sample	Temperature (°C)	Run Time (h)	Method
COME A	110	4.25	
COME B	110	3.00	All by the
Pacific biodiesel	110	11.35	AOCS Cd
PBSY	110	10.90	12b-92
SOB	110	5.05	

Table 3.6 The Effect of Gossypol Addition on COME A's Oxidative Stability

Sample	Gossypol Addition (ppm)	Temp (°C)	Run Time (h)	Method
COME A	0	110	4.15	
COME A-4	400	110	5.2	All by the
COME A-6	600	110	6.2	AOCS Cd
COME A-8	800	110	8.0	12b-92
COME A-10	1000	110	17.2	

3.6 References

- Almeida, S.C.A., Belchior, C.R., Nascimento, M.V.G., Vieira, L.S.R., & Fleury, G. (2002). Performance of a Diesel Generator Fueled with Palm Oil. *Fuel*, 81, 2097-2102.
- AOCS Official Method Cd 12b-92. (1997). 1-5.
- Caglayan, M.O., Kafa, S., & Yigit, N. (2005). Al-Pillared Clay for Cottonseed Oil Bleaching: an Optimization Study. *J Am Oil Chem Soc*, 82(8), 599-602.
- Chang, D.Y.Z., Gerpen, J.H.V., Lee, I., Johnson, L.A., Hammond, E.G., & Marley, S.J. (1996). Fuel Properties and Emissions of Soybean Oil Esters as Diesel Fuel. *J Am Oil Chem Soc*, 73(11), 1549-1555.
- Geller, D.P., Goodrum, J.W., & Campbell, C.C. (1999). Rapid Screening of Biologically Modified Vegetable Oils for Fuel Performance. *Trans ASAE*, 42(4), 859-862.
- Goodrum, J.W., Patel, V.C., & McClendon, R.W. (1996). Diesel Injector Carbonization by Three Alternative Fuels. *Trans ASAE*, 39(3), 817-821.
- Graboski, M.S., & McCormick, R.L. (1998). Combustion of Fat and Vegetable Oil Derived Fuels in Diesel Engines. *Prog Energy Combust Sci*, 24, 125-164.
- Jeong, G.T., Oh, Y.T., & Park, D.H. (2006). Emission Profile of Rapeseed Methyl Ester and its Blend in a Diesel Engine. *Appl Biochem Biotech*, 129, 165-178.
- Kalligeros, S., Zannikos, F., Stournas, S., Lois, E., Anastopoulos, G., Teas, Ch., & Sakellaropoulos, F. (2003). An Investigation of Using Biodiesel/Marine Diesel Blends on the Performance of a Stationary Diesel Engine. *Biomass Bioenerg*, 24, 141-149.
- Labeckas, G., & Slavinskas, S. (2006). The Effect of Rapeseed Oil Methyl Ester on Direct Injection Diesel Engine Performance and Exhaust Emissions. *Energy Convers Manage*, 47, 1954-1967.
- Lin, Y.C., Lee, W.J., & Hou, H.C. (2006). PAH Emissions and Energy Efficiency of Palm-Biodiesel Blends Fueled on Diesel Generator. *Atmos Environ*, 40, 3930-3940.

- Monyem, A., & Gerpen, J.H.V. (2001). The Effect of Biodiesel Oxidation on Engine Performance and Emissions. *Biomass Bioenerg*, 20, 317-325.
- Muniyappa, P.R., Brammer, S.C., & Nouredini, H. (1996). Improved Conversion of Plant Oils and Animal Fats into Biodiesel and Co-product. *Bioresour Technol*, 56, 19-24.
- O'Brien, R.D. (2004). *Fats and Oils: Formulating and Processing for Applications*. CRC Press: Boca Raton, 16-18.
- Puhan, S., Vedaraman, N., Ram, B.V.B., Sankarnarayanan, G., & Jeychandran, K. (2005). Mahua Oil (*Madhuca Indica* Seed Oil) Methyl Ester as Biodiesel Preparation and Emission Characteristics. (2005). *Biomass Bioenerg*, 28, 87-93.
- Raheman, H., & Phadatare, A.G. (2004). Diesel Engine Emissions and Performance from Blends of Karanja Methyl Ester and Diesel. *Biomass Bioenerg*, 27, 393-397.
- Rakopoulos, C.D., Antonopoulos, K.A., Rakopoulos, D.C., Hountalas, D.T., & Giakoumis, E.G. (2006). Comparative Performance and Emissions Study of a Direct Injection Diesel Engine Using Blends of Diesel Fuel with Vegetable Oils or Bio-diesels of Various Origins. *Energy Convers Manage*, 47, 3272-3287.
- Yücesu, H.S., & İlkiliç (2006). Effect of Cotton Seed Oil Methyl Ester on the Performance and Exhaust Emission of a Diesel Engine. *Energy Source, Part A*, 28, 389-398.

CHAPTER 4

**ULTRASONICALLY ASSISTED PRODUCTION OF BIODIESEL FROM
CRUDE COTTONSEED OIL**

Abstract

Transesterification of crude cottonseed oil with methanol in the presence of base catalyst by means of low frequency ultrasonic irradiation at room temperature (25°C) was investigated to evaluate the effects of methanol/oil molar ratio, reaction time, catalyst type and concentration and ultrasonic frequency on the biodiesel yield. Sodium hydroxide demonstrated the best activity. The high biodiesel yield obtained within shorter time under ultrasonic irradiation condition was attributed to the efficacy of cavitation, which could enhance the mass transfer between the methanol and crude cottonseed oil. The present results confirmed the high efficiency and feasibility of using ultrasonic energy to produce biodiesel.

4.1 Introduction

Biodiesel, the fatty acid alkyl ester, is gaining more and more attention in recent years since it may be at least a partial answer to the world's need for renewable energy. It can be produced by the transesterification process, which consists of a sequence of three consecutive reversible reactions, including conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides. The glycerides are converted into glycerol and yield one ester molecule in each step.

Transesterification can be catalyzed by acid (Williams, Mulcahy, Ford, Oliphant, Caldwell & Soriano, 2007; Zullaikah, Lai, Vali & Ju, 2005), base (Meka, Tripathi & Singh, 2007; Rashid & Anwar, 2008) or enzyme (Ranganathan, Narasimhan & Muthukumar, 2008). However, acid catalysis is generally slower and enzyme catalyst is more expensive than base catalyst. Therefore, base catalysts are preferred in the industrial scale. Commonly used base catalysts include sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide (NaOCH₃), and potassium methoxide (KOCH₃).

Stoichiometrically, a 3:1 molar ratio of alcohol to triglyceride is necessary to complete the reaction. In practice, excess amount of alcohol is added to enhance the biodiesel yield. The transesterification process can be affected by many factors, including the molar ratio of alcohol to oil, catalyst type and concentration, reaction time and temperature, etc. Among which the mixing efficiency is one of the most important factors since triglyceride and alcohol are immiscible. To strengthen the mass transfer between liquid-liquid heterogeneous systems, ultrasound can serve as a useful tool which has entered the popular consciousness. Many researches have demonstrated the feasibility

and proved the efficiency of using ultrasonic mixing to improve biodiesel production (Colucci, Borrero & Alape, 2005; Armenta, Vinatoru, Burja, Kralovec & Barrow, 2007; Stavarache, Vinatoru, Nishimura & Maeda, 2005; Ji, Wang, Li, Yu & Xu, 2006; Stavarache, Vinatoru, Maeda & Bandow, 2007; Hanh, Dong, Okitsu, Maeda & Nishimura, 2007).

It is known that ultrasound can generate cavitation that can efficiently improve the biodiesel production (**Figure 4.1**). Cavitation generally includes steps of generation, subsequent growth and collapse of cavities resulting in very high energy densities of the order of 1 to 10^{18} kW/m³ (Gogate, Tayal & Pandit, 2006). One kind of cavitation is called acoustic cavitation, in which bubbles containing mainly vapor reduce the ambient pressure sufficiently at essentially constant temperature and cause an ‘explosive’ vaporization into the cavities. Strong shock wave generated during the collapse of bubbles further disrupts the phase boundary, enhancing the mixing efficiency between immiscible triglycerides and alcohols. By applying the ultrasound, biodiesel production cost can be reduced significantly due to its high efficiency and low energy input.

The present work aims at studying the effect of ultrasonic irradiation on the production of biodiesel from crude cottonseed oil in the presence of base catalysts. Variables which affect the biodiesel yield, including methanol/oil molar ratio, catalyst type and concentration, reaction time, and ultrasound frequency, will be discussed.

4.2 Material and methods

4.2.1 Materials

Methanol was purchased from Fisher Scientific (Suwanee, GA, USA). NaOH (granular), KOH (pellets, ACS reagent), NaOCH₃ (anhydrous powder), and KOCH₃ (95%-99%) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Crude cottonseed oil was generously provided by the Elgin Cotton Oil Mill, Inc. (Elgin, TX, USA), the same raw material as mentioned in the Chapter 2, therefore, it has the same fatty acid profile and FFA content.

4.2.2 Apparatus

The ultrasonic system is comprised of ultrasound reactor, power supply amplifier (Model G 7520), and function generator (Model 182A), which converts a standard line voltage to a high-frequency electrical power. This electrical energy fed to the transducer, which is inside the soundproof enclosure, can be converted to mechanical vibrations of the same frequency.

4.2.3 Transesterification of Crude Cottonseed Oil

The amount of needed methanol was dependent on the defined methanol/oil molar ratio. The concentration of the base catalyst was based on the weight of crude cottonseed oil. An appropriate amount of catalyst dissolved in the methanol was added to the precisely prepared crude cottonseed oil. This mixture was then introduced to the ultrasound reactor. Ultrasound reaction was started at a desired frequency. After reaction, the product was kept overnight. The glycerol richer-phase, which stayed in the lower layer due to its relatively higher density, was separated from the methyl ester (biodiesel)

layer, the upper layer. The methyl ester layer was then washed to remove the excess alcohol residue, catalyst, and soap. Since water in biodiesel can lead to biological growth, the washed biodiesel was placed at 55°C oven to evaporate the water residue and then dried with anhydrous sodium sulphate.

4.2.4 Statistical Analyses

The biodiesel yield obtained under different ultrasound frequencies was analyzed statistically using the SAS program. Differences among individual mean yield were considered to be significant at $p < 0.05$.

4.3 Results and Discussion

Variables such as methanol/oil molar ratio, catalyst type and concentration, reaction time, and ultrasound frequency were investigated.

4.3.1 Effect of Methanol/Oil Molar Ratio

The methanol/oil molar ratio is known to be one of the most important variables affecting the biodiesel yield. In order to evaluate the effect of methanol/oil molar ratio on biodiesel yield, transesterification was conducted at different methanol/oil molar ratios (3/1, 6/1, 8/1, and 9/1) at room temperature (25°C) under 40 kHz ultrasound irradiation. **Figure 4.2** showed the relationship between the different molar ratios and the biodiesel yield when catalyzed by NaOH at different reaction times (from 10 s to 60 min). It demonstrated that at each of ten reaction times, the yield increased with increasing molar ratio from 3/1 to 6/1. The biodiesel yield greater than 90% could be achieved within 1 min. After about 10 min, the biodiesel yield of 95% could be reached. However, when the molar ratio equaled to 8/1 and 9/1, the yield apparently decreased.

Since transesterification is an equilibrium process, lower methanol/oil molar ratio may result in an incomplete transesterification. Increasing the methanol/oil molar ratio will shift the reaction to the ester formation direction. However when the methanol/oil molar ratio is set too high, the excessive alcohol may favor conversion of diglycerides to monoglycerides, and a slight recombination of esters and glycerol to monoglycerides because their concentrations keep increasing during the course of the reaction (Fillières, Benjelloun-Mlayah & Delmas, 1995). Also, the excess methanol, with one polar hydroxyl group, could act as an emulsifier and thereby increase the solubility of glycerol in the ester phase, making the separation more difficult. The glycerol remained in the solution could drive the equilibrium back to the left, reducing the esters conversion (Krisnangkura & Simamaharnnop, 1992).

4.3.2 Effect of Reaction Time

It could also be seen from **Figure 4.2** that, at the same methanol/oil molar ratio, there were no apparent differences for the yield along with the course of the reaction time from 10 s to 60 min. This means the ultrasonic irradiation is more efficient to produce biodiesel than the mechanical stirring. Hanh *et al.* (Hanh, Dong, Okitsu, Maeda & Nishimura, 2007) evaluated the reaction time to reach the steady state ethyl ester concentration under ultrasonic irradiation. Their results showed that the optimal time was less than 20 min at 25°C at the ethanol/oil molar ratio of 6/1. Armenta *et al.* (Armenta, Vinatoru, Burja, Kralovec & Barrow, 2007) observed that almost the entire transesterification was finished within the first 10 min when using ultrasonic energy to transesterify fish oil in the presence of base catalysts. Stavarache *et al.* (Stavarache,

Vinatoru & Maeda, 2007) also confirmed that the major part of the ultrasonically driven transesterification of vegetable oils under base catalysis took place in the first 3-10 min of the reaction.

This efficiency can be attributed to the fact that the emulsion droplets under ultrasonic irradiation become smaller, which increases contact (surface) area between the immiscible phases, thus enhancing the mass transfer, accelerating the reaction, and improving the production efficiency.

4.3.3 Effect of Catalyst Type and Concentration

Figure 4.3 shows the influence of catalyst type on the biodiesel yield. As can be seen, NaOH catalyst presented the best behavior. Moreover, the hydroxide catalysts showed better results than the counterpart methoxide catalysts. This observation was in agreement to those found by Encinar *et al.* (Encinar, González & Rodríguez-Reinares, 2005; Encinar, González & Rodríguez-Reinares, 2007), who evaluated the effect of catalyst types on methyl and ethyl ester yields. The different effects exhibited by these four kinds of catalysts could be explained by the fact that their chemical molecular weights were different. At the same weight concentration, the amount of methoxides available for each mole of triglyceride will differ. The effectiveness of catalysts might be correlated with the molar concentration of the catalyst formulation (Singh, Thompson & Gerpen, 2006). Since NaOH has the lowest molecular weight, it has the highest molar concentration, and the best performance in the biodiesel production.

The effect of catalyst concentration on the biodiesel yield is shown in **Figure 4.4**. When the concentration of NaOH was below 0.5 wt.% (by weight of crude cottonseed

oil), the lowest yields were obtained because the added NaOH was insufficient to catalyze the reaction for completion. In contrast, the best results were achieved at the concentration of 1 wt.%. Further addition of excessive amount of catalyst (1.5 wt.% and 3 wt.%) not only made the separation more complicated, but reduced the biodiesel yield. These results agreed with that discovered by Dorado *et al.* (Dorado, Ballesteros, López & Mittelbach, 2004), who optimized the parameters involved in the transesterification process of *Brassica carinata* oil. Encinar *et al.* (Encinar, González & Rodríguez-Reinares, 2005), Meher *et al.* (Meher, Dharmagadda & Naik, 2006), and Rashid *et al.* (Rashid & Anwar, 2008) also obtained similar results that there was a decrease in the yield with the increase in the catalyst concentration. This phenomenon can be attributed to the fact that at higher catalyst concentration, emulsion was formed and the dissolved soap can increase the methyl ester solubility in the glycerol, causing additional yield loss (Vicente, Martínez & Aracil, 2004).

4.3.4 Effect of Ultrasound Frequency

Four different frequencies (400 Hz, 4 kHz, 40 kHz, 400 kHz) were investigated to examine the effect of ultrasound frequency on biodiesel yield, while keeping other reaction conditions the same (methanol/oil molar ratio=6, NaOH concentration=1 wt.%, reaction time=15 min). The result is listed in the **Table 1**. There is no significant difference in any biodiesel yield ($p < 0.05$) at different frequencies, which indicates that there were no remarkable differences in the formation of the cavitation bubbles at the examined frequencies.

These results were in line with the observation of Stavarache *et al.* (Stavarache, Vinatoru, Nishimura & Maeda, 2005), who evaluated the influence of different frequencies (up to 100 kHz) on the biodiesel yield when transesterifying commercial edible grade vegetable oil with short chain alcohol. No remarkable results were found, though the transesterification yields were slightly lower at 40 kHz than at 28 kHz. However, it is already known that at higher frequencies the collapse of cavitation bubbles are not strong enough to impinge one liquid to the other, failing to generate intensive emulsification. The reason for this is that at very high frequency the rarefaction is extremely short. On the other hand, to produce a cavity in the liquid, a finite time is required to permit the molecules to be pulled apart. So when the rarefaction cycle approaches and becomes shorter than this time, it is more difficult and even impossible to achieve cavitation. In our case, since all the investigated frequencies were relatively low, there were no significantly different effects on the biodiesel yield.

4.4 Conclusions

The biodiesel yield of 95% could be achieved after 10 min reaction at room temperature (25°C), 6/1 of methanol/oil molar ratio, and 1 wt.% NaOH concentration under 40 kHz ultrasonic irradiation. Among the catalysts investigated, NaOH showed the best activity, which was ascribed to its highest molar concentration when the weight concentration was the same. Among the different ultrasonic frequencies examined, no significant different effects on the biodiesel yield were observed. Nevertheless, ultrasonic irradiation was an efficient way to produce biodiesel from crude cottonseed oil.

4.5 Figures and Tables

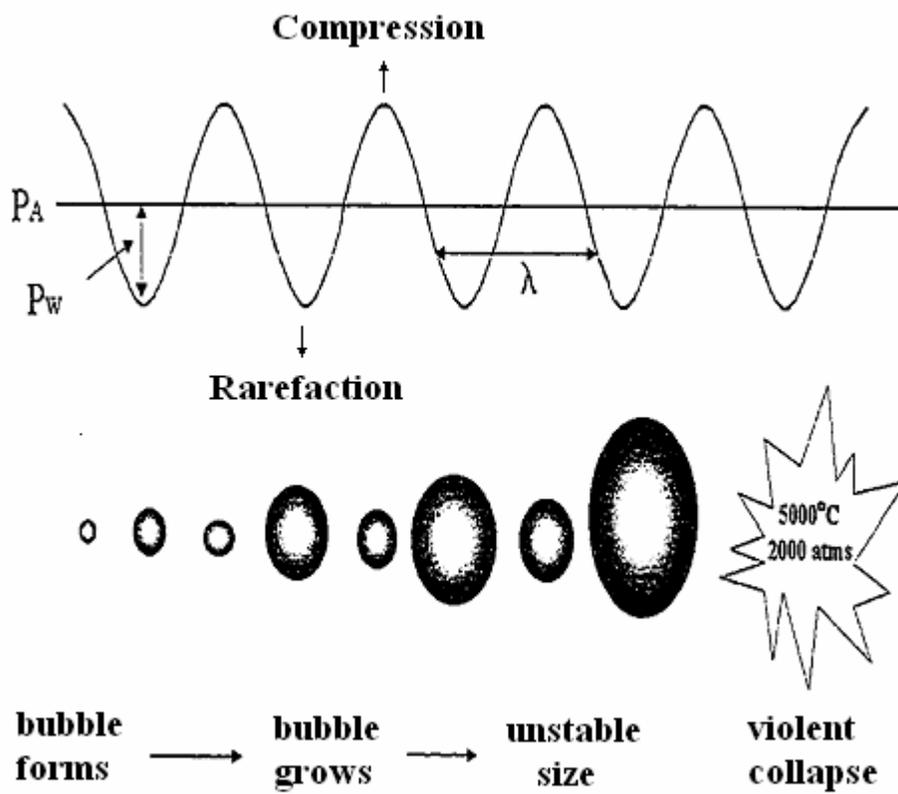


Figure 4.1 the Phenomenon of Cavitation

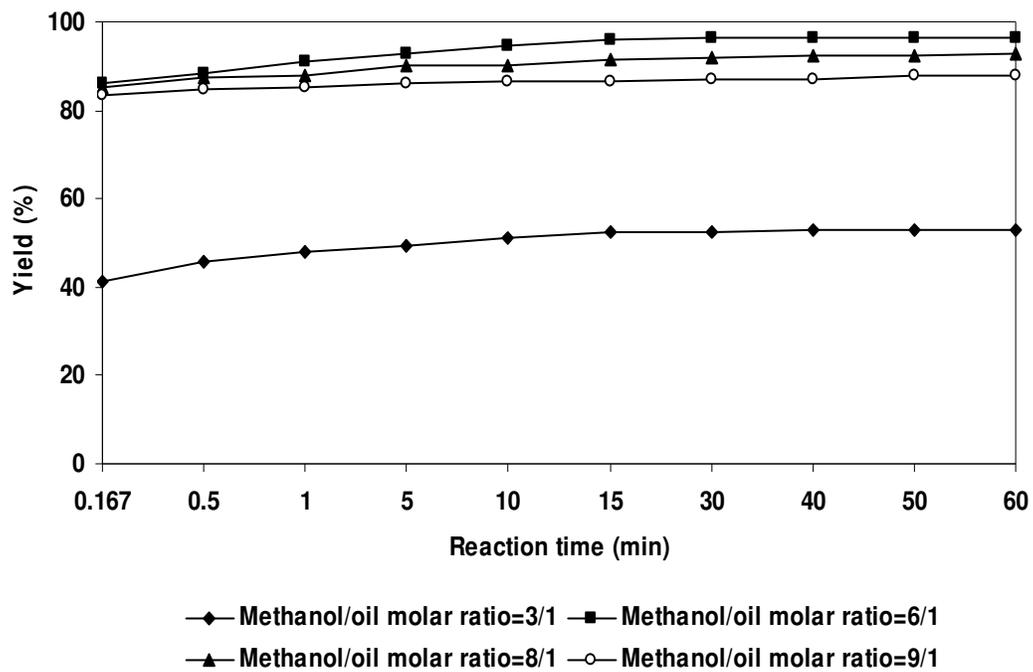


Figure 4.2 Effect of Methanol/oil Molar Ratio on the Biodiesel Yield.

Reaction Conditions: Temperature 25°C; Frequency 40 kHz; NaOH

Concentration 1 wt.%.

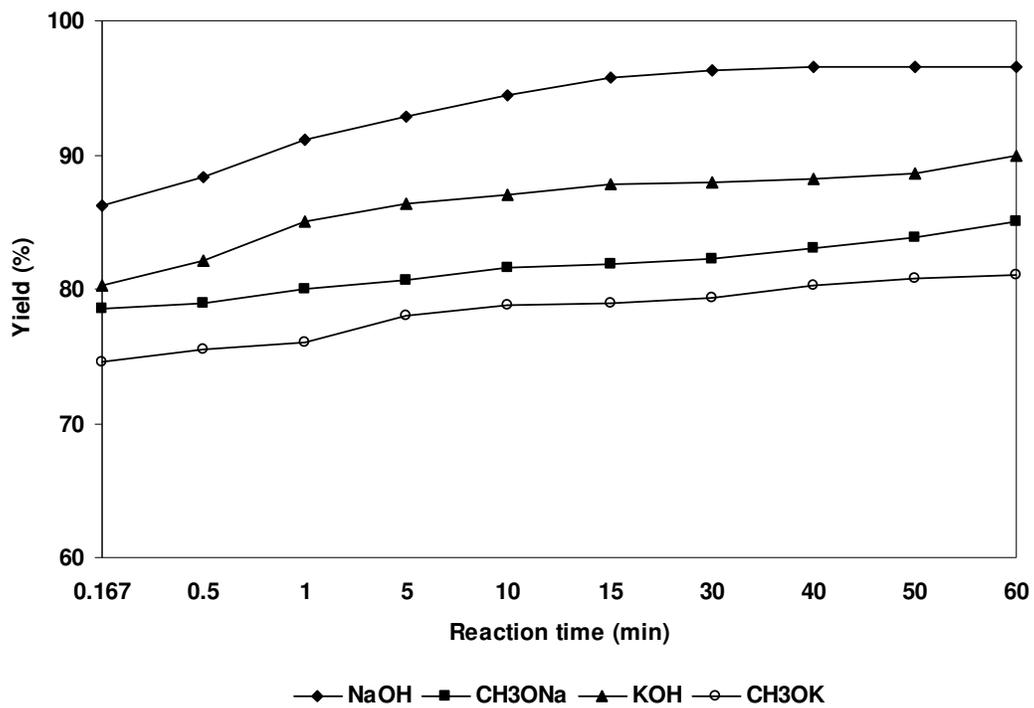


Figure 4.3 Effect of Catalyst Type on the Biodiesel Yield.

Reaction Conditions: Temperature 25°C; Frequency 40 kHz; Catalyst

Concentration 1 wt.%; Methanol/oil Molar Ratio 6/1.

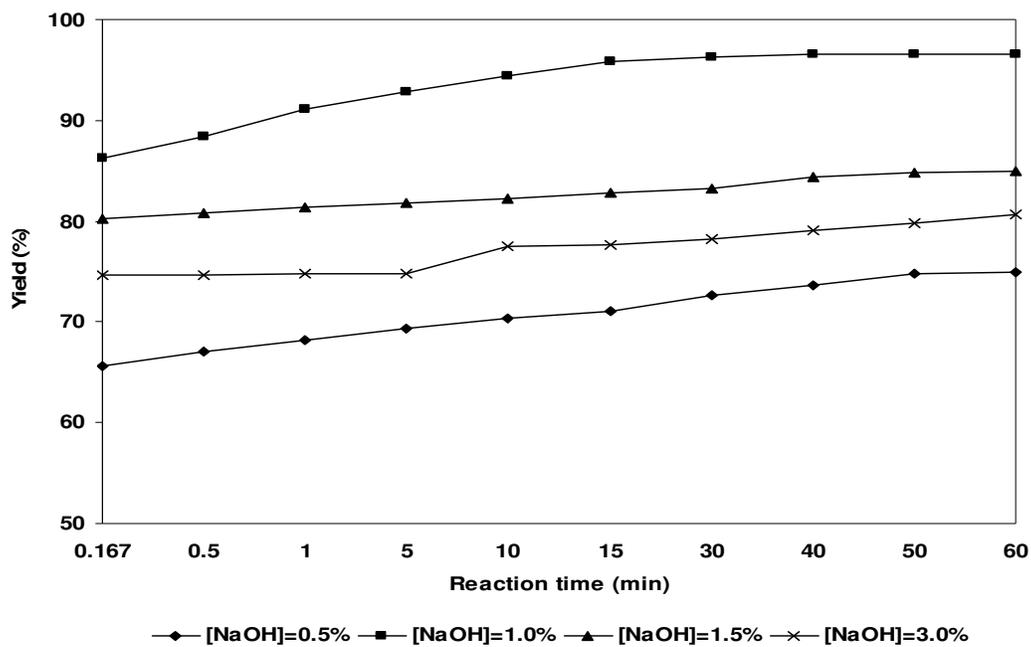


Figure 4.4 Effect of Catalyst Concentration on the Biodiesel Yield.

Reaction Conditions: Temperature 25°C; Frequency 40 kHz; Methanol/oil

Molar Ratio 6/1.

Table 4.1 Effect of ultrasound frequency on the biodiesel yield

Run	Frequency (Hz)	Yield (%)
1	40 k	96.0 ^a
2	400 k	96.6 ^a
3	4 M	96.2 ^a

Values in the last column with the same letter of superscript are not significantly different

($p < 0.05$, $n=3$); Reaction conditions: temperature 25°C; NaOH concentration 1 wt.%;

reaction time 15 min; methanol/oil molar ratio=6/1.

4.6 References

- Armenta, R.E., Vinatoru, M., Burja, A.M., Kralovec, J.A., & Barrow, C.J. (2007). Transesterification of Fish Oil to Produce Fatty Acid Ethyl Esters Using Ultrasonic Energy. *J Am Oil Chem Soc*, 84, 1045-1052.
- Colucci, J.A., Borrero, E.E., & Alape, F. (2005). Biodiesel from an Alkaline Transesterification Reaction of Soybean Oil Using Ultrasonic Mixing. *J Am Oil Chem Soc*, 82(7), 525-530.
- Cottonseed oil from Wikipedia. (2008). http://www.en.wikipedia.org/wiki/cottonseed_oil.
- Dorado, M.P., Ballesteros, E., López, F.J., Mittelbach, M. (2004). Optimization of Alkali-Catalyzed Transesterification of *Brassica Carinata* Oil for Biodiesel Production. *Energ Fuel*, 18, 77-83.
- Encinar, J.M., González, J.F., & Rodríguez-Reinares, A. (2005). Biodiesel from Used Frying Oil. Variables Affecting the Yields and Characteristics of the Biodiesel. *Ind Eng Chem Res*, 44, 5491-5499.
- Encinar, J.M., González, J.F., & Rodríguez-Reinares, A. (2007). Ethanolysis of Used Frying Oil. Biodiesel Preparation and Characterization. *Fuel Process Technol*, 88, 513-522.
- Fillières, R., Benjelloun-Mlayah, B., & Delmas, M. (1995). Ethanolysis of Rapeseed Oil: Quantitation of Ethyl Esters, Mono-, Di-, and Triglycerides and Glycerol by High-Performance Size-Exclusion Chromatography. *J Am Oil Chem Soc*, 72(4), 427-432.
- Gogate, P.R., Tayal, R.K., & Pandit, A.B. (2006). Cavitation: A Technology on the Horizon. *Curr Sci India*, 91, 35-46.
- Hanh, H.D., Dong, N.T., Okitsu, K., Maeda, Y., & Nishimura, R. (2007). Effect of Molar Ratio, Catalyst Concentration and Temperature on Transesterification of Triolein with Ethanol under Ultrasonic Irradiation. *J Jpn Petrol Inst*, 50, 195-199.
- Ji, J.B., Wang, J.L., Li, Y.C., Yu, Y.L., & Xu, Z.C. (2006). Preparation of Biodiesel with the Help of Ultrasonic and Hydrodynamic Cavitation. *Ultrasonics*, 44, e411-e414.

- Krisnangkura, K., & Simamaharnnop, R. (1992). Continuous Transmethylation of Palm Oil in an Organic Solvent. *J Am Oil Chem Soc*, 69(2), 166-169.
- Meher, L.C., Dharmagadda, V.S.S., & Naik, S.N. (2006). Optimization of Alkali-catalyzed Transesterification of *Pongamia Pinnata* Oil for Production of Biodiesel. *Bioresour Technol*, 97, 1392-1397.
- Meka, P.K., Tripathi, V., & Singh, R.P. (2007). Synthesis of Biodiesel Fuel from Safflower Oil Using Various Reaction Parameters. *Fuel*, 87, 265-273.
- Ranganathan, S.V., Narasimhan, S.L., & Muthukumar, K. (2008). An Overview of Enzymatic Production of Biodiesel. *Bioresour Technol*, 99, 3975-3981.
- Rashid, U., & Anwar, F. (2008). Production of Biodiesel through Optimized Alkaline-catalyzed Transesterification of Rapeseed Oil. *Fuel*, 87, 265-273.
- Singh, A., He, B., Thompson, J., & Gerpen, J.V. (2006). Process Optimization of Biodiesel Production Using Alkaline Catalysts. 22, 597-600.
- Stavarache, C., Vinatoru, M., & Maeda, Y. (2007). Aspects of Ultrasonically Assisted Transesterification of Various Vegetable Oils with Methanol. *Ultrason Sonochem*, 14, 380-386.
- Stavarache, C., Vinatoru, M., Maeda, Y., & Bandow, H. (2007). Ultrasonically Driven Continuous Process for Vegetable Oil Transesterification. *Ultrason Sonochem*, 14, 413-417.
- Stavarache, C., Vinatoru, M., Nishimura, R., & Maeda, Y. (2005). Fatty Acids Methyl Esters from Vegetable Oil by Means of Ultrasonic Energy. *Ultrason Sonochem*, 12, 367-372.
- Vicente, G., Martínez, M., & Aracil, J. (2004). Integrated Biodiesel Production: A Comparison of Different Homogeneous Catalysts Systems. *Bioresour Technol*, 92, 297-305.
- Williams, P., Mulcahy, F., Ford, J.T., Oliphant, J., Caldwell, & J., Soriano, D. (2007). Biodiesel Preparation via Acid Catalysis and Characterization. *Journal of Undergraduate Chemistry Research*, 6, 87-96.
- Zullaikah, S., Lai, C.C., Vali, S.R., & Ju, Y.H. (2005). A Two-step Acid-catalyzed Process for the Production of Biodiesel from Rice Bran Oil. *Bioresour Technol*, 96, 1889-1896.

CHAPTER 5

TRANSESTERIFICATION OF CRUDE COTTONSEED OIL TO PRODUCE BIODIESEL USING ULTRASONIC IRRADIATION: AN OPTIMIZED PROCESS APPLYING RESPONSE SURFACE METHODOLOGY

Abstract

Response surface methodology (RSM) based on central composite rotatable design (CCRD) was used to optimize the three important reaction variables: methanol/oil molar ratio (M), catalyst concentration (C) and reaction time (T) for transesterification of crude cottonseed oil under ultrasonic irradiation. A quadratic polynomial model was obtained to predict the methyl ester yield. 98% of the methyl ester yield could be reached at the deduced optimal condition: methanol/oil molar ratio of 6.2:1, catalyst concentration of 1% (by the weight of crude cottonseed oil) and reaction time of 8 min. Validation experiments confirmed the validity of the predicted model. Moreover, ultrasonic irradiation was proved to be an efficient, energy saving and economically feasible way to produce biodiesel.

5.1 Introduction

Biodiesel is currently of interest due to high energy demand, the limited resource of fossil fuel and environmental concerns. Made from vegetable oil, such as cottonseed oil, soybean oil, rapeseed oil or animal fat, biodiesel is a renewable, biodegradable, non-toxic and clean-burning fuel (Lang, Dalai, Bakhshi, Reaney & Hertz, 2001; Antolín, Tinaut, Briceño, Castaño, Pérez & Ramírez, 2002; Vicente, Martínez & Aracil, 2004), producing favorable effects on the environment (Hu, Du, Tang & Min, 2004; Shieh, Liao & Lee, 2003).

The most common method for producing biodiesel is through transesterification, a chemical process in which an alcohol, usually methanol, reacts with triglycerides to generate biodiesel and the by-product, glycerol in the presence of catalyst, usually alkaline (sodium hydroxide or potassium hydroxide) when the free fatty acid content in the raw material is below 1%.

To obtain increased biodiesel yields within shorter reaction times, ultrasonically-assisted production of biodiesel is currently the focus of new research (Colucci, Borrero & Alape, 2005; Stavarache, Vinatoru & Maeda, 2006; Ji, Wang, Li, Yu & Xu, 2006; Armenta, Vinatoru, Burja, Kralovec & Barrow, 2007). This process improves the mass transfer between two immiscible liquids, methanol and oils through cavitation, the phenomenon in which bubbles cause an explosive vaporization into the cavities. Stavarache *et al.* (Stavarache, Vinatoru, Nishimura & Maeda, 2005)) found the common mixing problems could be overcome by using low frequency (28 kHz and 40 kHz) ultrasounds when transesterifying commercially edible grade vegetable oil with short-

chain alcohols in the presence of base catalyst. The authors concluded that supersonic jets are created during the collapse of cavitation bubbles of methanol, generating nano-sized drops that are extremely efficient for mixing, thus abundantly enhancing the reaction efficiency (Stavarache, Vinatoru & Maeda, 2007).

It is well-known that using ultrasound for biodiesel production can improve mixing efficiency and reduce energy consumption. In addition, variables such as the methanol/oil molar ratio, reaction time, and the catalyst concentration could also have significant effects on the biodiesel yield using ultrasound, similar to the conventional method. To determine the optimal condition, Hanh *et al.* (Hanh, Dong, Okitsu, Maeda & Nishimura, 2007) evaluated these variables by transesterifying triolein with ethanol under ultrasonic irradiation. However, the process was time-consuming and complex since the interrelationships among the test variables were complicated.

Response surface methodology (RSM), a powerful tool in the optimization of chemical reactions, addresses this issue by providing: (1) an understanding of how the test variables affect the selected process response; (2) the determination of the interrelationships among the test variables; (3) and the characterization of the combined effect that all influential test variables may have on the process response. Because of these advantages, RSM has been increasingly involved in biodiesel production. For example, Ghadge and Raheman (Ghadge & Raheman, 2006) used this methodology to optimize the pretreatment process for reducing the free fatty acid (FFA) content of mahua oil to below 1% for maximum biodiesel production. In their study, it was found that three variables, including methanol quantity, acid catalyst concentration, and reaction time

could significantly affect the acid value of the product. Similarly, Tiwari *et al.* (Tiwari, Kumar & Raheman, 2007) deduced a quadratic polynomial model using RSM to optimize these three variables to reduce acid value of the *Jatropha* oil (*Jatropha curcas*) before its conversion to biodiesel. Li *et al.* (Li, Du & Liu, 2007) applied the same method developing a polynomial model which was used to predict the yield of biodiesel when utilizing whole cell biocatalyst. The authors adopted the central composite design to study the effect of *tert*-butanol quantity, methanol quantity, water content and dry biomass of the immobilized cell on biodiesel (methyl ester) yield. Most recently, RSM has been used for optimizing biodiesel production from waste rapeseed oil with high FFA (Yuan, Liu, Zeng, Shi, Tong & Huang, 2008).

Cottonseed oil biodiesel produced in our lab exhibited improved engine performance. Its stability was acceptable according to the ASTM D 6751, which was correlated to the content of pigments, such as gossypol (Fan, Wang, Chen, Geller, & Wan, 2008). However, little research has been conducted using cottonseed oil in the production of biodiesel using RSM, especially in the case of ultrasonic-assisted process. To address this issue, the study reported here investigated the ultrasonically assisted production of biodiesel (methyl ester in this experiment) from crude cottonseed oil by using RSM. The primary objective was to evaluate the suitability of RSM for optimizing the methanolysis of crude cottonseed oil, including the development of a mathematical model describing the relationships and subsequent effects of the primary process variables.

5.2 Material and methods

5.2.1 Reagents and Materials

Methanol was purchased from Fisher Scientific (Suwanee, GA, USA). Sodium hydroxide was bought from Sigma chemical company (St. Louis, MO, USA). Crude cottonseed oil derived from expeller (i.e. screw pressed cottonseed) was obtained from the Elgin Cotton Oil Mill, Inc. (Elgin, TX, USA). It was the same sample as described in Chapter 2, so it had the same fatty acid profile and FFA content. The ultrasonic reaction system is comprised of ultrasound reactor, power supply amplifier (Model G 7520), and function generator (Model 182A, 4MHz), which converts a standard line voltage to a high-frequency electrical power. This electrical energy fed to the transducer, which is inside the soundproof enclosure, can be converted to mechanical vibrations of the same frequency.

5.2.2 Experimental Design

A 3-factor experiment was conducted using a central composite rotatable design (CCRD) to examine effects of methanol/oil molar ratio, reaction time, and catalyst concentration on yield of methyl ester. The CCRD consisted of 20 experimental runs (eight factorial points, eight axial points, and four replicated center points) and provided sufficient information to fit a full second-order polynomial model. Results from previous research (Yuan, Liu, Zeng, Shi, Tong & Huang, 2008) were used to establish the center point of the CCRD for each factor: 6/1, 1%, and 8 min for methanol/oil molar ratio, catalyst concentration, and reaction time, respectively. **Table 5.1** provides the levels used

for each factor, and to avoid bias, the 20 experimental runs were performed in randomized order (**Table 5.2**).

5.2.3 Transesterification of Crude Cottonseed Oil

Transesterification of crude cottonseed oil with methanol in the presence of sodium hydroxide proceeded at room temperature (25°C) under 40 kHz ultrasonic irradiation. The amount of methanol needed was determined by the methanol/oil molar ratio. An appropriate amount of catalyst dissolved in the methanol was added to the precisely prepared crude cottonseed oil. This mixture was then introduced to the ultrasound reactor.

5.2.4 Statistical Analysis

The experimental data presented in **Table 5.2** was analyzed using the response surface regression (RSREG) procedure in SAS that fits a full second-order polynomial model:

$$y = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{ii} x_i^2 + \sum_{i=1}^3 \sum_{j=1}^2 \beta_{ij} x_i x_j$$

where y is % methyl ester yield, x_i and x_j are the independent study factors, and β_0 , β_i , β_{ii} , and β_{ij} are intercept, linear, quadratic, and interaction constant coefficients, respectively.

An α level of 0.05 was used to examine the statistical significance of the fitted polynomial model. The RSREG procedure uses canonical analysis to estimate stationary values for each factor. Using the fitted model, response surface contour plots were constructed for each pair of study factors while holding the other factor constant at its estimated stationary point. Confirmatory experiments were carried out to validate the

model using combinations of independent variables that were not a part of the original experimental design but within the experimental region.

5.3 Results and Discussion

5.3.1 RSM Analysis of Transesterification

Table 5.3 listed the regression coefficients and the corresponding p -values for the second-order polynomial model. It could be seen from the p -values of each model term that the regression coefficients of the linear term M , C , the quadratic term, M^2 , C^2 , and the interaction term, TC , MC had significant effects on the yield (p -value <0.05). Among them, M , C , C^2 , MC were significant at 1% level, while M^2 and TC were significant at 5% level.

Using the determined coefficients (**Table 5.3**), the predicted model in terms of uncoded factors for methyl ester yield is:

$$Y_{\text{yield}} = -123.93 - 1.36T + 32.02M + 188.97C + 0.49TM - 0.59TC - 4.44MC - 0.05T^2 - 1.99M^2 - 66.06C^2$$

Where Y_{yield} is the response, that is, the methyl ester yield, and T , M , and C are the actual values of the test variables, reaction time, methanol/oil molar ratio, and catalyst concentration, respectively.

It could be concluded from **Table 5.3** that the linear effects of M , C and the quadratic effect of C^2 were the primary determining factors on the methyl ester yield as they had the largest coefficient. Meanwhile, the quadratic effect of M^2 and the interaction effect of MC were the secondary determining factors with medium coefficient. Other terms of the model showed no significant effect on Y_{yield} . Among them, M and C had

positive coefficient, exhibiting the enhancement on the yield. However, all the other terms had negative coefficient.

Table 5.4 shows the analysis of variance (F -test) and the p -value for this model. The F -value is 28.57 and the p -value is smaller than 0.0001, demonstrating the suitability of the deduced model. The R^2 value (=0.963) indicates that the quadratic model was able to predict 96.3% of the total variance and only 3.7% of the total variance was not explained by the model.

5.3.2 Effect of Parameters

Contour plots (**Figure 5.1a-5.1c**) are profiled to show the relationships between the dependent and independent variables of the developed model. Each contour curve presents the effect of two variables on the methyl ester yield, holding the third variable at constant level. Remarkable interaction between the independent variables can be observed if the contour plots have an elliptical profile. **Figure 5.1a** shows the strong interaction between methanol/oil molar ratio (M) and catalyst concentration (C). This can also be confirmed by the small p -value (0.0001) for MC term. It can also be seen from the **Figure 5.1a** that the methyl ester yield increased with increasing catalyst concentration at the low concentration. However, when the catalyst concentration was more than its center point, the reverse trend was observed. The similar pattern was observed when increasing the methanol/oil molar ratio. This could be due to the fact that the positive coefficient for C and M played the main role when the catalyst concentration and methanol/oil molar ratio were at lower level, while at higher level, the interaction term MC and quadratic term M^2 and C^2 showed more significant negative effect, leading to the decrease of the

yield. This was consistent with the physical explanation. Since the methanol and triglyceride in the crude cottonseed oil are immiscible, addition of catalyst can facilitate the transesterification reaction, and rapidly increase the yield. However, when the catalyst concentration was too high, soap could be quickly formed which made the separation of glycerol from biodiesel more difficult, thus reducing the yield. Similarly, the increase of the methanol amount, on one hand, will drive the reaction to the right since the transesterification reaction is an equilibrium process; on the other hand, excess methanol will help increase the solubility of glycerol resulting in the reaction driven to the left, thus decreasing the yield.

Figure 5.1b shows the effect of reaction time and catalyst concentration on the methyl ester yield. At a certain level of catalyst concentration, there is no significant change in methyl ester yield when increasing the reaction time. Similar results are observed in the **Figure 5.1c** when the level of methanol/oil molar ratio is fixed. This could be explained by the higher p -value (0.6124) for the T term in the model, indicating the non-significant effect. It can also be observed from the **Figure 5.1b** that when the catalyst concentration was about 1%, the methyl ester yield could be greater than 90% in less than 5 min. Compared with conventional mechanical stirring method, transesterification under ultrasonic irradiation was more efficient. This was also confirmed by many other researchers (Armenta, Vinatoru, Burja, Kralovec & Barrow, 2007; Stavarache, Vinatoru & Maeda, 2007). The advantage of ultrasonic irradiation was attributed to the effect of cavitation, in which strong shock wave was generated during

the collapse of bubbles that further disrupted the phase boundary and enhanced the mixing efficiency between immiscible triglycerides and alcohols.

5.3.3 Attaining Optimum Conditions and Model Verification

RIDGE analysis for maximization suggested the optimal values for the test variables in uncoded unit were as follows: reaction time=8 min, catalyst concentration=1%, methanol/oil molar ratio=6.2:1. Under the above optimum conditions of the variables, the model predicted that the maximum yield could be 99%. Verification experiments were performed at the suggested optimal conditions to examine the adequacy of the predicted model. The actual value was 98% for the methyl ester yield. Hence, the quadratic model was considered to be suitable to predict the methyl ester yield.

5.3.4 The Advantages of Using Ultrasonic Irradiation to Produce Biodiesel

It could be clearly seen from RSM results that methyl ester produced by using ultrasonic irradiation exhibited many advantages. Compared with conventional mechanical stirring method, it could not only reduce the transesterification processing time, but also decrease reaction temperature due to the increased chemical activity in the presence of cavitation. These will reduce the biodiesel production costs and make biodiesel more competitive in price than diesel fuel.

5.4 Conclusions

In this study, RSM was proved to be a powerful tool for the optimization of methyl ester production under ultrasonic irradiation at room temperature. A second-order model was successfully developed to describe the relationships between methyl ester yield and test variables, including methanol/oil molar ratio, catalyst concentration and

reaction time. The optimal conditions for the maximum methyl ester yield were found to be at methanol/oil molar ratio of 6.2:1, catalyst concentration of 1% (by the weight of crude cottonseed oil), reaction time of 8 min. Validation experiment further confirmed the accuracy of the model. The transesterification process under ultrasonic irradiation could be more efficient, making biodiesel production more competitive in price than diesel fuel.

5.5 Figures and Tables

Table 5.1 Independent Variable and Levels Used for CCRD in Methyl Ester Production

Variables	Symbol	Levels				
Reaction Time (min)	T	0.43	3.5	8.0	12.5	15.57
Methanol/oil Molar Ratio (mol/mol)	M	0.95	3	6	9	11
Catalyst Concentration (wt.%)	C	0.16	0.5	1	1.5	1.8

Table 5.2 CCRD Arrangement and Responses for Methyl Ester Production

Treatment	Random	Level of Variables			Yield (%) (response)	
		T, min	M, mol/ mol	C, wt. %	Experimental	Predicted
1	8	12.5	9	1.5	95.5	97.3
2	12	8	6	1	96.0	97.6
3	7	3.5	9	1.5	73.3	84.9
4	14	15.6	6	1	98.4	96.3
5	2	12.5	3	0.5	23.9	15.5
6	19	8	6	1	97.6	97.6
7	1	3.5	3	0.5	22.9	24.3
8	9	8	6	1	98.0	97.6
9	20	8	6	1	98.0	97.6
10	13	0.43	6	1	97.0	93.2
11	6	12.5	3	1.5	41.7	51.7
12	4	12.5	9	0.5	86.8	87.8
13	18	8	6	1.8	91.0	75.7
14	3	3.5	9	0.5	76.8	70.1
15	16	8	11	1	90.3	86.0
16	5	3.5	3	1.5	63.6	65.8
17	17	8	6	0.16	21.5	29.6
18	10	8	6	1	97.0	97.6
19	15	8	0.95	1	10.0	8.4
20	11	8	6	1	98.0	97.6

T: Reaction time, M: Methanol/oil molar ratio, C: Catalyst concentration

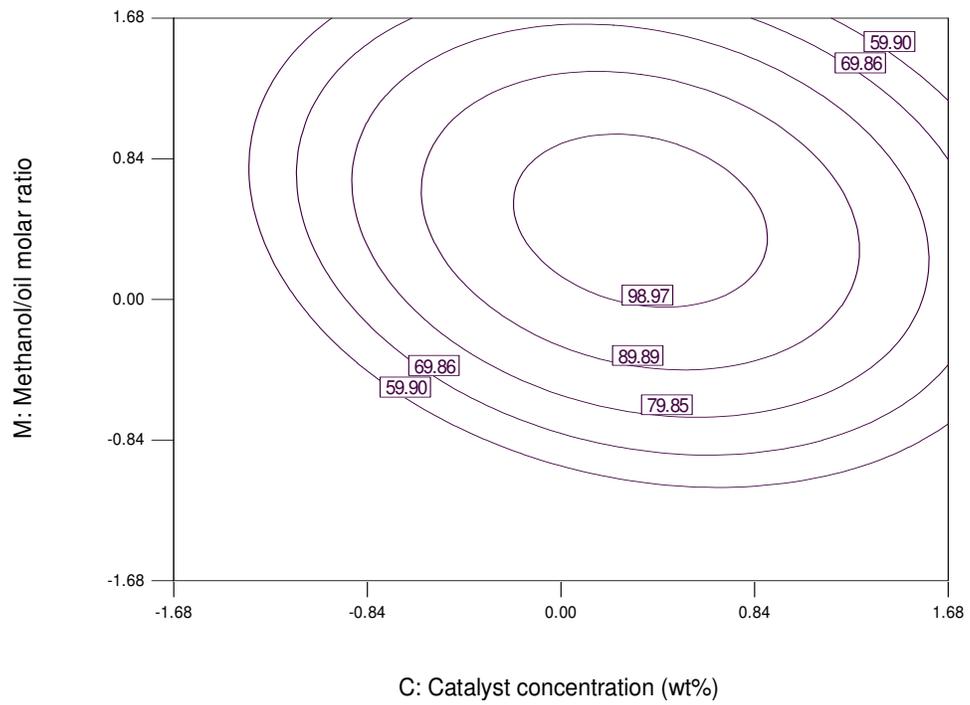
Table 5.3 Regression Coefficients of Predicted Quadratic Polynomial Model for Methyl Ester Production

Terms	Regression Coefficients	<i>p</i> -value
Intercept		
β_0	-123.93	0.0005
Linear		
β_1	-1.36	0.6124
β_2	32.02	0.0001
β_3	188.97	0.0001
Quadratic		
β_{11}	-0.05	0.6643
β_{22}	-1.99	0.0489
β_{33}	-66.06	0.0001
Interaction		
β_{12}	0.49	0.6611
β_{13}	-0.59	0.0482
β_{23}	-4.44	0.0001

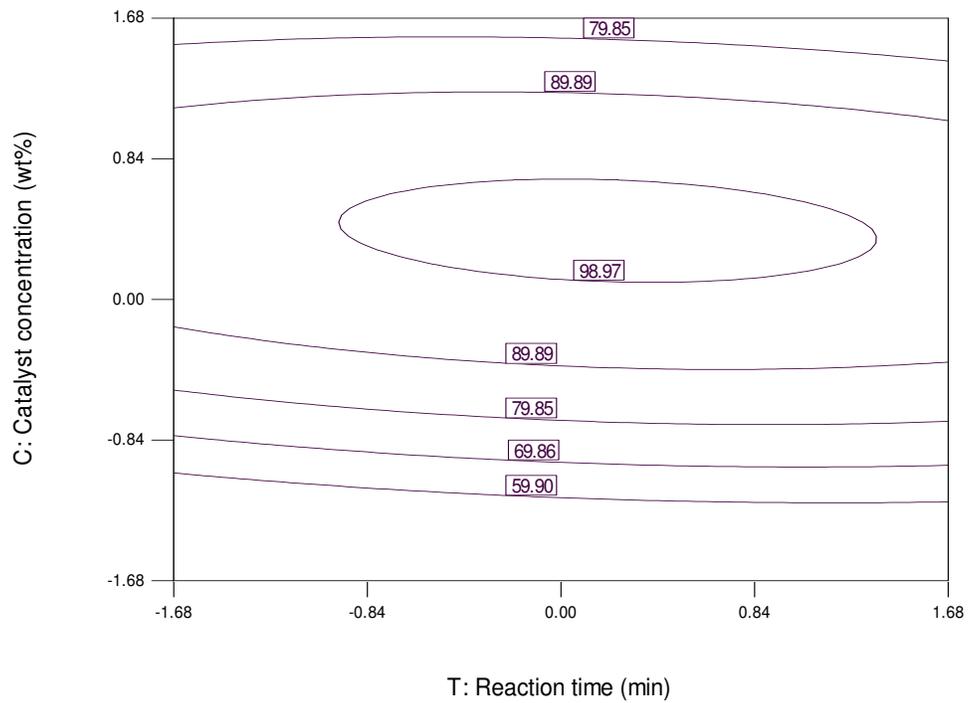
Table 5.4 Analysis of Variance (ANOVA) for the Quadratic Model

Variance Source	Sum of Squares	Degrees of Freedom	Mean Square	<i>F</i> -value	<i>p</i> -value
Regression	18034.588	9	2003.843	28.569	<0.0001
Linear	9709.719	3	3236.573	46.145	<0.0001
Quadratic	7602.995	3	2534.332	36.133	<0.0001
Interaction	721.874	3	240.625	3.431	0.0603
Residual error	701.397	10	70.140		
Total error	18735.985	19			

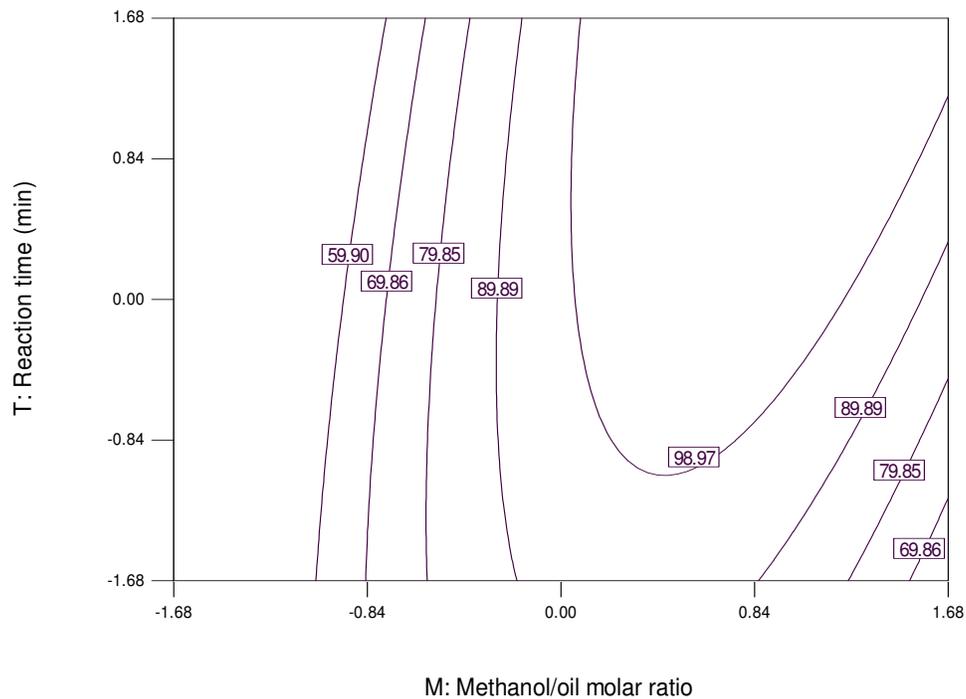
R²=0.963



(a)



(b)



(c)

Figure 5.1 Contour Plot of Methyl Ester Yield (wt.%) in Terms of Coded Factors:

The Effect of Methanol/oil Molar Ratio and Catalyst Concentration (a),
 Reaction Time and Catalyst Concentration (b), Methanol/oil Molar Ratio
 and Reaction Time (c) on Methyl Ester Production. The third variable is
 held at zero level.

5.6 References

- Antolín, G., Tinaut, F.V., Briceño, Y., Castaño, V., Pérez, C., & Ramírez, A.I. (2002). Optimisation of Biodiesel Production by Sunflower Oil Transesterification. *Bioresour Technol*, 83, 111-114.
- AOCS official method Ca 5a-40. (1997).
- Armenta, R.E., Vinatoru, M., Burja, A.M., Kralovec, J.A., & Barrow, C.J. (2007). Transesterification of Fish Oil to Produce Fatty Acid Ethyl Esters Using Ultrasonic Energy. *J Am Oil Chem Soc*, 84, 1045-1052.
- Colucci, J.A., Borrero, E.E., & Alape, F. (2005). Biodiesel from an Alkaline Transesterification Reaction of Soybean Oil Using Ultrasonic Mixing. *J Am Oil Chem Soc*, 82(7), 525-530.
- Ghadge, S.V., & Raheman, H. (2006). Process Optimization for Biodiesel Production from Mahua (*Madhuca indica*) Oil Using Response Surface Methodology. *Bioresour Technol*, 97, 379-384.
- Hanh, H.D., Dong, N.T., Okitsu, K., Maeda, Y., & Nishimura, R. (2007). Effects of Molar Ratio, Catalyst Concentration and Temperature on Transesterification of Triolein with Ethanol under Ultrasonic Irradiation. *Journal of the Japan Petroleum Institute*, 50(4), 195-199.
- Hu, J.B., Du, Z.X., Tang, Z., & Min, E.Z. (2004). Study on the Solvent Power of a New Green Solvent: Biodiesel. *Industry and Engineering Chemistry Research*, 43, 7928-7931.
- Ji, J.B., Wang, J.L., Li, Y.C., Yu, Y.L., Xu, Z.C. (2006). Preparation of Biodiesel with the Help of Ultrasonic and Hydrodynamic Cavitation. *Ultrasonics*. 44, e411-e414.
- Lang, X., Dalai, A.K., Bakhshi, N.N., Reaney, M.J., & Hertz, P.B. Preparation and Characterization of Bio-diesels from Various Bio-oils. *Bioresour Technol*, 80, 53-62.
- Li, W., Du, W., & Liu, D.H. (2007). Optimization of Whole Cell-catalyzed Methanolysis of Soybean Oil for Biodiesel Production Using Response Surface Methodology. *J Mol Catal B-Enzym*, 45, 122-127.
- Shieh, C.J., Liao, H.F., & Lee, C.C. (2003). Optimization of Lipase-catalyzed Biodiesel by Response Surface Methodology. *Bioresour Technol*, 88, 103-106.

- Stavarache, C., Vinatoru, M., & Maeda, Y. (2006). Ultrasonic versus Silent Methylation of Vegetable Oils. *Ultrason Sonochem*, 13, 401-407.
- Stavarache, C., Vinatoru, M., & Maeda, Y. (2007). Aspects of Ultrasonically Assisted Transesterification of Various Vegetable Oils with Methanol. *Ultrason Sonochem*, 14, 380-386.
- Stavarache, C., Vinatoru, M., Nishimura, R., & Maeda, Y. (2005). Fatty Acids Methyl Esters from Vegetable Oil by Means of Ultrasonic Energy. *Ultrason Sonochem*, 12, 367-372.
- Tiwari, A.K., Kumar, A., & Raheman, H. (2007). Biodiesel Production from *Jatropha* Oil (*Jatropha curcas*) with High Free Fatty Acids: An Optimized Process. *Biomass Bioenerg*, 31, 569-575.
- Vicente, G., Martínez, M., & Aracil, J. (2004). Integrated Biodiesel Production: A Comparison of Different Homogeneous Catalysts Systems. *Bioresour Technol*, 92, 297-305.
- Fan, X.H., Wang, X., Chen, F., Geller, D.P., & Wan, P.J. (2008). Engine Performance Test of Cottonseed Oil Biodiesel. *The Open Energy and Fuels Journal*, 1, 40- 45.
- Yuan, X.Z., Liu, J., Zeng, G.M., Shi, J.G., Tong, J.Y., & Huang, G.H. (2008). Optimization of Conversion of Waste Rapeseed Oil with High FFA to Biodiesel Using Response Surface Methodology. *Renew Energ*, 33, 1678-1684.

CHAPTER 6

OTHER APPROACHES TO PRODUCE BIODIESELS

Abstract

The price of feedstock oil is one of the most significant factors affecting the economic viability of biodiesel manufacturer. Many approaches were investigated to reduce the biodiesel production cost. The present work gave a preliminary study of two approaches to economically produce biodiesel. One was the use of waste cooking oil (WCO) as raw material. The other was the application of *in situ* transesterification on biodiesel production from crude cottonseed oil. When using the same optimal conditions as illustrated in Chapter 5, WCO could be converted to biodiesel with 90% conversion. HPLC and TLC results proved the feasibility of both approaches.

6.1 Introduction

Though biodiesel is technically feasible and environmentally acceptable, it should be noted that it is not economically competitive. The high cost of virgin vegetable oil as the source of biodiesel impedes the industrial profitability. This is the main hurdle for biodiesel commercialization. Therefore, many approaches have been taken in order to reduce production costs and make biodiesel more competitive with petroleum diesel.

One approach is to utilize low cost non-edible oils feedstocks, such as waste cooking oils (WCO) as the raw material. At present, waste oils are sold commercially as animal feed. However, since 2002, the European Union (EU) has enforced a ban on feeding these mixtures to animals to prevent the return of harmful compounds back into the food chain through the animal meat. In fact, most of the used cooking oil is poured into the sewer system of the cities. This will worsen the pollution of rivers, lakes, seas and underground water, leading to the negative effect on the environment and human health. Therefore, the disposal of waste oils in a safe way is required since it may contaminate the environment. The utilization of waste oils for producing biodiesel is one of the efficient and economical approaches to solve the problem.

Considerable research has been conducted to investigate the production of biodiesel from waste oil under acid (Zheng, Kates, Dubé & McLean, 2006), alkaline (Encinar, González & Rodríguez-Reinares, 2005) and enzyme (Watanabe, Shimada, Sugihara & Tominaga, 2001; Chen, Ying & Li, 2006) catalyses. Waste cooking oils exhibit properties quite different from those of refined and crude oils. The high temperatures of particular cooking processes and the water from the foods accelerate the

hydrolysis of triglycerides and increase the free fatty acid (FFA) content in the oil. Acid catalysis is more efficient when the amount of FFA in the oil exceeds 1% (Freedman, Pryde & Mounts, 1984). Zheng *et al.* (Zheng, Kates, Dubé & McLean, 2006) studied the kinetics of acid-catalyzed transesterification of waste frying oil in excess of methanol to produce biodiesel. They concluded that it was a pseudo-first-order reaction, provided that the methanol/oil molar ratio was close to 250:1 at 70°C or in the range of 74:1-250:1 at 80°C. Under these conditions, high yield of biodiesel (99± 1%) could be obtained at a stirring rate of 400 rpm, using a feed molar ratio oil:methanol:acid of 1:245:3.8. Though acid-catalyzed transesterification is insensitive to FFA in the feedstock, it requires longer reaction time and higher temperature. Many researchers recommended using acid-catalysis as a pretreatment step followed by an alkaline-catalyzed step. Wang *et al.* (Wang, Ou, Liu & Zhang, 2007) adopted this kind of two-step catalyzed process to prepare biodiesel from waste cooking oil. In the first step, FFAs of waste cooking oil were esterified with methanol catalyzed by ferric sulfate. In the second step, the triglycerides in the waste cooking oil were transesterified with methanol (methanol/oil molar ratio=6) catalyzed by 1.0 wt.% potassium hydroxide at 65°C for an hour. After this two-step catalysis process, the final product with 97.02% conversion of biodiesel was obtained. However, the two-step process is more complex in the instrumentation than the alkaline-catalyzed process, thus resulting in an increase in equipment and operating costs. Çetinkaya *et al.* (Çetinkaya & Karaosmanoğlu, 2004) investigated the optimum conditions under alkaline catalysis for biodiesel production from restaurant-originated used cooking oil. One alternative reaction condition suitable for pilot-scale and industrial-

scale biodiesel production were found to be: Oil/alcohol molar ratio, 1:6; temperature, $55 \pm 1^\circ\text{C}$; NaOH amount, 1% (by the weight of the oil); stirring speed, 40 rpm; pressure, atmospheric; and reaction time, 60 min.

Nowadays, low frequency ultrasonication receives more and more interest for biodiesel production (Stavarache, Vinatoru & Maeda, 2006; Armenta, Vinatoru, Burja, Kralovec & Barrow, 2007; Stavarache, Vinatoru, Nishimura & Maeda, 2005; Hanh, Dong, Starvarache, Okitsu, Maeda & Nishimura, 2008). It was proved to be an efficient, energy saving and economically feasible way. This process can enhance the mass transfer between two immiscible liquids, methanol and oils through cavitation. The application of ultrasound on biodiesel production from WCO will further reduce the biodiesel production cost.

Another approach is to use *in situ* transesterification process to produce biodiesel. By using this approach, the transesterification reagents might be able to access triglycerides resident in oilseeds and achieve their transesterification directly. This could simplify the whole reaction steps since solvent extraction and oil cleanup prior to biodiesel synthesis become unnecessary. Many researchers investigated this approach for biodiesel production. Georgogianni *et al.* compared *in situ* transesterification of both sunflower seed oil (Georgogianni, Kontominas, Pomonis, Avlonitis & Gergis, 2008) and cottonseed oil (Georgogianni, Kontominas, Pomonis, Avlonitis & Gergis, 2008) with conventional transesterification. The authors found that *in situ* transesterification gave similar ester yields to those obtained by conventional transesterification, which indicated the former method could be an alternative, efficient and economical process. Hass *et al.*

(Haas, Scott, Foglia & Marmer, 2007) made a reasonable conclusion that *in situ* approach might be valid for the production of biodiesel from virtually any lipid-bearing material after the authors explored the general applicability of this approach to feedstocks other than soybeans, such as distillers dried grains with solubles, the co-product of the production of ethanol from corn, and meat and bone meal, a product of animal rendering.

The present work simply showed a preliminary study of the use of WCO as raw material for biodiesel production by using 40 kHz ultrasonic irradiation. Meanwhile, *in situ* alkaline transesterification of flaked cottonseed was further investigated.

6.2 Materials and methods

6.2.1 Materials

Methanol and sodium hydroxide were purchased from Fisher Scientific (Suwanee, GA, USA). WCO was obtained from New China restaurant (Clemson, SC, USA). Every day this restaurant produces many WCO which is used for cooking various Chinese dishes. So the WCO may contain some food particles, phospholipids etc. Identification of fatty acids composition of WCO was performed by comparison of retention times with fatty acid standard purchased from SUPELCO (Supelco park, Bellefonte, PA, USA). The ultrasonic reaction system is the same as described in Chapter 4 and 5.

6.2.2 Transesterification of WCO

Before transesterification, the WCO was filtered under vacuum to remove any solid impurities. FFA content of the WCO was measured according to A.O.C.S. Official Method Ca 5a-40.

FFA content was 2.8%, calculated as oleic acid. According to Gerpen (Gerpen, 2005), the transesterification reaction can still be catalyzed with an alkaline catalyst up to about 5% FFAs, but additional catalyst must be added to compensate for the catalyst lost to soap. Since the acid-catalyzed pretreatment of WCO will increase the operation cost, direct alkaline-catalysis is preferred. Extra alkaline (sodium hydroxide) was added to neutralize the FFAs.

6.2.3 Fatty Acid Profile of WCO

Shimadzu's GC-FID system was used for the analyses of fatty acid profile of the WCO. It consists of a GC-17A, a flame ionization detector, and a DB-WAX capillary column (60 m×0.25 mm, thickness=0.25 μm; J&W Scientific). The initial temperature for oven was set at 140 °C and held for 5 min. Then the temperature increased from 140 °C to 220°C at the ramp of 4°C/min and held at 220°C for 25 min. The injector and detector were maintained at 200°C and 220°C, respectively. Helium was used as a carrier gas and the split ratio was 50/1. Supelco™ 37 Component FAME Mix was as the standard. COME A was also as the reference.

6.2.4 Water Determination

The water content was measured by direct coulometric Karl Fischer titration according to ISO 12937(2000) using the 756 KF Coulometer (Metrohm Company, Switzerland). The water content in the WCO was 0.1%.

6.2.5 Sample Preparation for *in situ* Transesterification of Flaked Cottonseed

Flaked cottonseeds were first dried overnight in the oven at about 70~77°C to remove the moisture and then mixed with methanol in which sodium hydroxide were

already dissolved. The mixtures were placed in the capped bottle, sealed tightly. According to the reference (Haas, Scott, Marmer & Foglia, 2004), the molar ratio of methanol/oil/NaOH for the flaked cottonseed as the raw material was equal to 543/1/2.

6.2.6 Methods for *in situ* Transesterification of Flaked Cottonseed

1. The bottle (contained sample) was placed in the water bath (55°C). Sampling and TLC analysis were performed hourly.

2. The bottle (contained sample) was placed at Roto mixer. Mixing of the methanol and flaked cottonseed was conducted like orbital shaking. The reaction was performed at room temperature. Sufficient speed was maintained to keep the flaked cottonseed well suspended. Sampling and TLC analysis were conducted hourly to check the reaction conversion.

3. Two bottles, one containing flaked cottonseed and the other containing crude cottonseed oil (both were mixed with methanol in which sodium hydroxide were already dissolved) were placed in the ultrasonic water bath. The reaction was conducted at room temperature. Sampling and TLC analysis were carried out hourly.

6.3 Results

Figure 6.1, 6.2, and 6.3 show the GC chromatogram of Supelco™ 37 Component FAME Mix Standard, WCO biodiesel, and COME A, respectively. From the known fatty acid profile of the standard and COME A, it can be concluded that the WCO primarily contains oleic acid, palmitic acid, and linoleic acid. It can also be seen from **Figure 6.4** that methyl esters were obtained from WCO. TLC (**Figure 6.5**) shows the apparent conversion of crude cottonseed oil to biodiesel by *in situ* transesterification. These results

demonstrated the feasibility of the two approaches (including the use of WCO as raw material and *in situ* transesterification) to produce biodiesel.

6.4 Figures

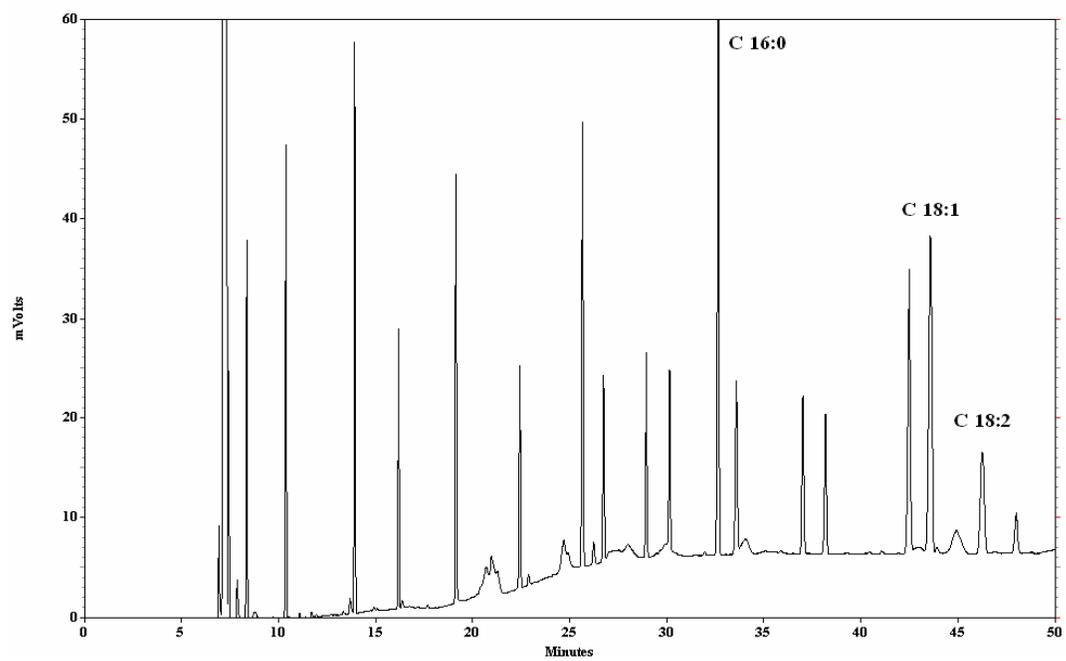


Figure 6.1 GC Chromatogram of Supelco™ 37 Component FAME Mix Standard

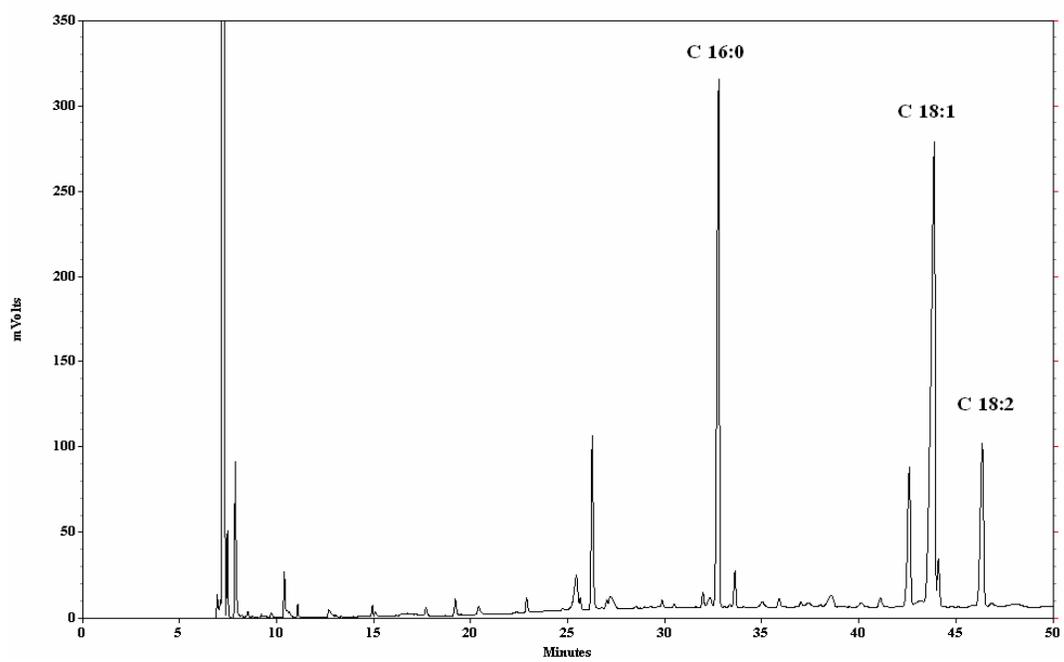


Figure 6.2 GC Chromatogram of WCO Biodiesel

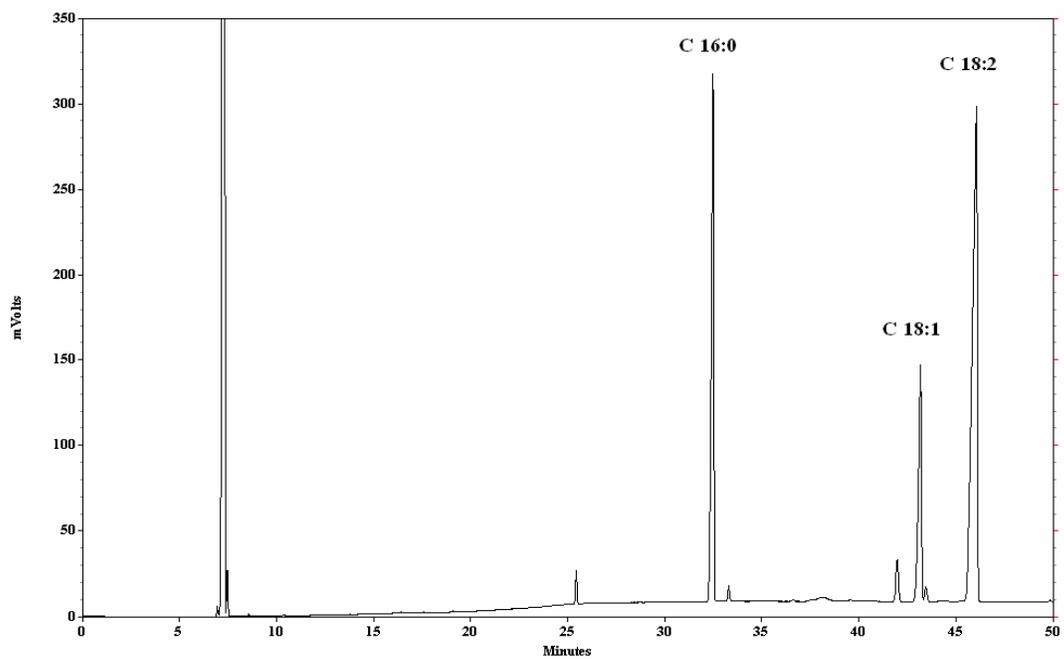


Figure 6.3 GC Chromatogram of COME A

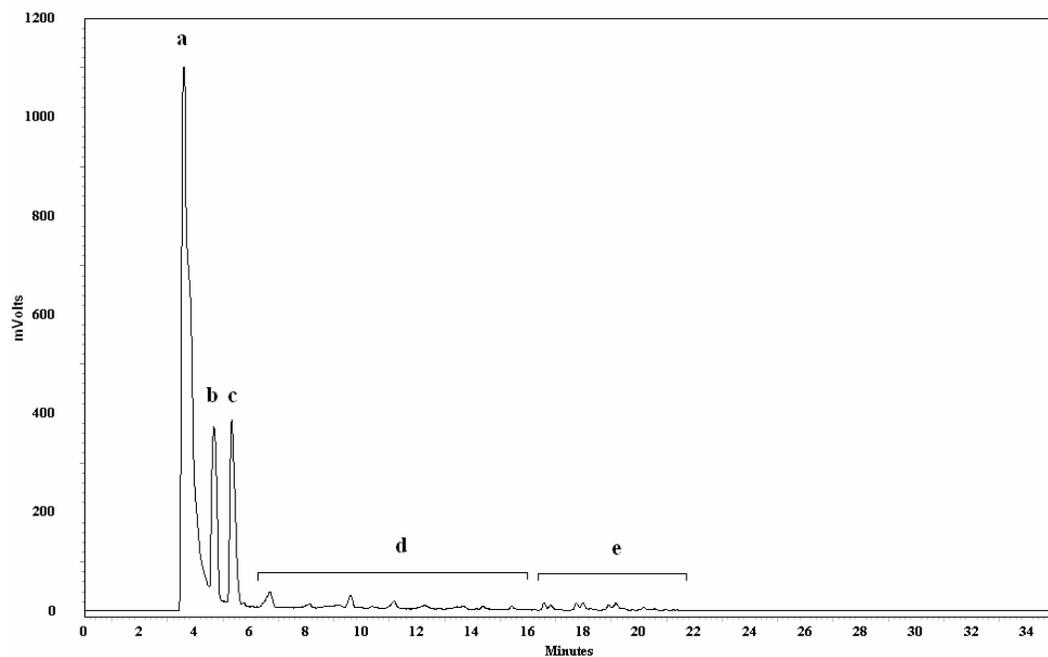
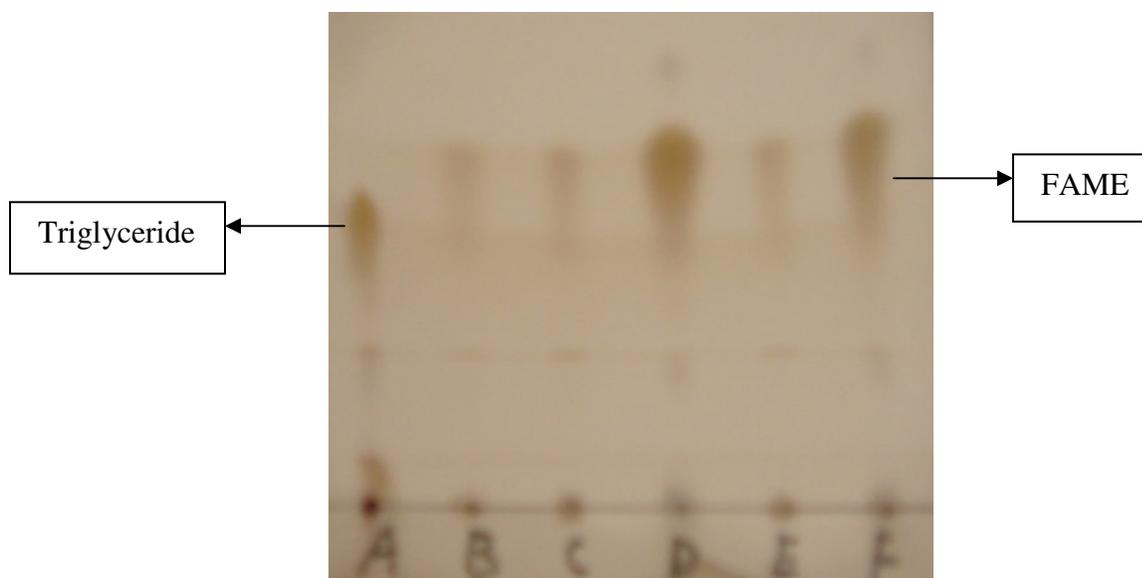


Figure 6.4 HPLC chromatogram of biodiesel from WCO

a C18:1 (oleic acid methyl ester), **b** C18:2 (linoleic acid methyl ester), **c** C16:0 (palmitic acid methyl ester), **d** diglycerides, **e** unreacted triglycerides present in the biodiesel



TLC analysis for all methods

Figure 6.5 TLC Results for *in situ* Transesterification of Crude Cottonseed Oil

A: crude cottonseed oil extracted from flaked cottonseed; B: *In situ* transesterification conducted on the Roto mixer at room temperature; C: *In situ* transesterification conducted in the water bath (55°C); D: transesterification of crude cottonseed oil in the ultrasonic water bath; E: *In situ* transesterification of flaked cottonseed in the ultrasonic water bath; F: biodiesel standard

6.5 References

- Armenta, R.E., Vinatoru, M., Burja, A.M., Kralovec, J.A., & Barrow, C.J. (2007). Transesterification of Fish Oil to Produce Fatty Acid Ethyl Esters Using Ultrasonic Energy. *JAOCS*, 84, 1045-1052.
- Chen, G., Ying, M., & Li, W.Z. (2006). Enzymatic Conversion of Waste Cooking Oils into Alternative Fuel-Biodiesel. *Appl. Biochem. Biotech.*, 129-132, 911-921.
- Çetinkaya, M., & Karaosmanoğlu, F. (2004). Optimization of Base-Catalyzed Transesterification Reaction of Used Cooking Oil. *Energ. Fuel.*, 18, 1888-1895.
- Encinar, J.M., González, J.F., & Rodríguez-Reinares, A. (2005). Biodiesel from Used Frying Oil. Variables Affecting the Yields and Characteristics of the Biodiesel. *Ind. Eng. Chem. Res.*, 44, 5491-5499.
- Freedman, B., Pryde, E.H., & Mounts, T.L. (1984). Variables Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils. *JAOCS*, 61, 1639-1643.
- Georgogianni, K.G., Kontominas, M.G., Pomonis, P.J., Avlonitis, D., & Gergis, V. (2008). Alkaline Conventional and *In Situ* Transesterification of Cottonseed Oil for the Production of Biodiesel. *Energ. Fuel.*, 22, 2110-2115.
- Georgogianni, K.G., Kontominas, M.G., Pomonis, P.J., Avlonitis, D., & Gergis, V. (2008). Conventional and *In Situ* Transesterification of Sunflower Seed Oil for the Production of Biodiesel. *Fuel Process. Technol.*, 89, 503-509.
- Gerpen, J.V. (2005). Biodiesel Processing and Production. *Fuel Process. Technol.*, 86, 1097-1107.
- Haas, M.J., Scott, K.M., Foglia, T.A., & Marmer, W.N. (2007). The General Applicability of *In Situ* Transesterification for the Production of Fatty Acid Esters from a Variety of Feedstocks. *JAOCS*, 84, 963-970.
- Haas, M.J., Scott, K.M., Marmer, W.N., & Foglia, T.A. (2004). *In Situ* Alkaline Transesterification: An Effective Method for the Production of Fatty Acid Esters from Vegetable Oils. *JAOCS*, 81, 83-89.

- Hanh, H.D., Dong, N.T., Starvarache, C., Okitsu, K., Maeda, Y., & Nishimura, R. (2008). Methanolysis of Triolein by Low Frequency Ultrasonic Irradiation. *Energy Convers. Manage.*, 49, 276-280.
- Stavarache, C., Vinatoru, M., & Maeda, Y. (2006). Ultrasonic versus Silent Methylation of Vegetable Oils. *Ultrason. Sonochem.*, 13, 401-407.
- Stavarache, C., Vinatoru, M., Nishimura, R., & Maeda, Y. (2005). Fatty Acids Methyl Esters from Vegetable Oil by Means of Ultrasonic Energy. *Ultrason. Sonochem.*, 12, 367-372.
- Wang, Y., Ou, S., Liu, P.Z., & Zhang, Z. (2007). Preparation of Biodiesel from Waste Cooking Oil via Two-Step Catalyzed Process. *Energy Convers. Manage.*, 48, 184-188.
- Watanabe, Y., Shimada, Y., Sugihara, A. & Tominaga, Y. (2001). Enzymatic Conversion of Waste Edible Oil to Biodiesel Fuel in a Fixed-Bed Bioreactor. *JAOCS*, 78(7), 703-707.
- Zheng, S., Kates, M., Dubé, M.A., & McLean, D.D. (2006). Acid-Catalyzed Production of Biodiesel from Waste Frying Oil. *Biomass Bioenerg.*, 30, 267-272.