IN SITU EXTRACTION AND TRANSESTERIFICATION OF *JATROPHA CURCAS* L. SEEDS USING SUPERCRITICAL FLUIDS FOR THE SYNTHESIS OF BIODIESEL

STEVEN LIM

UNIVERSITI SAINS MALAYSIA

2013

IN SITU EXTRACTION AND TRANSESTERIFICATION OF *JATROPHA CURCAS* L. SEEDS USING SUPERCRITICAL FLUIDS FOR THE SYNTHESIS OF BIODIESEL

by

STEVEN LIM

Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy

December 2013

ACKNOWLEDGEMENTS

First and foremost, I would like to dedicate this thesis to my parents, brother and sister for their unwavering support and encouragement throughout the duration of my research work. Their care and advice remained the main driving force for me to continue to persevere against all odds.

I would also like to express my heartiest gratitude to my main supervisor, Assoc. Prof. Dr. Lee Keat Teong for his guidance and support which allowed me to overcome many challenges in my research study. His passion and desire to success would continue to be a role model for me in my future career. Apart from him, I would also like to extent my tribute to my co-supervisor, Prof. Dr. Subhash Bhatia who had retired earlier. His profound knowledge and high motivation had sparked me to remain diligent and passionate in my research.

In addition, I would also like to express my appreciation to all the lecturers and staffs of School of Chemical Engineering, Universiti Sains Malaysia who had lent their help and support to me in one way or the other throughout my research study. It would be too long to list down their names one by one but their cooperation and kindness would remain carved in my heart for eternity. The financial support provided by Universiti Sains Malaysia in the form of Vice-Chancellor Scholarship and Postgraduate Research Grant Scheme (PRGS) (8043031) was also gratefully acknowledged.

Last but not least, I would like to thank all my friends and colleagues especially Ms. Pang Yean Ling who had remained with me throughout the ups and downs in my research life. Without them, my experience would not be so wonderful and I would always cherish the memories for the rest of my life. Thanks to all of you!

TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION

CHAPTER 2: LITERATURE REVIEW

CHAPTER 3: MATERIALS AND METHODS

CHAPTER 4: RESULTS AND DISCUSSION

CHAPTER 5: PROCESS MODEL STUDY

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF SYMBOLS

Symbol	Description	Unit
A_{eff}	Effective surface area for mass transfer	m^2
A_i	Pre-exponential factor, *i* = 1,2,3,4,5 and 6	min^{-1}
α	Distance of the axial runs from the centre	Dimensionless
C_{Ai}	concentration of solute in solvent at time t	g/m^3
C_{TG}	Concentration of triglyceride	mol/m^3
C_{MeOH}	Concentration of methanol	mol/m^3
D_{eff}	Effective diffusivity	m^2/min
d_p	Particle diameter	m
dW_A/dt	rate of change of mass of solute	g/min
ΔH	Enthalpy of reaction	J/mol
ΔS	Entropy of reaction	J/mol
ΔG	Gibb's free energy of activation	J/mol
E_{ai}	Activation energy, *i* = 1,2,3,4,5 and 6	J/mol
E_c	Extraction content	% w/w
E_e	Extraction efficiency comparison	% w/w
e	Ratio of the mass of recovered solute to the initial mass of feed	Dimensionless
ε	Error observed in the equation	Dimensionless
F-value	Ratio of model mean square to residuals mean square	Dimensionless
F_e	FAME efficiency	% w/w
F_y	FAME yield	% w/w
k	Number of variables in RSM	Dimensionless
$k^{'}$	Apparent mass volumetric mass transfer coefficient	min^{-1}

k''	Apparent reaction rate constant	min^{-1}
$k.a$	volumetric mass transfer coefficient	min^{-1}
k_c	Mass transfer coefficient	m/min
K_e	Equilibrium constant	Dimensionless
k_i	Reaction rate constants, $i = 1,2,3,4,5$ and 6	min^{-1}
$M_{extract}$	Extraction efficiency	% w/w
M_{wet}	Moisture content	% w/w
η	Effectiveness factor	Dimensionless
n_c	Number of centre runs in RSM	Dimensionless
n_F	Number of factorial points in RSM	Dimensionless
Φ	Thiele modulus	Dimensionless
R	Gas constant	$J\ mol^{-1}\ K^{-1}$
R^2	Coefficient of determination	Dimensionless
r_{TG}	Rate of change of triglyceride concentration	$mol\ m^{-3}\ min^{-1}$
T	Reaction temperature	K
t	Reaction time	min
t'	Initial reaction time when TG is first detected	min
V	Volume of reactants	m^3
x	Independent variable	Dimensionless
X_{exp}	Experimental values	Dimensionless
X_{pred}	Predicted values	Dimensionless
X_{TGE}	Conversion of triglyceride	Dimensionless
Y	Response (Yield)	Dimensionless
y_i	Concentration	mol/dm^3

LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
ASTM	ASTM International
AT	Acid-catalyzed *in situ* transesterification
ATR	Attenuated total reflection
CaO	Calcium oxide
CCRD	Central composite rotatable design
CEP	Constant extraction phase
CG	Constantinou and Gani
CO	Carbon monoxide
CO_2	Carbon dioxide
CSR	Co-solvent to solid ratio
DCP	Diffusion-controlled phase
DG	Diglyceride
DoE	Design of experiment
DTG	Derivative thermogravimetric analysis
FAAE	Fatty acid alkyl ester
FAME	Fatty acid methyl ester
FFA	Free fatty acids
FFB	Fresh fruit bunch
FID	Flame ionization detector
FT-IR	Fourier tranform infrared spectroscopy
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
GHG	Greenhouse gas

GY	Glycerol
HCl	Hydrochloric acid
H_2SO_4	Sulfuric acid
HHV	Higher heating value
KBr	Potassium bromide
KOH	Potassium hydroxide
JCL	*Jatropha curcas* L.
Li-CaO	Lithium doped calcium oxide
MG	Monoglyceride
N_2	Nitrogen gas
NaOH	Sodium hydroxide
NO_x	Nitrogen oxide
OEM	Original engine manufacturer
RBD	Refined, bleached and deodorized
REP	Reducing extraction phase
RMSE	Root mean square error
RSM	Response surface methodology
SCF	Supercritical fluid
SE	Cconventional two-step soxhlet extraction
SEM	Scanning electron microscopy
SET	Supercritical *in situ* extraction and transesterification
SO_2	Sulfur dioxide
SO_4/SnO_2	Sulfated tin oxide
SrO	Strontium oxide
SSQ	Sum of square error

SSR	Solvent to solid ratio
TG	Triglyceride
TGA	Thermal gravitational analysis
THF	Tetrahydrofuran
TTP	Three-phase partitioning
VOC	Volatile organic compound
WO_3/ZrO_2	Tungstated zirconia
ZrO_2	Amorphous zirconia

LIST OF APPENDICES

PENGEKSTRAKAN DAN TRANSESTERIFIKASI *IN SITU* BENIH *JATROPHA CURCAS* L. MENGGUNAKAN CECAIR LAMPAU GENTING UNTUK BIODIESEL SINTESIS

ABSTRAK

Jatropha curcas L. (JCL) ialah minyak tanaman baharu yang tidak boleh dimakan tetapi mempunyai potensi yang besar sebagai stok suapan untuk penghasilan biodiesel. Dalan kajian ini, proses pengekstrakan dan transesterifikasi *in situ* lampau genting (SET) yang dibangunkan dari proses intensifikasi dicampur bersama-sama dengan metanol untuk penghasilan biodiesel dari JCL dalam sebuah reaktor kelompok bertekanan tinggi. Pencirian sifat-sifat bahan mentah telah dijalankan ke atas benih-benih minyak JCL untuk menentukan ciri-ciri fizikal dan kimia. Pra-rawatan benih-benih pepejal termasuk saiz zarah pepejal (0.5-2.0 mm), tanpa petala dan rawatan haba pada lima suhu (45°C-105°C) dan dua tempoh yang berbeza (12j dan 24j) turut disiasat. Ia didapati bahawa benih-benih JCL tanpa petala mempunyai kesan utama terhadap hasil produk, diikuti dengan penapisan dan rawatan haba. Proses SET telah dijalankan dalam julat suhu proses antara 240°C dan 320°C, tekanan proses antara 4.0 MPa dan 24.0 MPa, nisbah metanol kepada benih pepejal (SSR) antara 2.5 ml/g dan 15.0 ml/g, ruang pemuatan antara 90.0 ml/g dan 18.0 ml/g, nisbah n-hexane kepada benih pepejal antara 0 ml/g dan 6.0 ml/g, tunggakan masa proses antara 0 min dan 35 min dan kelajuan putaran antara 0 rpm dan 500 rpm. Pelarut-pelarut bersama yang digunakan untuk mengurangkan keterlaluan proses adalah n-pentane, n-heptane, tetrahidrofuran (THF), toluene, gas nitrogen (N_2) dan gas karbon dioksida (CO_2). Jumlah kandungan mereka diubah dari 1.0 ml/g ke 5.0 ml/g untuk cecair dan dari 10 bar ke 50 bar untuk gas. Ia didapati bahawa n-pentane dan CO_2 boleh mengurangkan suhu optimum operasi dan jumlah metanol untuk proses SET kerana menggalakkan ketercampuran yang lebih tinggi antara reaktan. Analisis statistik reka bentuk eksperimen (DoE) telah digunakan untuk mengkaji kesan interaksi antara suhu operasi, tunggakan masa, nisbah metanol kepada pepejal dan amaun CO_2. Pengoptimuman berangka berdasarkan model statistik yang dibangunkan memberi hasil asid lemak metil ester (FAME) yang optimum pada 92.0 wt. % dalam keadaan berikut: 5.9 SSR, 300°C, 12.3 min dan 20 bar CO_2. Kajian tentang toleransi benda asing terhadap kandungan air dan asid lemak bebas (FFA) dari 5.0 wt.% ke 30.0 wt.% dan kestabilan haba dari suhu 280°C ke 320°C untuk proses SET juga dijalankan. Ia boleh disimpulkan bahawa proses SET mempunyai toleransi yang lebih tinggi terhadap jumlah air dan FFA pada kandungan permulaan dalam benih-benih JCL berbanding dengan proses konvensional. Ini dapat mengurangkan keterlaluan langkah-langkah pra-rawatan untuk benih-benih JCL serta membenarkan penggunaan julat stok suapan yang lebih luas. FAME dalam proses SET juga menunjukkan kestabilan haba yang tinggi tanpa kemerosotan yang banyak dalam keadaan proses di bawah kajian. Analisis pencirian awal mengesahkan bahawa hasil sampingan yang dijana boleh diproses semula untuk aplikasi tenaga yang lain. FAME yang dihasilkan juga didapati mematuhi had kualiti antarabangsa EN 14214 dan ASTM 6751. Model-model matematik berdasarkan kajian kinetik juga dibangunkan untuk meramalkan hasil produk. Kajian mendapati bahawa proses reaksi mematuhi tindak balas perintah pertama palsu. Akhir sekali, satu mekanisme proses yang lengkap untuk menggambarkan proses SET juga dikemukakan.

‘

IN SITU EXTRACTION AND TRANSESTERIFICATION OF *JATROPHA CURCAS* L. SEEDS USING SUPERCRITICAL FLUIDS FOR THE SYNTHESIS OF BIODIESEL

ABSTRACT

Jatropha curcas L. (JCL) is an emerging non-edible oil plant which has a high potential as the feedstock for biodiesel production. In this study, supercritical *in situ* extraction and transesterification process (SET) developed from process intensification was applied together with methanol for the production of biodiesel from JCL in a high pressure batch reactor. Raw material characterizations were performed on the JCL oil seeds in this study to determine their physical and chemical properties. Pre-treatments of the solid seeds including solid particle size (0.5-2.0 mm), de-shelling and heat treatment at five different temperatures (45°C-105°C) and two different durations (12h and 24h) were also investigated. It was discovered that de-shelling of JCL seeds had highest influence on the product yield, followed by sieving and heat treatment. SET process was conducted in the process temperature range of 240°C to 320°C, process pressure of 4.0 MPa to 24.0 MPa, methanol to solid seeds ratio (SSR) of 2.5 ml/g to 15.0 ml/g, space loading of 90.0 ml/g to 18.0 ml/g, n-hexane to solid seeds ratio of 0 ml/g to 6.0 ml/g, process holding time of 0 min to 35 min and stirring speed of 0 rpm to 500 rpm. Co-solvents which were being employed in the process to reduce the process severity were n-pentane, n-heptane, tetrahydrofuran (THF), toluene, nitrogen gas (N_2) and carbon dioxide gas (CO_2). Their amounts were varied from 1.0 ml/g to 5.0 ml/g for liquid and 10 bar to 50 bar for gases. It was found that n-pentane and CO_2 could further reduce the optimum operating temperature and amount of methanol for SET process due to promoting higher miscibility between reactants. Statistical analysis design of experiment (DoE) was used to study the interaction effect between operating temperature, holding time, methanol to solid ratio and amount of CO_2. Numerical optimization based on the statistical model developed provided an optimum fatty acid methyl ester (FAME) yield of 92.0 wt. % under the following conditions: 5.9 SSR, 300°C, 12.3 min and 20 bar of CO_2. Studies on impurities tolerance for water and free fatty acid contents (FFA) from 5.0 wt.% to 30.0 wt.% and thermal stability from 280°C to 320°C for SET process were also carried out. It was concluded that SET process had higher tolerance towards the initial amount of water and FFA in JCL seeds compared to conventional acidic catalyzed transesterification process. This could reduce the severity of the pre-treatment steps for JCL seeds and allowed a wider range of feedstock to be applied. FAME in SET process also exhibited high thermal stability without significant degradation for the process conditions under study. Preliminary characterization analysis confirmed that the by-products generated could be re-used for other higher-value applications. The FAME produced was also found to fulfill the limits of international standards of EN 14214 and ASTM 6751. Mathematical models based on kinetics study were also developed in order to predict the yield of products according to different reactants and process conditions. It was found that the reaction process followed a pseudo first order reaction. Lastly, a complete process mechanism describing the SET process was also proposed.

CHAPTER 1

INTRODUCTION

1.1 Global Demand for Sustainable Energy

Since the commencement of industrial revolution in the late 18th and early 19th century, energy has become an indispensable factor for human to preserve economic growth and maintain basic standard of living. The widespread of industrial revolution in Europe has been largely attributed by the high availability and accessibility of coal as the primary source of energy. Meanwhile, the advent of automobiles, airplanes and electricity has been made possible by the energy usage of petroleum in the twentieth century. Since then, coal and petroleum have become the main source of energy to human beings (Avinash *et al.*, 2014). Until today, energy has been continuously derived from conventional sources such as coal, petroleum and natural gas. Despite the discoveries of various alternative energies particularly renewable energy from biofuels and solar, fossil fuels remain as the largest contributor to satisfy the global energy demand. From 2008 to 2012, the combined total of petroleum, natural gas and coal represents more than 83% of the world total primary energy consumption as shown in Figure 1.1 (EIA, 2011).

The energy generated from the combustion of fossil fuels has indeed enabled many technological advancements and social-economy growth which otherwise may be impossible. However, it simultaneously creates several environmental concerns which can threaten the sustainability of our eco-system. One of the primary concerns will be the emissions of greenhouse gases (GHG's) and other types of air pollutants such as sulphur dioxide (SO_2), hydrocarbon and volatile organic compounds (VOC's) (Chattopadhyay and Sen, 2013). Realizing the fossil fuels as a double-edged sword, many different types of alternative energy have been explored which have the possibility of satisfying the world energy demand while simultaneously ensuring the sustainability of the environment. One such renewable energy in particular will be biodiesel which is mainly derived from vegetable oils or animal fats and has shown great potential to serve as a substitute to petroleum-derived diesel for diesel engine. Malaysia is one of the countries which actively advocates for the commercial production and usage of biodiesel as fossil fuels replacement due to its rich palm oil resources.

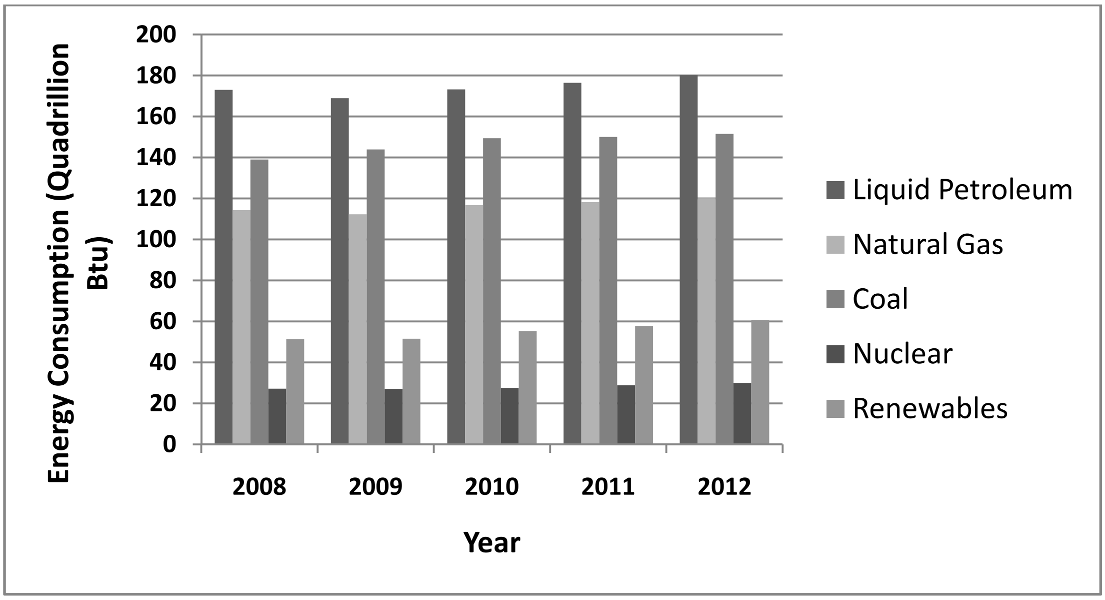

Figure 1.1: Global energy consumption in terms of fuel types from 2008 to 2012 (EIA, 2011)

1.2 Biodiesel as Transportation Fuel

Biodiesel, which can also be known as fatty acid alkyl ester (FAAE), is mainly produced from transesterification of vegetable oils or animal fats with the addition of methanol as shown in Figure 1.2. Transesterification process is the reversible reaction of lipid feedstocks (which are composed of triglyceride molecules) with an alcohol to form monoalkyl esters of long chain fatty acids and glycerol as main by-product. According to the reaction stoichiometry, the reaction requires a 3:1 molar alcohol-to-oil ratio, but excess alcohol is usually added to drive the equilibrium toward the products side for higher conversion. FAAE has similar composition and characteristics when compared to petroleum-derived diesel such as cetane number, energy content, viscosity and phase changes (Agarwal, 2007). Therefore, when blended together with petroleum-derived diesel, it can be used in most compression-ignition diesel engine without any modification. The potential of biodiesel as transportation fuel was bolstered when ASTM International (ASTM), an international renowned standard organization, approved new quality specifications for biodiesel blends in 2008 (Schill, 2008). The new fuel standards enabled as much as 5.0 wt. % of biodiesel to be blended with mineral diesel without the need for re-labelling in diesel selling stations. Many original engine manufacturers (OEM's) worldwide had also begun accepting biodiesel fuel blends as high as 20.0 wt.% in their engines which paved the way for wider spread of biodiesel usage in transportation sector.

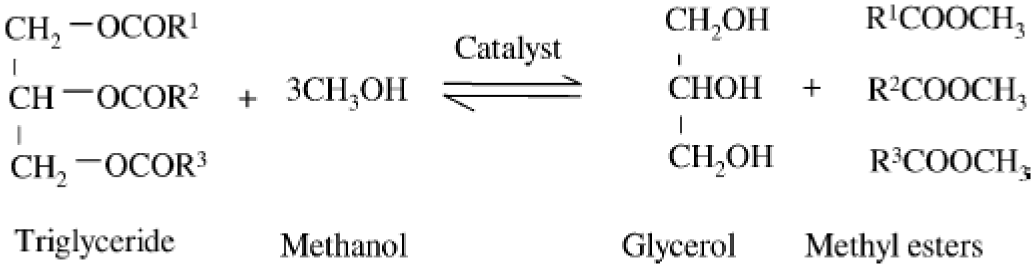

Figure 1.2: General equation for transesterification of triglyceride from lipid feedstock with methanol (Diasakou *et al.*, 1998)

1.2.1 Biodiesel Feedstocks

Biodiesel can be produced from a wide range of different feedstocks depending on their lipid content and properties. The cost of raw material may reach up to three quarters of the total biodiesel production cost including purification and refinement and therefore selection of appropriate feedstock will be paramount (Huang *et al.*, 2013). Currently, the most common commercial feedstock for first generation biodiesel or FAME is edible oils such as soybean, rapeseed, canola, sunflower, palm, coconut and even corn oil. Their wide availability, established supply infrastructure and high oil quality rendered them to be the most convenient and cost effective raw material for biodiesel production (Moser, 2009). Even though the biodiesel quality may vary from different feedstock material, most of them still meet the requirements regulated by international standards, EN 14214:2003 and ASTM D6751. However, this practice has raised objections from various organizations, claiming that biodiesel is competing resources with the food industry for human consumption. Consequently, biodiesel production from edible oils is being accused of creating food supply shortage and indirectly increases the price of the food. In the view that food for human should be prioritized, a possible solution to this issue is to produce biodiesel from second generation non-edible oils such as *Jatropha curcas* L. (JCL) seeds, beef tallow, waste cooking oil and algae. JCL has recently been discovered as a feasible feedstock for biodiesel production as it does not compete with food sources and can be grown in non-arable lands. A research report carried out by Goldman Sachs Global Investment Research cited JCL as one of the most promising candidates for biodiesel production owing to its high efficiency and economic value on par with sugar cane (Currie, 2007).

1.2.2 Production Methods

There are many ways to reduce the high viscosity of vegetable oil to make it suitable for internal combustion diesel engines. These methods include dilution, microemulsions, pyrolysis, catalytic cracking and transesterification (Bezergianni and Dimitriadis, 2013). Among all these technologies, transesterification of oil to fatty acid alkyl esters seems to be the best choice as the physical properties/characteristics of FAAE are very close to petroleum-derived diesel. The process is also relatively simpler and thus requires only minimal capital cost. The popular transesterification production of biodiesel normally focus on either catalyst or non-catalyst route. For the catalyst method, traditional chemical reactions employ different kinds of homogeneous or heterogeneous catalysts, such as sodium or potassium hydroxides (NaOH and KOH), sulphuric acid (H_2SO_4), ion exchange resins and lipases. However, synthesis of biodiesel by homogeneous catalytic transesterification reaction has several drawbacks: it required intensive purification, recovery of glycerol is difficult, wastewater produced retains fatty acids and formation of water which interferes with the reaction (Talebian-Kiakalaieh *et al.*, 2013). In addition, alkaline transesterification is low in selectivity, leading to undesirable side reactions. Although the usage of heterogeneous catalyst can overcome the separation barrier, its catalyst synthesis route is relatively tedious and expensive. Moreover, the leaching of the solid catalyst during the reaction and disposal of spent catalyst still remained a major concern (Lam *et al.*, 2010).

Lipase has been used a a biocatalyst for synthesis of biodiesel from vegetable oils or animal fats and can overcome the problems of conventional chemical processes (Tupufia *et al.*, 2013). However, due to the high price of the enzyme and the time consuming reaction process, this method is not widely used in large scale production. Biodiesel may also be prepared from liquid vegetable oil via a non-catalytic method with supercritical alcohol. Compared with the traditional chemistry method, this novel method requires no catalyst, and nearly complete conversions can be achieved in a very short time (Saka and Kusdiana, 2001). Consequently, it can successfully resolve most problems in the conventional chemical processes. Moreover, co-solvents, such as carbon dioxide (CO_2), hexane and calcium oxide (CaO), added into the reaction mixture can decrease the severity of the operating conditions.

Conventionally, pre-extracted oil from the oil-bearing material using either mechanical or chemical extraction techniques will be fed into the transesterification process together with short-chain alcohol (usually methanol) to be reacted. Recently, process intensification for biodiesel production has promoted the development of *in situ* extraction and transesterification or also known as catalytic reactive extraction process. In the process, oil-bearing material such as oil seeds will be in contact directly with the reaction media. Research showed that this process has the potential to produce FAME with yield significantly greater than those obtained from conventional reaction with pre-extracted seed oils (Kaul *et al.*, 2010; Shuit *et al.*, 2010).

1.2.3 Advantages as Sustainable Energy

Biodiesel has been proven to be one of the best alternatives for diesel fuels in diesel-powered buses, trucks and private vehicles since it is biodegradable, renewable, clean, non-toxic, and has low emission profile. Its emission profiles were found to contain reduced amount of carbon monoxide (CO), CO_2, particulate matter and unburned hydrocarbons compare to mineral diesel (Chattopadhyay and Sen, 2013). Furthermore, the physical properties such as cetane number, energy content, viscosity and phase changes of biodiesel are similar to those of petroleum-derived diesel fuel. Consequently, its properties are highly compatible to existing energy supply chain and mixable with mineral diesel in large ratio without any major engine modifications. Its established production infrastructure and easy know-how technology also helped to transform biodiesel as one of the most ideal replacements for fossil fuels in the coming decades.

1.3 Development of Biodiesel in Malaysia

The usage of biodiesel as renewable energy has been greatly promoted by Malaysia, given the wide availability of crude palm oil as feedstock material for biodiesel production and the need to address the energy supply issue. This can be shown through the National Biofuel Policy and the 5th fuel policy which emphasized the usage of biodiesel and other biofuels as energy sources for Malaysia (Lim and Lee, 2010). Malaysian biodiesel production had increased from 1.10 thousand barrels per day in 2006 to 4.50 thousand barrels per day in 2009 (IndexMundi, 2010). Under the current transportation fuel policy, it is expected that a minimum of B5 biodiesel blend (mixture of 95% mineral diesel and 5% biodiesel) mandate to be implemented in 2013 with B10 blend to be implemented a year after in Malaysia after ensuring most of the blending facilities are in place. This will create a huge demand for biodiesel and at the same time spur the growth of local biodiesel industry. However, challenges remain to be tackled as palm oil plantation has been linked with massive deforestation, extinction of wildlife and competition as food source. Therefore, utilizing non-edible oil as feedstock material for biodiesel production will be the trend in the near future. In this context, JCL is regarded as one of the prime candidates for biodiesel production to supplement the existing palm oil feedstock.

1.4 *Jatropha curcas* L.

Recently, *Jatropha curcas* L. (JCL) has successfully captured considerable interest from the mass media and scientific community due to its suitability and advantages as an alternative feedstock for biodiesel production. Firstly originated from Central America, JCL was introduced into India by Portugese traders since 1600s for its medicinal application. Nowadays, JCL is mainly cultivated in tropical and subtropical regions such as Mexico, India and Africa. The oil in the seeds is extracted for manufacture of soaps, candles, lubricants and dyes. JCL is still a relatively wild plant and unexplored until the publication of its research finding pertaining to its promising potential as biodiesel feedstock (Foidl *et al.*, 1996). In 2010, a team of researchers from Kazusa DNA Research Institute, Japan had successfully sequenced the whole genome of JCL which in turn spurred more fundamental research works to improve its properties and applications (Sato *et al.*, 2010).

1.5 Supercritical *in situ* Extraction and Transesterification

Conventional method for the production of biodiesel from JCL and other types of oil seeds involve various stages; oil extraction, purification (degumming, deacidification, dewaxing, dephosphorization, dehydration, etc.) and esterification/transesterification. These processes constitute a significant portion of the overall production cost while in the meantime, generate waste streams which incurred additional loss of yield. Development of catalytic *in-situ* extraction, esterification and transesterification or simply term as reactive extraction has the potential to cut down the processing cost significantly while maintaining high product yield. The process differs from the conventional biodiesel production process in which the oil-bearing material contacts with alcohol directly instead of reacting with pre-extracted oil. In another words, extraction and transesterification proceed in one single step, with alcohol acting both, as an extraction solvent and a transesterification reagent. Therefore it eliminates the requirement of two separate processes; the costly hexane oil extraction process and transesterification reaction process, thus reducing processing time, cost and amount of solvent required.

Meanwhile, the utilization of supercritical fluids (SCF's) technology will eliminate the needs for addition of expensive heterogeneous catalyst. SCF's are fluids above their critical temperature and pressure with gas like diffusivities and liquid like viscosities. Their unique features enable SCF's to form homogenous phase with the reactants and subsequently enhance the diffusion rates without the aid of third-party catalyst. In addition, the usage of homogeneous or heterogeneous catalyst results in a more complex process while requiring extra separation step post-reaction. Without addition of catalyst, this can help to reduce product contamination and purification process thus reduces the overall biodiesel production cost.

In order to obtain the advantages of both processes, a novel process termed as supercritical *in situ* extraction and transesterification (SET) is developed in this study which combines the application of reactive extraction with SCF's. In this whole new intensification process, solid oil seeds will be reacted directly with short-chain alcohol (methanol) to produce FAME under supercritical conditions without any addition of catalyst. Theoretically, this process is able to enjoy ample of benefits from the combination process while overcoming most of the weaknesses in the inherent biodiesel production system. Currently there is no detailed scientific study regarding the development of SET process for JCL oil seeds published in the literature.

1.6 Problem Statement

One of the major obstacles which prevent large-scale commercialization of biodiesel to completely substitute petroleum-derived diesel lies within its cost of production. Currently, the cost of pure biodiesel (100%) is still much higher than diesel fuel. This high cost is largely attributed to the cost of virgin vegetable oil as feedstock and processing technology such as large usage of solvent and catalyst. Thus, biodiesel is still not economically feasible and this justifies the need for more advanced research and technical development. First generation biodiesel that is available in the market nowadays is produced from edible oils such as palm oil and rapeseed oil as the raw material. However this becomes a big international issue since food is used to produce fuel while many people in the world still die because of starvation. Therefore, research on the production of biodiesel via non-edible oil is necessary. Many types of non-edible oil can be used as the feedstock for the production of biodiesel such as the oil extracted from sea mango, castor bean, sandbox tree and JCL. The oil content in JCL seeds is quite high and even higher than the oil palm fresh fruit bunch (Currie, 2007). Therefore, JCL seeds actually have a good potential as feedstock for the production of biodiesel.

Unfortunately, the transesterification of vegetable oil with alcohol to biodiesel is typically catalyzed by NaOH or KOH as the homogenous basic catalyst. Free fatty acids (FFA) are strong poison to these homogeneous catalysts and also lead to the formation of soap which will complicate the separation of products. The FFA content in the oil is considered low if it is lower than 1.0 wt% (usually in refined oil), but for some crude oil (like unrefined JCL seeds oil), recycled oils and greases, the FFA content can exceed 10.0 wt% (Gui *et al.*, 2008). Therefore acid catalyst such as H_2SO_4 is used. However, using homogeneous acids and bases as catalysts presents not only environmental threats like corrosion but also causes difficulty in the separation of products. Likewise, the cost for solid heterogeneous catalyst synthesis is relatively higher and leaching of catalyst active sites is still a primary concern (Lam *et al.*, 2010). Therefore, there is an urgent need to develop alternative process pathway to overcome all the limitations above.

Apart from that, there are still a lot of inconveniences and disadvantages in the production of biodiesel using conventional method. For the conventional method, biodiesel need to go through several pre-processes before it can be generated. The processes include the solvent extraction of oil from the oil seeds, solvent recovery via evaporation and purification of raw oil before subjecting to transesterification process. Meanwhile, production of biodiesel via SET method is just a one step process where the extraction and reaction occur simultaneously. Besides, other chemical reagents and substances which are normally required in the conventional method can be minimized using the SET process. For instance, large amount of hexane needs to be used as solvent to extract the oil before employing methanol as the reactant. However, in the SET method, only methanol is needed for extraction and production with significant shorter reaction time. In overall, SET method is believed to have the potential to produce high yield of biodiesel at a faster rate and reduction of waste streams generation. This can lead to a huge reduction of operating cost and thus render biodiesel to be more economically competitive to fossil fuels.

Nevertheless, for SET, the mass transfer barrier which involves 3 phases simultaneously (solid, liquid and gas) and the supercritical conditions which consume a lot of energy might render this process not viable for industrial application. Moreover, the fundamental knowledge and information pertaining to similar SET process are still limited in the literature. Therefore, there is a need to further optimize this process by lowering the process condition severity while at the same time retaining the high biodiesel yield compared to conventional process.

1.7 Objectives

The main aim for this research is to produce biodiesel from JCL seeds by using *in situ* extraction and transesterification with supercritical fluids. Specific objectives can be broken down into 5 parts as listed below:

1. To perform raw material characterization (particle size, moisture content and free fatty acid content) on JCL oil seeds and investigate the effect of solid pretreatment (heat treatment, grounding and sieving) towards SET process
2. To optimize the process parameters in a batch reaction under different primary variables including reaction time, temperature, molar ratio of solvent/co-solvent to solid seeds and agitation rate using one factor at a time method and Design of Experiment (DoE)
3. To determine the effect of different co-solvents (alkanes, aromatic hydrocarbon and CO_2) and impurities towards lowering process severity of the SET process
4. To analyze the properties of FAME and by-products from the SET process
5. To study the kinetics of the SET and propose a suitable process mechanism

1.8 Scope of Study

JCL is an emerging non-edible oil plant which has a high potential as the feedstock for biodiesel production. In this study, SET developed from process intensification was applied together with supercritical fluids for the production of biodiesel from JCL in a high pressure batch reactor. Characterizations of solid JCL seeds were performed with Scanning Electron Microscopy (SEM), surface area analysis, particle size analyzer, Thermal Gravitational Analysis (TGA) and Fourier Tranform infrared spectroscopy (FT-IR). Its oil, water and FFA content were also determined for subsequent experimental calculations. Pre-treatments of the solid seeds including solid particle size (0.5-2.0 mm), de-shelling and heat treatment at five different temperatures (45°C-105°C) and two different durations (12h and 24h) were also investigated to obtain cost-effective fatty acid methyl ester (FAME) yield.

SET process was conducted in the process temperature range of 240°C to 320°C, process pressure of 4.0 MPa to 24.0 MPa, methanol to solid seeds ratio of 2.5 ml/g to 15.0 ml/g, space loading of 90.0 ml/g to 18.0 ml/g, n-hexane to solid seeds ratio of 0 ml/g to 6.0 ml/g, process holding time of 0 min to 35 min and stirring speed of 0 rpm to 500 rpm. Co-solvents which were being employed in the process to reduce the process severity were n-pentane, n-heptane, tetrahydrofuran (THF), toluene, nitrogen gas (N_2) and carbon dioxide gas (CO_2). Their amounts were varied from 1.0 ml/g to 5.0 ml/g for liquid and 10 bar to 50 bar for gases.

Statistical analysis design of experiment (DoE) was used to study the interaction effects between operating temperature (280°C to 300°C), holding time (0 to 30 min), methanol to solid ratio (2.5 mg/l to 7.5 ml/g) and amount of CO_2 (10 bar to 50 bar) towards both the extraction efficiency and FAME yield. The optimum product yield was obtained based on the RSM for the range of conditions proposed. Studies on impurities tolerance for water and FFA contents from 5.0 wt.% to 30.0 wt.% and thermal stability from 280°C to 320°C for SET process were also carried out.

In order to ensure the sustainability of the process by re-utilizing all the products in a close-loop life-cycle scheme, product characterization will be vital. The solid residue post-reaction was subjected to SEM, surface area analysis and TGA characterization and compared to un-reacted JCL seeds. Polar liquid compounds collected from SET process were analyzed with Gas Chromatography-Mass Spectrometry (GC-MS) to identify their components for re-utilization. The FAME produced was also characterized for several important fuel properties to validate that they are within the limits of international standards. Mathematical models based on kinetics study were also developed for both extraction and reaction study in order to predict the yield of products according to different process conditions. Lastly, a relevant process mechanism representing SET process based on the experimental observations and results was proposed.

1.9 Organization of the Thesis

This thesis will consist of six different chapters. All of them are arranged in a sequential manner to allow readers to follow the research work systematically.

The first chapter, which is the introduction chapter, will provide a general overview on the outline of this research. It covers the global development of renewable energy as well as in Malaysia. It will also provide background information on the importance of biodiesel, JCL as feedstock and SET process as a feasible biodiesel production process. The problem statement, research objectives and scope of the study can be found here in detailed.

The second chapter compiled all the literature reviews relevant in this research work from past and present. Past research work in transesterification process for the development of biodiesel will be presented in details including their process pathway, methodology, mechanism and fundamental process chemistry. Present progress in SET process will also be explored to provide information on the current status quo in the related research field. Updated scientific information on the process optimization, DoE, kinetic modeling, thermodynamics and product application will also be covered to gain insights into the future challenges and benefits in this research work.

The third chapter will cover the research methodology and analysis employed in this research work. It includes the detailed description of the SET process procedures, experimental rig, consumables and analytical instruments applied throughout the study. In addition, the implementation of statistical tools for kinetic modeling and in particularly, RSM with Central Composite Rotatable Design (CCRD) will be provided in this chapter. This chapter is presented in such a way that other researchers can repeat the experimental work if necessary.

In Chapter Four, all the experimental results obtained are presented followed by their respective discussions. The first part consists of raw material characterization and results from preliminary study. This is followed by investigation of the effect of solid pre-treatments and process parameters study in SET process towards extraction efficiency and FAME yield. The potential of various co-solvents to help lower the process severity is also discussed in detail. The significant interaction effects between primary variables affecting SET process are also explored in depth with the help of RSM. Impurities tolerance for water and FFA content and thermal stability of methyl esters in JCL are also presented. Lastly, product characterization on the final FAME and by-products are discussed with their potential to be re-utilized as product in other applications.

Chapter Five gives the comprehensive analysis on the kinetic modeling for SET process. It was divided into two parts to investigate the extraction and reaction process occurred in this study separately. The mathematical model which represented the SET process is calculated and validated in this chapter together with other thermodynamic data. Based on the information gathered, an adequate reaction mechanism for SET process is proposed.

Lastly, Chapter Six will include the executive summary of the research work comprising of the significant findings, observations and discussions involved. Recommendations for future studies to enhance the SET process will be suggested to ensure high sustainability in biodiesel production.

CHAPTER 2

LITERATURE REVIEW

2.1 *Jatropha curcas* L. as Biodiesel Feedstock

Jatropha is a genus from the family of Euphorbiaceae which consists of more than 170 of different plants, shrubs and trees species. Most of them are succulent plants with water-retaining features which makes them highly adaptable to semi-dry climates or soil conditions. Euphorbiaceae plants normally produce anti-nutritional compounds with high toxicity to human bodies and *Jatropha* plants are not exception. Extraction from several *Jatropha* plants has identified several toxic compounds such as lectin, protease inhibitors, carcinogenic phorbol and phytate (Openshaw, 2000). Due to the presence of these poisonous ingredients, consuming untreated *Jatropha* seeds can lead to human fatality. Moreover, its sap is notorious for its skin-irritant effect and therefore should avoid pro-long skin contact. Several notable species from the *Jatropha* genus include *Jatropha cuneata* (used for basketmaking), *Jatropha integerrima* (ornamental), *Jatropha pohliana* and *Jatropha curcas (*biodiesel*).*

2.1.1 Botanical Characteristics

JCL is a perennial semi-evergreen shrub and fully-grown tree which can reach up to 6 m in height. It has two flowering seasons, each lasting for 2 months which normally ranging from November-December and April-May. Its leaves are large and broad with green in colour. Each JCL's fruit bears 2-3 seeds weighing between 600 to 700 mg. Its seed are brown in colour when fully ripen. However, the seed contains highly poisonous toxalbumin curcin which can be fatal when consumed by human. JCL can grow in semi-arid areas with average rainfall as low as

500 mm/year (Carels, 2009). Minimum rainfall for JCL to survive is around 300 mm/year but it will usually need at least 600 mm/year to bear fruits and flowers. Optimum rainfall for JCL is approximately between 1000 and 1500 while higher precipitation will be detrimental due to more susceptible to fungal attack. It thrives well in degraded land too as it do not demand a lot of cultivation attention. JCL is found to grow well on sandy and loamy soil with about neutral pH ($6.0 < pH < 8.0$). Clay and shallow soils are deemed as unsuitable as they might hamper its deep root development. However, scientific research shows that adequate fertilization (chemical or organic matter) can help to overcome poor soil condition.

The seed yields for JCL had been reported from on-site plantation data ranging from 100 kg to 5 tonne dry seed/ha/year (Achten *et al.*, 2008). Trees with yield higher than 2 tonnes dry seed/ha/year should generally be selected as new plantation sources although out-crossing seeds from high yield plants may not guaranteed the same results as their parent trees. Older JCL trees with higher toxicity content are discovered to have a higher resistance to pests and diseases which will reduce the requirement for pesticides and chemicals. Planting density for JCL trees are recommended to be within the range of 1100 to 2500 trees/ha. Wider spacing will promote higher yield due to less competition but will decrease the overall yield per hectare. For inter-cropping practices, Singh and co proved that inter-cropping JCL plantation with groundnuts can help with weed control which subsequently leads to improve yield (Singh *et al.*, 2007). JCL plants can grow quickly and will form a thick bushy fence in about half a year. In 2 to 3 years time, it can form thick branches with approximately 4 m in height. Normal JCL trees can last for more than 50 years though their optimum economical lifespan is about 30 to 50 years.

2.1.2 Characteristics of JCL as Biodiesel Feedstock

Mature JCL fruits will change their colours from green to yellow-brown. They can be harvested either by shaking the branches or hand-picking, though both will require a substantial amount of labour work. JCL seeds are then separated from the fruit pericarp. Raw JCL seeds can undergo oil extraction without any pretreatment either through mechanical pressing (small scale) or solvent extraction (large scale). Average oil content reported from literature from oil extraction of raw JCL seeds normally ranged from 30-40% (Pramanik, 2003) although certain species can reach up to 61-80% (Belewu *et al.*, 2010). JCL seeds can be further separated into seed shell and seed kernel as shown in Figure 2.1. Seed kernel contains primarily oil and protein while protected by a white thin layer of seed coat made up of fibre. Most of the oil is stored in the seed kernel and by separating the seed shell from the seeds, approximately 20% higher oil extraction yield can be obtained (Karaj *et al.*, 2008). Dry matter in shell and kernel are reported to be 91.17% and 94.65% respectively.

Characteristic of extracted JCL oil can differ greatly according to different environment, cultivation conditions and genetics. Table 2.1 shows the comparison of several main characteristics between mineral diesel, JCL oil and *Jatropha* biodiesel. Research studies have also shown that processing and storage of JCL oil can affect its quality. In order to produce high quality fuel in the form of biodiesel, certain criteria must be fulfilled. In general, high quality fuel must possess characteristics as below:

- Low content of phosphorus, sulfur, ash and moisture
- Low content of contaminants
- High oxidative stability

- Low acid value
- Low viscosity
- High heating value
- Low pour and cloud point

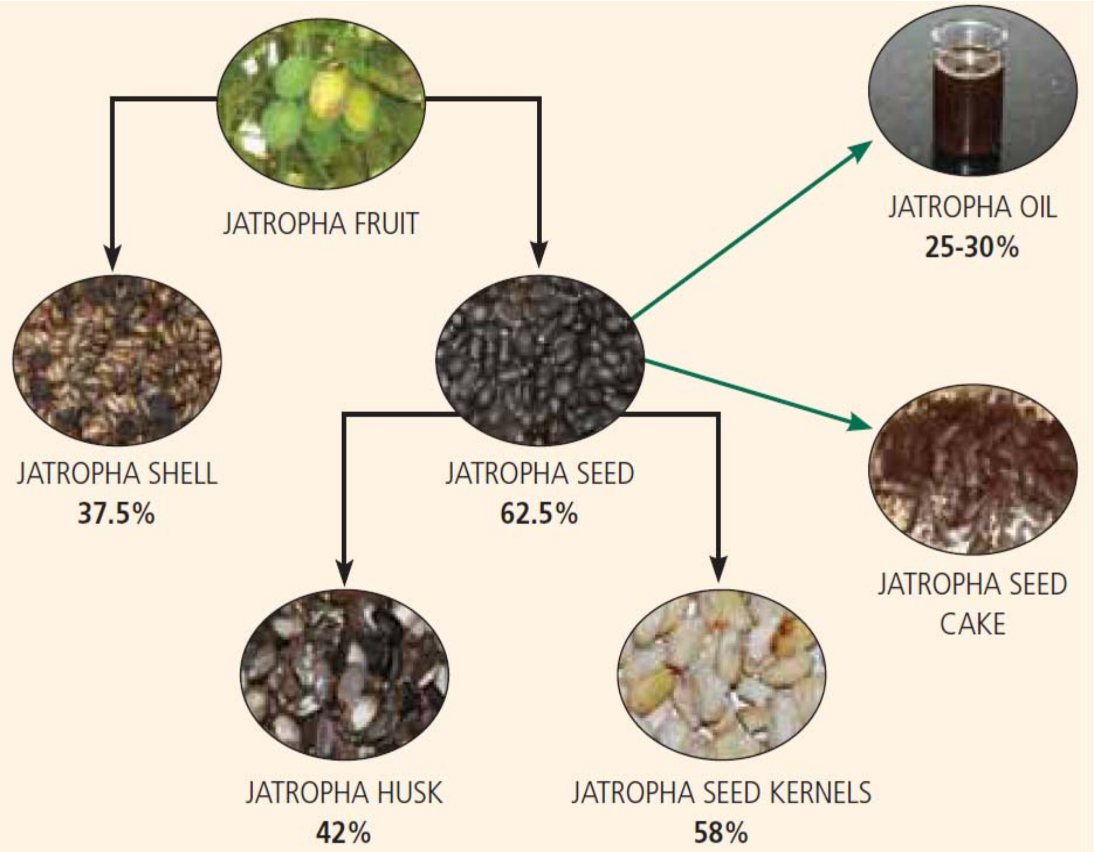

Figure 2.1: A typical composition of JCL fruit (Brittaine and Lutaladio, 2010)

Table 2.1: Comparison of properties between *Jatropha* biofuels and mineral diesel (Achten *et al.*, 2008; Belewu *et al.*, 2010; Parawira, 2010)

Parameters	Unit	Mineral diesel	*Jatropha* oil	*Jatropha* biodiesel
Density (15/40°C)	kg/l	0.84-0.85	0.86-0.93	0.86-0.88
Cloud point	°C	-14.0	2.0	4.0
Flash point	°C	80	210-240	170-192
Pour point	°C	-20	4.0	2.0
Cetane number	-	47.8	38.0-51.0	57-62
Sulfur content	%	1.0-1.2	0-0.13	negligible
Kinematic viscosity (at 40°C)	cSt	4.0-8.0	37.0-54.8	4.84-5.65
Ash content	%	0.01	0.8	0.012
Carbon residue	%	0.17	1.0	0.20
Net calorific value	MJ/l	42-46	38.20	38.45-41.00
FFA content	%	-	5.00-8.50	< 1.00
Moisture content	%	0.02	1.4	0.025

Crude JCL oil is relatively viscous and slow-drying. It is odourless and colourless when fresh but becomes yellowish after standing. FFA content of crude JCL oil can vary from as low as 2-3 wt.% to 10-14 wt.%, depending on the extraction conditions. Low FFA content is required to improve the biodiesel storage stability. There are four main types of fatty acids in JCL oil which are palmitic (C16:0), steric (C18:0), oleic (C18:1) and linoleic acids (C18:2). Oleic and linoleic acids are unsaturated fatty acids with double bonds and usually constitute over 50% of the composition of JCL oil. Average fatty acid composition for JCL is shown in Table 2.2. Although its high unsaturation content will improve the fuel's cold flow properties, it will be prone to oxidation during long term of storage which should be taken into consideration as well. Combustion of *Jatropha* biodiesel in internal combustion engine has been proven to lead to reduction in several critical atmospheric pollutants such as hydrocarbons, CO_2, CO, sulfates, polycyclic aromatic hydrocarbons and particulate matter (Pandey *et al.*, 2011). Emission of carbon dioxide equivalent from usage of *Jatropha* biodiesel is found to be about 78% lower than the usage of corresponding mineral diesel and thus can contribute significantly towards carbon reduction. However, its higher oxygenated content will also give rise to the increase emission of nitrogen oxide (NO_x) compare to conventional diesel.

Table 2.2: Average fatty acid composition of JCL oil (Achten *et al.*, 2008)

Fatty acid composition	Weight percentage (%)		Average saturated fatty acid (%)	Average unsaturated fatty acid (%)
	High	Low		
Palmitic acid (C16:0)	16.91	12.17	22.30	-
Stearic acid (C18:0)	9.71	2.89		
Oleic acid (C18:1)	50.09	33.95	-	77.50
Linoleic acid (C18:2)	41.64	29.12		
Others*	1.94	1.585		

*Minority fatty acids include capric acid (C10:0), myristic acid (C14:0), palmitoleic acid (C16:1), linolenic acid (C18:3) and arachidic acid (C20:0)

2.1.3 Status of JCL plantation in Malaysia

Initial effort to develop JCL plantation in Malaysia was spearheaded by Malaysian Rubber Board (MRB) in 2008. Various JCL strains were bought from neighboring countries such as Thailand, Myanmar and Indonesia and tested on a 2 hectares plantation. The plantation was scheduled to be expanded to 38 hectares within one year. In addition, MRB encouraged farmers to produce JCL plants in marginal lands which were not suitable for other types of commercial plantation. In 2009, another government agency, Forest Research Institute of Malaysia (FRIM), initiated a JCL plantation project in Terengganu. The JCL plantation would be developed into commercial scale using the vast idle coastline along the Terengganu state (Lane, 2012). Currently, most of the major JCL plantations were being developed and expanded in East Malaysia by private companies such as Mission Biotechnology and Bionas Group. Mission Biotechnology was expected to possess up to 1 million hectares of JCL plantation by 2010. On the other hand, Bionas Group was able to acquire up to 3.3 million hectares of JCL plantation through step-wise contracting method with local land owners in Sabah and Sarawak (Mofijur *et al.*, 2012). Development of JCL plantation in Malaysia is expected to grow at a moderate pace without affecting the development of palm oil plantation.

2.2 Lipid Extraction for Biodiesel Production

For first generation biodiesel derived from edible oils, lipid or oil extraction from the oil-bearing solid material has to be performed prior to transesterification process to harvest the oil in liquid form. For instance, palm oil is normally extracted from the fresh fruit bunch (FFB) while rapeseed oil is harvested from the plant seeds. In the view that almost two-thirds of the total oils and fats production is comprised of oil seeds, optimizing lipid extraction techniques will thus be extremely crucial (Dominguez *et al.*, 1994). Currently, various types of extraction techniques are available depending on the associated feedstock and required quality of extraction product. For JCL oil extraction process, the most popular methods are mechanical extraction, chemical extraction with solvents, three-phase partitioning extraction and supercritical fluid extraction.

2.2.1 Mechanical Extraction

One of the most traditional extraction methods for JCL oil seeds is mechanical extraction using oil expeller in the form of hydraulic or screw press. It can be fed directly with the whole seed or the kernels or a mixture of both either manually or engine-driven. Under usual circumstances, engine-driven press can achieve 10-15% higher extraction efficiency compare to manual operated press (Tewari, 2007). In order to obtain higher oil yield, the seeds are normally passed through the expellers for two or three times. Its simplicity and low cost make it a favorite among people especially in rural areas. (Karaj and Muller, 2011) managed to obtain maximum oil extraction efficiency at 89.4% w/w from JCL seeds using mechanical screw press. They discovered that specific energy consumption and oil recovery efficiency were correlated to material throughput following a strict pattern. This enabled them to determine the optimal oil recovery by manipulating the operation parameters. In a more recent study, Evon and co successfully obtained highest JCL oil yield of 70.6% with good press cake quality (residual oil content less than 8%) by using a continuous twin-screw extruder (Evon *et al.*, 2013). Nevertheless, oil extraction efficiency using mechanical pressing is generally lower than other extraction methods while generates heats which might damage both the oil and the seeds.

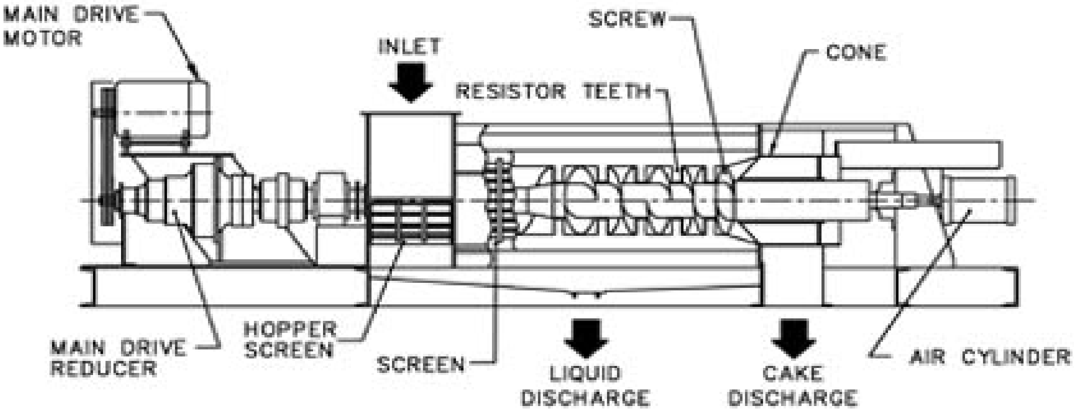

Figure 2.2: Schematic diagram of a screw press for oil extraction (Corporation, 2006)