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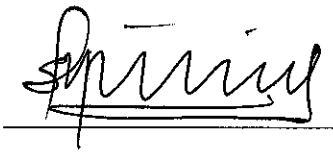

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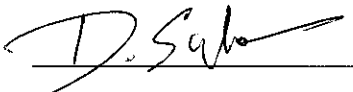

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DEDICATION

This thesis is dedicated to my lovely father M. Mekuria Hailegiorgis and lovely mother Weizero Yegile Abebe.

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ABSTRACT

Raw material and processing costs are adversely affecting the economic viability of biodiesel technology. In-situ transesterification of non edible oil seed particles such as jatropha curcas can minimize the costs of feedstock, oil extraction and purification; slow conversion rates due to limited solubility of oil in methanol can be enhanced by using phase transfer catalysts; microwave pretreatment of seeds can make oil molecules more reactive. In the present work, these three concepts were utilized together to investigate in-situ transesterification of microwave pretreated jatropha curcas seed particles in the presence of alkaline phase transfer catalysts (PTC) such as cetyltrimethylammonium bromide (CTMAB), benzyltrimethylammonium hydroxide (BTMAOH) and crown ether (CE); BTMAOH was observed to be better than CTMAB and CE. It was observed that use of alkaline BTMAOH as a PTC and microwave heat pretreatment of jatropha curcas seed particles have substantially increased the reaction rate of in-situ transesterification reaction. Optimum conditions for in-situ transesterification in presence of alkaline BTMAOH were established using response surface methodology (RSM). At optimum condition, yield of fatty acid methyl esters (FAME) observed was 89.8±1.37% w/w in 103 minutes while yield of fatty acid ethyl esters (FAEE) achieved was 99.4±0.4% w/w in 95 minutes. With microwave heat pretreatment of jatropha curcas seed particles, in-situ transesterification reaction rate was enhanced; at optimum condition, yield of fatty acid methyl esters achieved (FAME) was 93.7±1.53% w/w in 37 minutes at 38°C while yield of fatty acid ethyl esters (FAEE) was 99.5±0.12% w/w in 30 minutes at 30°C reaction temperature. Order of the reaction for the conversion of triglycerides was around one for in-situ methanolysis as well as in-situ ethanolysis reaction. Microwave pretreatment of seed particles enhanced the apparent reaction rate constant of triglycerides conversion from 0.01637 to 0.04328min^{-1} for in-situ methanolysis and from 0.03013 to 0.05497min^{-1} for in-situ ethanolysis at 30°C reaction temperature.

Alkaline phase transfer transesterification of fatty oils reaction mechanism based reaction kinetics model equations were developed. Experimental observations were compared with the model equations to identify significant model parameters related to intrinsic reaction rate constant, rate of complex formation and partition coefficients. Estimated yield of biodiesel from the model equation for triglyceride conversion compare well with the experimental results.

ABSTRAK

Daya maju ekonomi teknologi biodiesel dikekang oleh kos bahan mentah dan kos pemprosesan yang tinggi. Trans-esterifikasi in-situ keatas zarah daripada benih minyak bukan makanan seperti biji buah jarak (jatrophacurcas) dapat mengurangkan kos bahan mentah, pengekstrakan dan pemurnian; kadar ubah yang perlahan disebabkan kelarutan terhad minyak di dalam metanol boleh dipertingkatkan dengan menggunakan pemangkin pemindahan fasa (PTC); pra-rawatan gelombang mikro keatas benih minyak boleh meningkatkan tahap tindak-balas molekul minyak. Tesis ini menggunakan ketiga-tiga konsep serentak untuk menyiasat pengaruh PTC alkali, khasnya cetyltrimethylammonium bromide (CTMAB), benzyltrimethylammonium hydroxide (BTMAOH) dan crown ether (CE); BTMAOH didapati lebih baik daripada CTMAB dan CE terhadap trans-esterifikasi in-situ keatas zarah biji buah jarak yang melalui pra-rawatan gelombang mikro. Penggunaan PTC alkali BTMAOH dan pra-rawatan gelombang mikro keatas zarah biji buah jarak telah meningkatkan kadar tindak-balas trans-esterifikasi in-situ dengan ketara. Keadaan operasi optimum trans-esterifikasi in-situ bersama PTC alkali BTMAOH telah dipilih dengan menggunakan kaedah RSM. Pada keadaan optimum, penghasilan metil ester asid lemak (FAME) adalah 89.8±1.37% dalam tempoh 103 minit sementara hasil dari etil ester asid lemak (FAEE) adalah 99.4±0.4% dalam 95 minit. Pra-rawatan gelombang mikro keatas zarah biji buah jatropha telah menunjukkan peningkatan kadar tindak-balas trans-esterifikasi in-situ; pada keadaan operasi optimum, penghasilan FAME adalah 93.7±1.53% dalam tempoh 37 minit dan suhu tindak-balas 38°C sementara penghasilan FAEE adalah 99.5±0.12% dalam 30 minit pada 30°C. Tahap tindak-balas trigliserida adalah sekitar satu untuk metanolisis in-situ dan juga untuk ethnolisis in-situ. Pra-rawatan gelombang mikro keatas zarah benih minyak meningkatkan pemalar nyata untuk kadar tindak-balas trigliserida daripada 0.01337 kepada 0.04328 min-1 bagi metanolisis in-situ dan daripada 0.03013 kepada 0.05497 min-1 untuk etanolisis

in-situ pada suhu tindak-balas 30°C. Persamaan model kinetik juga telah dibina untuk menjelaskan mekanisme transesterifikasi benih minyak di bawah pengaruh PTC alkali. Perbandingan di antara eksperimen dan persamaan model kinetik dibuat untuk mengenal pasti parameter model penting yang berkaitan dengan pemalar intrinsik kadar tindak-balas, kadar pembentukan kompleks dan pekali pembahagian. Anggaran penghasilan biodiesel daripada persamaan model kinetik menunjukkan perbandingan yang baik dengan penghasilan dari eksperimen.

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CHAPTER 1

INTRODUCTION

1.1 Background of the study

Global energy consumption is rising rapidly with increasing population and modernization. The total world energy demand is estimated to rise from 505 quadrillion British thermal unit (BTU) in 2008 to 770 quadrillion BTU in 2035 as presented in Figure 1.1. About 88% of the world energy consumption is based on fossil fuels. World liquid energy consumption is also estimated to increase from 85.7 million barrels per day in 2008 to 112.2 million barrels per day in 2035 [1-4]. At the existing production rate, the global proven reserves of crude oil and natural gas are estimated to be fully consumed in a half century [5].

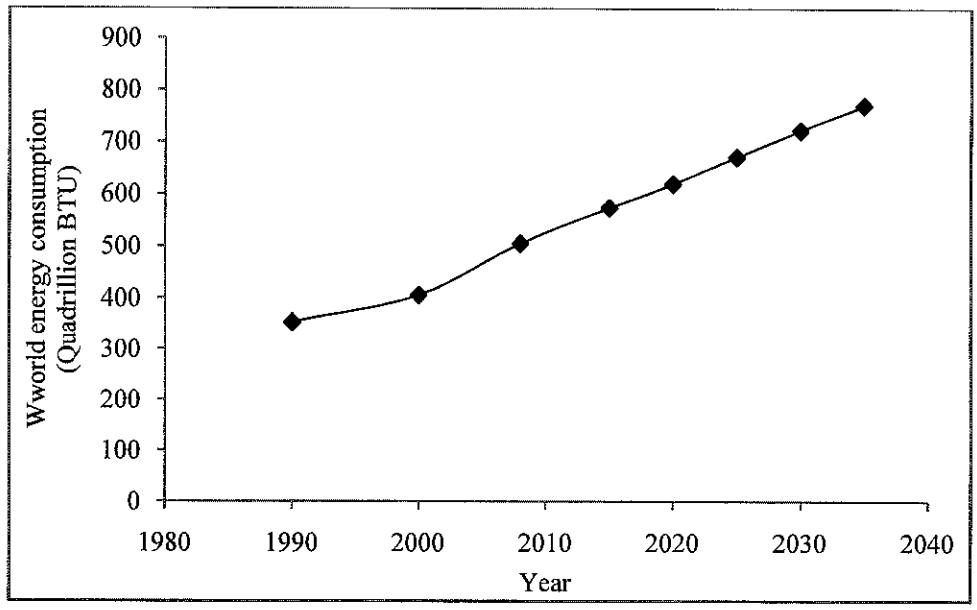


Figure 1.1: Projected world energy consumption from 1990 to 2035 in quadrillion BTU (source: IEO 2011[2])

With the increasing demand for energy from the fossil fuels, the environment and its ecosystems are getting polluted by the emission of greenhouse gases such as carbon dioxide. Carbon dioxide emissions related to use of energy was also estimated to increase from 30.2 billion metric tons in 2008 to 43.2 billion metric tons in 2035[1]. Associated global warming, melting of the polar ice cap, glaciers, rising sea levels and devastating weather patterns can affect life on earth irrecoverably. Exploration for alternative renewable fuels and chemical feedstocks with zero net carbon dioxide emissions is necessary for sustainable development. Currently renewable energy fuels account for about 11% of the total world energy supply [5].

Biomass, obtained by photosynthesis, is a versatile renewable feedstock that can be converted into different types of bio-fuels (solid, liquid and gas) [5, 6]. It contributes up to 77.4% of the current renewable energy supply. Bio-fuels include bio-ethanol, bio-methanol, biodiesel and bio-hydrogen. Biodiesel is gaining increasing attention as it can substitute effectively for petro diesel [7]. Biodiesel can be produced by transesterification of a wide range of feedstocks such as vegetable oils, animal fats, used frying oils, etc with alcohols [8, 9]. The feedstock source can be region specific. Thus, soybean oil is used in the United States; rapeseed oil (canola oil) is used in Europe while palm oil is used in Indonesia and Malaysia. Biodiesel offers promising benefits such as biodegradability, good lubricity, high cetane number, high flash point, higher combustion efficiency and low polluting emission to the environment compared to petro-diesel [9, 10].

Transesterification is a chemical reaction between triglycerides present in the oils or fats and alcohols such as methanol or ethanol to form esters and glycerol in the presence of a catalyst or at high pressure and temperature[11, 12]. The molecular weight of ester molecule is about one-third of its parent vegetable oil molecule and has a viscosity approximately one tenth of the viscosity of vegetable oils and twice that of petro-diesel fuel. The physical characteristics of esters produced by transesterification are very close to those of petro-diesel fuel. Vegetable oils or animal fats are esters of saturated and unsaturated mono-carboxylic acids with the tri-hydric alcohol glycerides. The most common fatty acids of vegetable oils are palmitic acid (C16:0, no double bond), stearic acid (C18:0, no double bond), oleic acid (C18:1, one

double bond) and linoleic acid (C18:2, two double bond). All the three OH groups can be esterified with alcohol [13, 14]. Stiochiometrically, one mole of triglycerides reacts with three moles of alcohol to produce three moles of esters and a mole of glycerol as shown in Figure 1.2.

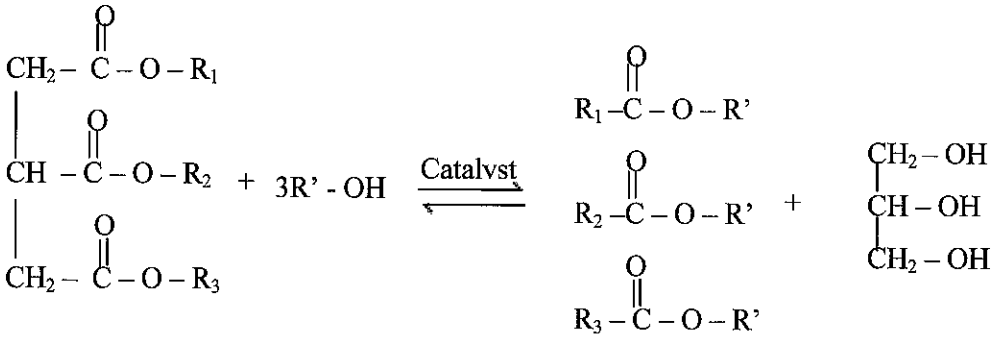


Figure 1.2: Transesterification reaction of vegetable oils

As vegetable oils are sparingly soluble in lower alcohols, the transesterification reaction is slow due to the limited mass transfer rate between the two immiscible phases [15]. Several techniques such as mixing, co-solvent addition, higher temperature, higher pressure, super critical alcohol, ultrasonication and microwave irradiation have been investigated to enhance the reaction rates [16-18].

The global markets for biodiesel are entering a period of rapid, transitional growth, creating both uncertainty and opportunity. In years 2008 to 2012, the global edible oil production increased from 137.7 to 150 million tons; about 85% was used as food while about 13% was used for biodiesel production and the remaining 2% for other non-food industrial inputs[19]. Currently, more than 95% of biodiesel is made from edible oil sources such as rapeseeds, soybeans, sunflower and palm [14, 20]. The capacity for biodiesel production increased from 2.2 million tons per year in 2002 to 46.5 million tons per year in 2011; however, biodiesel production was only 1.9 million tons per year in 2002 and 18.3 million tons per year in 2011 as presented in Figure 1.3 [1, 2, 19, 21]. Biodiesel industry had to compete with food processing industry for the all important raw material - edible oils. This resulted in the rise of edible oil prices affecting the economics of biodiesel production as well as food prices. Even now, it has been reported that feedstock cost alone accounts for 75% of the biodiesel production cost [8].

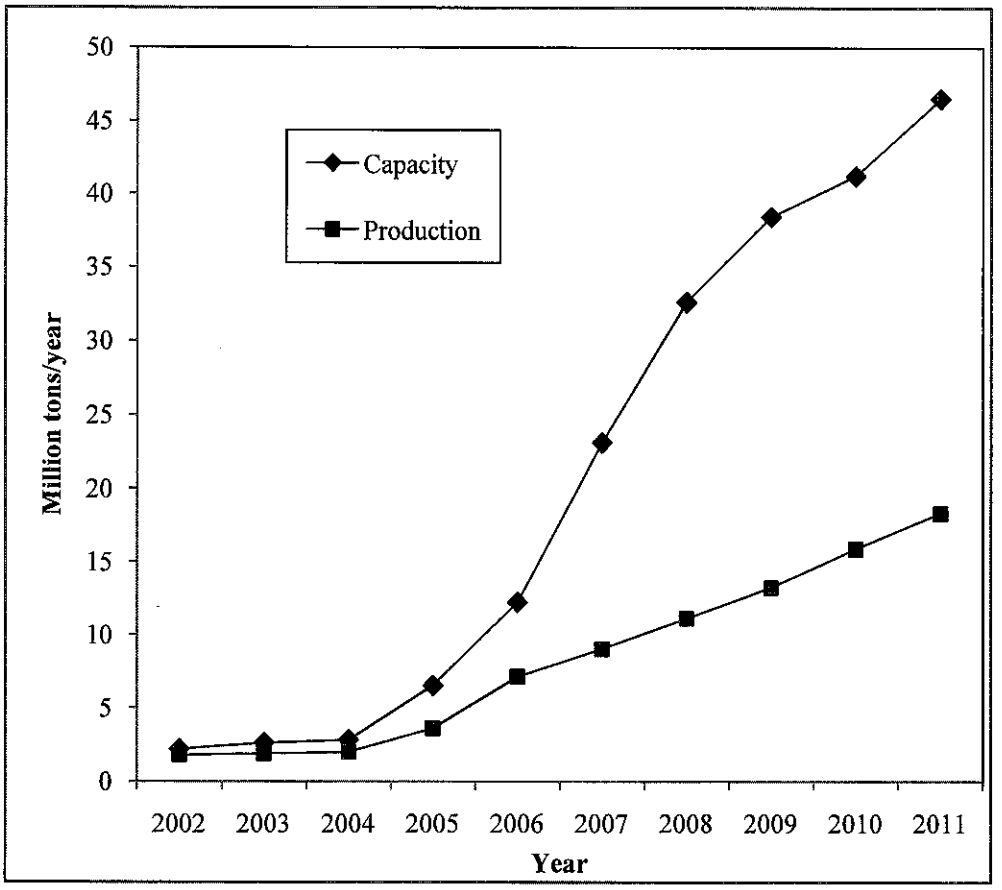


Figure 1.3: World biodiesel production and capacity from 2002 to 20011 [1, 2, 19, 21]

Production of biodiesel from non-edible oil sources such as jatropha, algae, used cooking oil and animal fats can potentially decrease the high edible oil feedstock costs for biodiesel production. In recent years jatropha is identified as a potential alternative non-edible oil bearing plant source to edible oils in different parts of the world such as Central and South America, India, Africa, South East Asia, etc [22, 23]. Planting jatropha as a source of oil for biodiesel production is gaining more attention particularly in tropical and subtropical countries because of its easy propagation, drought resistance, and adaptation to wide agro-climatic conditions, high oil content (35-60%) and versatility use of the plant. Jatropha can grow in marginal and waste lands with no possibility of fertile land use competing with food production. This enables non-arable lands to be utilized for jatropha plantation that will provide high oil yield for biodiesel production in return. India is proven to be a good example as the country planted jatropha along the sides of railroads with the yield obtained from

such practice reported to be 1.5-2 tons per hectare [24]. The plant bears fruit starting from the second years of its plantation and economic yield can be obtained from 5th years on wards. The plant has an average life of 50 years [25, 26]. The matured jatropha reported to give up to 4kg of seeds per plant per year. However, the economic yields can be considered from 1.5-4kg per plant/per year. In poor soil conditions it is reported to be about 1.5-2kg seeds/plant [8, 24].

Energy demand in Malaysia is expected to grow at a rate of 5 to 7.9% for the next 20 years due to its fast growing industrialized economy [5]. Natural gas (43.4%), crude oil (38.2%), coal (15.3%) and the renewable resources (3.1%) contribute to the required energy mix [5]. Malaysia is a major palm oil producer and exporter. The government of Malaysia adopted the National Biofuel Policy in 2006 to further promote the production and consumption of biodiesels [5, 27]. In the same year, Envo diesel has been introduced to further strengthen the utilization of biodiesel as a renewable diesel. Envo diesel was a mixture of 5% blend of processed palm oil with 95% petro-diesel. Even though 92 biodiesel projects were approved in the period 2006-2007, due to the challenges posed by high palm oil price only 14 of them were built. Of the 14 biodiesel plants, only 8 of them were put in operation in the year 2008 [24, 28]. At the end of 2011, even though the biodiesel plants in operation were increased to more than 20 biodiesel plants, with a total production capacity of 2.62 million ton per year, only 2 plants were in operation and producing biodiesel below capacity. The rest are either-non operational or producing other bio-chemical products due to high demand of palm oil for food industries at global level. With the high cost of feedstock biodiesel producers in Malaysia will continue to face a difficult environment. Malaysian government modified its biodiesel oil feedstocks strategy to include alternative non-edible feedstocks such as jatropha curcas. The government of Malaysia encouraged jatropha curcas as a next potential biodiesel feedstock at the Sabah Development Corridor launched in 2008. Malaysia has about 1.5 million ha of estimated marginal land that can be used for jatropha plantation even though its current plantation is at a gradual level [24]. Forest Research Institute Malaysia (FRIM) has conducted a research work for exploring alternative non-edible feedstocks to complement palm oil for the production of biodiesel. It produced biodiesel from non-edible oil sources of jatropha curcas, bintangor laut (Collyphylum innophylum

L.), perah (elateriospermum tapos) and industrial effluents. FRIM installed a pilot biodiesel producing plant with a capacity of producing 20,000 liters of biodiesel per month such that multi feedstock biodiesels were produced and its blend as B20 was successfully tested on FRIM vehicles [29]. Bionas Murabahah Berhad (BMB), a local company, has also built Bionas Jatropha Biofuels processing, storage and supply facilities at Kuching Port, Sarawak, Malaysia with a production capacity of 50,000 metric tons per year of jatropha biodiesel. Some other ventures such as Alam Widuri Sdn Bhd, Mission Biotechnologies Sdn Bhd, Agro Innaz Sdn Bhd, etc, are in the process of expanding jatropha curcas plantation as a complement to palm oil.

Apart from the feedstock costs, even processing costs need to be reduced. Conventionally biodiesel is produced by transesterification of extracted and purified oils from oil bearing plant sources. Recovery of oil from oil bearing seeds can be accomplished using mechanical methods (expelling and extrusion) and chemical methods (solvent extraction). Vegetable oil can be extracted mechanically using mechanical expeller or extruder; however, mechanical extraction can extract only 75 – 80% of the available oils in the oil seeds resulting in high amount of oil loss with the remaining residue [30, 31]. In addition, oil extracted using mechanical methods needs further purification processes such as degumming, deacidification, dewaxing, dephosphorization, dehydration, etc which also increases the cost of vegetable oil. Solvent extraction using hexane is found to be the main technology to achieve high oil recovery from the seed particularly in the United States of America [32]. In such units, hexane recovery is one of the significant step; studies have shown that even in plants operating efficiently, 1.25 liters of hexane is lost for every metric ton of solvent used [33]. Thus, oil extraction using hexane is a costly process due to solvent (hexane) cost, extraction cost, solvent hexane recovery and additional hexane cost to top up hexane lost during solvent recovery; in addition hexane losses can contribute to atmospheric pollution and global warming [34]. Generally, the extraction and purification of oil contributes up to 70% of total oil production costs [35, 36].

In-situ transesterification of oilseeds is one such option developed by Harrington and D'Arcy-Evans [37] that can combine oil extraction step with transesterification step using oil seeds of sunflower. They observed increase in the overall yield of

biodiesel due to possibly better utilization of lipids that could have been lost through imperfect hull-kernel during oil extraction. This process was further investigated by different researchers using soybean seeds [3, 32], sunflower seeds [36, 38] and jatropha seeds [35, 39].

1.2 Problem Statement

Biodiesel is an attractive renewable option to complement dependence on petro diesel. Biodiesel can be produced by transesterification of vegetable oils with methanol in presence of a suitable catalyst. Presently, more than 95% of biodiesel is made from edible oil sources such as rapeseeds, soybeans, sunflower and palm which are available in large scale from the agricultural industry. Usage of edible oils has an adverse effect on its price due to its demand by food processing industry. Also, extraction and purification of oil from the oil seeds adds to the feedstock price. The wastes released during purification process such as degumming, deacidification, dewaxing, dephosphorization, dehydration, etc., threaten the environment. Limited solubility of oils in alcohols reduces reaction rates. It is necessary to keep the cost of production under control to make the biodiesel technology viable by using alternative cheap feedstocks and effective environmental friendly reaction pathways. The general review presented suggests that in-situ transesterification of non-edible seeds as feedstock is a possibility that can keep the cost of feedstock and processing low. Application of phase transfer catalysis and microwave pretreatment of seed particles can enhance the reaction rates.

In the present work, it is proposed to use in-situ transesterification of jatropha curcas seeds as a non-edible oil sources. To enhance the slow reaction rate of transesterification due to limited solubility of alcohol and oil, it is proposed to investigate various phase transfer catalysts (PTC) along with microwave pretreatment of jatropha curcas seeds.

1.3 Research Objectives

The objectives of this research work are:

1. To investigate alkaline in-situ transesterification of microwave irradiation pretreated jatropha curcas seed particles with methanol and ethanol in the presence of phase transfer catalysts; this includes:

    i) Investigation of the catalytic effect of cetyltrimethylammonium bromide (CTMAB), benzyltrimethylammonium bromide (BTMAOH) and crown ether (CE) as phase transfer catalysts during in-situ transesterification reaction and identification of the better PTC

    ii) Investigation of the effect of microwave pretreatment of jatropha curcas seed particles ; and

    iii) Optimization of reaction parameters by statistical experimental design technique of response surface methodology (RSM).

2. To develop reaction mechanism of phase transfer catalysis assisted transesterification reaction and model reaction kinetics based on phase transfer catalysis enhanced transesterification reaction mechanism.

1.4 Scope of the Study

To achieve the aforementioned objectives, jatropha seed particles were prepared and characterized for their oil content and quality. Effects of alkaline and phase transfer catalysts {such sodium hydroxide (NaOH), cetyltrimethylammonium bromide (CTMAB), benzyltrimethylammonium hydroxide (BTMAOH), crown ether (CE), alkaline CTMAB, alkaline BTMAOH and alkaline CE}, effect of reactant ratio (methanol or ethanol to jatropha seeds), mixing speed, reaction temperature on in-situ transesterification of jatropha curcas seed particles as well as microwave heat pretreated jatropha curcas seed particles on in-situ transesterification of jatropha curcas with methanol/ethanol were investigated in a batch reactor. Optimum operating

conditions were established using response surface methodology (RSM). Conversions of triglycerides with time at different reaction conditions were measured to develop reaction mechanism of alkaline PTC assisted transesterification reaction and develop reaction mechanism based kinetics model equations.

1.5 Organization of the Thesis

This thesis is presented in six chapters. The literature review of related research works are described in chapter 2. Historical and technical development of vegetable oil (biodiesel) as a fuel, different techniques used to utilize vegetable oil as biodiesel, the advantage and disadvantages of biodiesel as a diesel fuel, biodiesel production technology, different research works conducted to increase the rate of transesterification reaction and reduce the cost of biodiesel processing, variables affecting biodiesel processing technology, biodiesel quality and international standards are discussed in chapter 2.

Chapter 3 reports the research methodology of the study. In this chapter the materials required for the experimental work, the experimental methodology used to prepare jatropha curcas seed particles and characterize the physical and chemical properties of jatropha curcas oil, experimental set up and procedures of in-situ transesterification experiments are briefly presented. The methods of analysis of the quality of biodiesel and the calculation methodology to quantify experimental results of in-situ transesterification reaction were also described in chapter 3.

Chapter 4 presents the experimental results and discussion. It discusses results on the physical and chemical properties of jatropha oil, the effect of phase transfer catalysis and microwave irradiation heat pretreatment of jatropha curcas seeds on in-situ transesterification of jatropha curcas. It also presents the individual and interaction effects of reaction variables, the optimum operating conditions and biodiesel quality of the present work as compared with the international standards.

Chapter 5 discusses reaction kinetics of in-situ transesterification of jatropha curcas seed particles which includes empirical reaction kinetics result, phase transfer

catalysis reaction mechanism of transesterification and mathematical modeling of mechanism based reaction kinetics of PTC assisted in-situ transesterification and validations of the model with the experimental result.

The thesis is concluded in chapter 6, presenting the final conclusions, contributions of the research work and recommendation for the future work.

CHAPTER 2

LITERATURE REVEIW

2.1 Historical background of vegetable oil as a fuel

Energy consumption per capita is an indicator of economic growth and quality of living. Pre-industrial revolution society primarily depended on renewable agriculture and animal power for their energy needs. Combustion of wood and biomass (solid waste from agricultural produce) provided low efficiency energy. Combustion of coal to release high efficiency energy ushered in the era of industrial revolution in the late 18^{th} century to energize mechanical machines for industrial uses and transportation. Discovery of other fossil fuels like petroleum and natural gas with higher calorific value accelerated industrialization and economic development. Increased use of fossil fuels contributed to generation of pollutants and greenhouse gases such as oxides of nitrogen, sulfur and carbon as well as fossil fuel is getting depleted resulting in unsustainable energy source for long term energy supply. For sustainable development, efficient use of renewable resources which include biomass and vegetable oils is necessary [7, 12].

Rudolf Diesel developed an engine that could run on vegetable oils as fuel in the year 1893 [12, 40]. Its performance was poor compared to petroleum diesel fuel due to higher viscosity of vegetable oils. In a remarkable speech in the year 1902, Rudolf Diesel said "the use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal-tar products of the present time." However, due to the widespread availability of low viscosity petroleum diesel at low cost since the 1920's, diesel engines were adopted to utilize petro-diesel [41].

Thus, except during the periods of energy shortages and high oil prices, vegetable oil fuels received little attention [20, 42]. A mechanism was required to decrease its viscosity so as to burn vegetable oil properly in the diesel engine. Different methods have been proposed to reduce the viscosity of vegetable oil such as blending with solvents, pyrolysis, transesterification etc [41, 43]. The transesterification reaction converts vegetable oil into "biodiesel" consisting of three smaller molecules which are much less viscous and easy to burn in a diesel engine. First patent for the production of biodiesel was awarded in 1977 to Parente [20, 44]. An Austrian company, Gaskoks established the first industrial-scale plant in 1989 [42]. Still the economics of biodiesel production is not favorable due to high cost of vegetable oils and processing steps. Also, the quantity of vegetable oils that can be spared for biodiesel production is very small to be able to replace petro-diesel in its entirety.

Presence of mercaptans in petro-diesel, though useful to provide the necessary lubrication for operating diesel engines, generates pollutants such as oxides of sulfur. Present day environmental concerns require drastic reduction of sulfur compounds in petro-diesel [12]. It has been observed that lubricity of sulfur free petro-diesel can be restored by addition of biodiesel in small proportions. This strategy can complement usage of biodiesel (renewable resource) along with petro-diesel while reducing pollution by SO_X emissions. Use of biodiesel has also a potential advantage in reducing the emission of carbon dioxide. Biodiesel is biodegradable, non-toxic and environmentally friendly as compared to petro diesel and can be run in diesel engines with same or better performance as compared to normal diesel fuel [45].

2.2 Biodiesel feedstock oil yields

Vegetable oils and fats are esters of various fatty acids with glycerol and can be transesterified with lower alcohols to produce biodiesel. The wide range of vegetable oils and fats sources are available for producing biodiesel as an alternative energy resource [8, 9] enabling biodiesel as attractive alternative to diesel fuel. Cultivation of oil seeds depends mainly on climate, soil conditions and cultivation practice.

Oils and fats can be edible or non-edible. Production of edible oils such as palm, sunflower, rapeseeds, soybeans etc., received great attention due to their need for food processing. Presently, cost of vegetable oil source itself accounts for 75% of the biodiesel production cost [8, 24]. Production of biodiesel using edible oils is constrained by ever increasing price of edible oils due to its unavoidable need for the food industry. Selecting the cheapest feedstock is vital to ensure low cost of biodiesel production. Various oil bearing plants have different oil yielding capacity per hectare. Oil yield of different edible oil bearing plants is given in Table 2.1 in the order of volume of oil per hectare along with percentage of oil in the oil-bearing seeds. Palm tree gives the highest oil yield of about 5950 liters per hectare.

Table 2.1: Oil yield for major edible oil crops [4, 14, 20, 46, 47]

Type of oil	Oil yield (liter/ha)	Oil yield (%)
Palm	5950	30–60
Coconut	2689	63–65
Olives	1212	45–70
Rapeseed	1190	38–46
Peanuts	1059	45–55
Sunflower	952	25–35
Soybeans	446	15–20
Corn	172	48

Use of non-edible oil sources such as jatropha, algae, used cooking oil and animal fats can make the technology economically viable. Non-edible oils from sources such as jatropha curcas, karanja (Pongamia pinnata), tobacco (Nicotiana tabacum), rubber plant (Hevea brasiliensis), castor, micro-algae, etc., are not suitable for human consumptions due to the presence of toxic compounds in the oil. The plantation cost of non-edible oil in terms of per kg is less than that of edible oil costs[48]. Oil yield of different non-edible oil bearing plants is given in Table 2.2 in the order of volume of oil per hectare along with percentage of oil in the oil bearing seeds. Jatropha curcas gives the highest oil yield of about 1892 liters per hectare.

Among the non-edible oil sources, jatropha has an immense potential for producing oil that finds large scale industrial uses [49].

Table 2.2: Oil yield for major non-edible oil crops [4, 14, 20, 46, 47]

Type of oil	Oil yield (litre/ha)	Oil yield (%)
Jatropha curcas	1892	Seed: 35-40, kernel: 50-60
Castor	1413	45–50
Pongamia pinnata	225-250	30-40
Rubber seed	80-120	40-50
Sea mango	N/A	54
Cotton	325	18–25
Karanja	27–39	-
Moringa oleifera	N/A	35–40

2.2.1 Oil composition of different feedstocks

The fatty acid composition of oils from different sources is another important factor that should determine the properties of biodiesel produced. Different fatty acid compositions of vegetable oils can be caused by climatic conditions, cultivation practice, soil type, growing season, plant maturity and plant genetic variations [50, 51]. The fatty acid compositions of different edible and non-edible oils are shown in Table 2.3. The major oil compositions are generally similar in both edible and non-edible oils with the exception of castor oil. The major fatty acids that constitute the oils are oleic, linoleic, stearic and palmitic acids as presented in Table 2.3. Those fatty acids are further categorized as saturated and unsaturated fatty acids. Saturated fatty acids includes stearic, palmitic and dihydroxystearic acids whereas unsaturated fatty acids includes oleic, linoleic, ricinoleic, and eicosenoic acids. The composition of the oils especially the type and quantity of the unsaturated fatty acids affects the stability of the oil. Of the unsaturated fatty acids type, oleic acids is the most stable since its oxidation rate is lower than linoleic and linolenic acids [31, 52].

Table 2.3: Fatty acid oil compositions of different edible and non-edible oils [8, 14, 47]

	Lauric	**Myristic**	**Palmitic**	**Stearic**	**Oleic**	**Linoleic**	**Linolenic**	**Arachidic**	**Others**
Edible oil sources	**12:0**	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**	**18:3**	**20:0**	
Soybeans	-	<0.5	7.0-11	2-6	19-34	43-56	5-11	<1	
Rapeseed	-	-	3.49	0.85	64.1	22.3	8.23	-	
Palm		0.5–2	32.0–45	2–7	38–52	5–11	-		
Sunflower		<1.0	3.0–6	1–3	4–35	<1.5	44–75	0.6–4	
Corn		0.2–1	8.0–12	2–5	19–49	34–62	<2		11
Coconut	44–52	13.0–19	8.0–11	1–3	5–8	0–1	-	0–0.5	6–10
Peanuts			6.0–9	3–6	52–60	13–27	-	02–4	1-4
Olives		0.1–1.2	7.0–16	1–3	65–80	4–10	-	0.1–1.3	-
Non-edible oil sources									
Jatropha		0.5–1.4	12.0–17	5–9.5	37–63	19–41		0.3	
Castor			2.0	1	7	5			Ricinoleic 86–90
Moringa oleifera			6.5	6	72.2	1		4.0	Eicosenoicacid 2, C22:0-7.1
Cotton			4.0–7	2–5	12–34	17–24	35–60	0.3–1	-

2.2.2 Jatropha curcas as source of biodiesel feedstock

Jatropha curcas plant is a small or large shrub tree of about 4-7m tall and it belongs to a family of Euphorbiaceace [4, 22, 47] that consists of around 800 species. Its fruits and wood can be used for numerous purposes such as biomass energy, biocides (insecticide, molluscicide, fungicide and nematicide) [8]. Studies have shown that the oil can be used in cosmetics industry for manufacturing of candle, paraffin, fatty nitrogenous derivatives, surfactants, detergents and soap [49, 53]. In recent years jatropha is identified as a potential non-edible oil bearing plant, an alternative source to edible oils in different parts of the world such as Central and South America, India, Africa, South East Asia, etc[8, 9, 23, 26, 54, 55]. Planting jatropha as a source of oil for biodiesel production is gaining more attention particularly in tropical and subtropical countries because of its easy propagation, drought resistance, and adaptation to wide agro-climate conditions, high oil content (35-60%) and multiple use of the plant. Jatropha can grow in marginal and waste lands with no possibility of fertile land use competing with food production. This enables non-arable lands to be utilized for jatropha plantation that will provide high oil yield for biodiesel production in return. India is proved to be a good example as the country planted jatropha along the sides of railroads with the yield obtained from such practice is reported to be 1.5-2 tons per hectare[24].

The plant bears fruit starting from the second year of its plantation and economic yield can be obtained from 5^{th} year onwards. The plant has an average life of 50 years [25, 26]. The matured jatropha reported to give up to 4kg of seeds per plant per year. However, the economic yields can be considered from 2-4kg per plant/per year. In poor soil conditions it was reported to be about 1.5-2kg seeds/plant [8, 24]. As presented on Table 2.2, jatropha curcas was also found to give the highest oil yield of 1892 liters per hectare when compared to other non-edible oil sources such as castor, pongamia pinnat, rubber trees, etc,. Thus, besides its non-edible oil sources and many other advantages discussed earlier, jatropha curcas was also found preferable due to its high oil yield per land area of plantation.

The fresh jatropha curcas seed are oblong, gray in color and the seed resembles castor oil seed. The seeds are 10 to 20mm long and weigh 0.5 to 0.7 grams [49]. The

seed on average composed of 6.2% moisture, 18% protein, 38% fat, 17% carbohydrate, 15.5% fiber and 5.3% ash. The kernel of jatropha curcas yields 50-60% oil. Jatropha produces oil composed of oleic, linoleic, palmitic and stearic acids as shown in Table 2.4. Oleic acid constitutes the majority of the oils component (37-63%) followed by linoleic acid (29-35) of principal fatty acids [31, 56-59]. The high content of oleic acid helps the acid more resistance to oxidation and makes it more suitable for process requiring good oxidation stability such as biodiesel processing [49, 60]. Studies conducted by Özcan and Seven 2003 [61] indicated that the oxidation of oleic acid is lower than linoleic and linolenic acid; oleic acid is the most stable unsaturated fatty acid as compared to linoleic acid which makes jatropha curcas oil to be suitable as a feedstock for the production of biodiesel. It was also reported that the higher the saturated fatty acids, the higher the cloud point of the corresponding biodiesel [62].

Table 2.4: Fatty acid compositions of jatropha oils investigated by different researchers [31, 56-59]

Fatty acid	structure	Formula	Mol. weight	% mass[31]	% mass[56]	% mass[57]	% mass[58]	% mass[59]
Myristic	14 : 0	$C_{14}H_{28}O_2$	228.376	0.12	-	-	-	-
Palmitic	16 : 0	$C_{16}H_{32}O_2$	256.428	19.5	17.4	14.1	13.73	15.18
Palmitolic acid	16:1	$C_{16}H_{30}O_2$	258.248	-	-	-	-	0.99
Stearic	18 : 0	$C_{18}H_{36}O_2$	284.481	6.8	6.0	6.7	5.79	
Oleic	18 : 1	$C_{18}H_{34}O_2$	282.465	41.3	50.3	47	42.37	41.17
Linoleic	18 : 2	$C_{18}H_{32}O_2$	280.450	31.4	23.2	31.6	37.52	31.25
Linolenic	18 : 3	$C_{18}H_{30}O_2$	278.434	0.2	-	-	0.59	0.08
Arachidic	20:0	$C_{20}H_{40}O2$	312.14	0.12	-	-	0.09	-

The fuel properties of jatropha oil, jatropha oil methyl esters (jatropha biodiesel) and petrol diesel are presented in Table 2.5 for comparisons [49, 63]. Properties of jatropha oil such as heating value and specific gravity are found to be in the range of most vegetable oils. The report indicated that properties such as density, cloud point and pour point are higher than petroleum diesel indicating the unsuitability of direct use of jatropha oil as a diesel fuel[64]. On the other hand the high flash point of jatropha oil indicates the oil handling is safe from safety point of view [65].

The viscosity of jatropha oil is also quite high (about 35.5 mm^2/s as compared to 2.7 mm^2/s of petro-diesel); hence its direct use as a fuel is not suitable as it affects the performance of diesel engines. Jatropha oil viscosity needs to be reduced for its use as a diesel fuel. However, as shown in Table 2.5, the viscosity of jatropha oil was reduced by a substantial amount after it was transesterified with methyl alcohol. Thus, jatropha methyl esters (biodiesel) can then be directly used as a diesel fuel or blended with petroleum diesel. Generally, for all reasons discussed above, jatropha curcas is found to be the best non-edible alternative oil candidate for the production of biodiesel.

Table 2.5: Comparison of fuel properties of jatropha oil, jatropha oil methyl ester and diesel fuel[49, 63].

Property	**Unit**	**Jatropha oil**	**Jatropha oil methyl ester**	**Diesel**	**ASTM D6751-02**	**DIN EN 14214**
Density at 288K	kg/m^3	918	880	850	875–900	860–900
Viscosity at 313 K	mm^2/s	35.4	4.84	2.70	1.9–6.0	3.5–5.0
Flash point	K	459	435	343	>403	>393
Pour point	K	267	267	253	–	–
Water content	%	5	Nil	0.02	<0.03	<0.05
Acid value	mgKOH/g	11.0	0.24	0.35	<0.8	<0.50
Saponification value	–	194	190	–	–	–
Iodine value	–	101	104	–		–
Sulfur content	%	0.02	Nil	–	0.05	–
Calorific value	MJ/kg	33	37.2	42	–	–
Cetane number		23	51.6	46	–	–

2.3 Vegetable oil extraction and purification

The process of extracting vegetable oil from oil seeds is not an easy task. The vegetable oil processing industry involves the extraction and processing of oils from vegetable oil bearing sources. Before extraction of oils from the seeds, the seeds need to be cleaned, prepared (i.e. dried) and in some cases dehulled, flaked and conditioned. The extraction processes are generally mechanical (boiling for fruits, pressing for seeds and nuts) or involve the use of solvent such as hexane (chemical extraction).

2.3.1 Mechanical extraction

Mechanical extraction method is a means of separating oils from the seeds using mechanical forces to expel out the oils present in the seeds. It has been used since long years ago and has been widely applied. Mechanical extraction has potential for producing chemical free, edible-grade oil. In mechanical oil extraction, to obtain the oils from oil bearing sources, the seeds are mechanically pressed at high pressure and the oil is expelled out. However, mechanical oil-expression equipment and processes are cost ineffective as the oil extraction efficiency is quite low (75-80% oil extraction) [66]. Other problems associated with mechanical extractions are the design of the extractor is suitable only for one or very few particular type of seeds. The crude vegetable oil obtained need also be further treated and refined through using processes such as degumming, neutralization and bleaching [67]. The less efficiency of mechanical extraction associated with additional requirement of oil purification processes can result in high cost of oil.

2.3.2 Chemical extraction

Oil can also be extracted from oil bearing sources using chemical extraction methods. Extraction of oils using chemical method is a process which involves extracting oil from oil-bearing materials by treating it with a low boiling solvent. As compared to mechanical extraction method, chemical extraction method is the most efficient

process that recovers almost all the oils except only 0.5% to 0.7% of residual oil that can be left in the raw material [67]. Chemical extraction method has also the capability to handle large quantities. The most commonly used chemical as a solvent is hexane. Oil extraction using hexane is found to be the main technology to achieve high oil recovery from the seed particularly in the United States of America [32]. Direct hexane extraction is the most cost-effective oil recovery method for a plant with an extraction capacity of over 300, 000 kg/day [68]. Hexane recovery is one of the significant processes of oil extraction plant, however, studies has shown that for efficiently operating plant 1.25 liters of hexane is lost for every one metric ton of solvent process [33]. Thus, oil extraction using hexane is a costly process due to solvent (hexane) cost, extraction cost, hexane recovery and additional hexane cost to top up hexane lost during solvent recovery; in addition use of hexane can increase the formation of atmospheric smog and global warming and it is classified as one of a hazardous air pollutant [34].

The chemical (solvent) extraction process consists of treating the raw material with hexane and recovering the oil by distillation. Evaporation followed by condensation recovers the hexane from the extracted oil-hexane mixture. The hexane thus recovered is reused for further extraction. The low boiling point of hexane (68°C) and the high solubility of oils and fats in it are the properties exploited in the solvent extraction process. The main drawback of the chemical extraction method is that, high solvent cost and solvent recovery cost and environmental pollution due to traces of hexane that may emit to the atmosphere during extraction [32].

2.4 Biodiesel production technology

Vegetable oils are not suitable for direct use as internal combustion engine fuel due to their high viscosity, (27-54 mm^2/s compared to 2.7 mm^2/s of petro-diesel fuel), lower volatility and high reactivity due to its unsaturated hydrocarbon. Direct use of vegetable oil has shown several problems such as

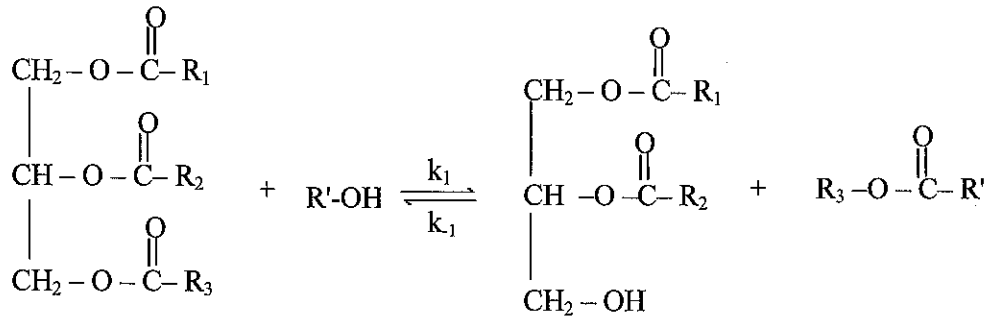
- coking and trumpet formation on the injectors
- oil ring sticking,
- thickening and gelling of the lubricating oil,

- reduced power and fuel economy [69].

To overcome the problems posed by direct use of vegetable oils, different methods such as dilution, micro emulsion, pyrolysis and transesterification were proposed to modify the chemical and physical properties of vegetable oil [46]. However, transesterification is the most suitable method to lower the viscosity of vegetable oil and commercially established process to convert vegetable oils or animal fats to biodiesel [14].

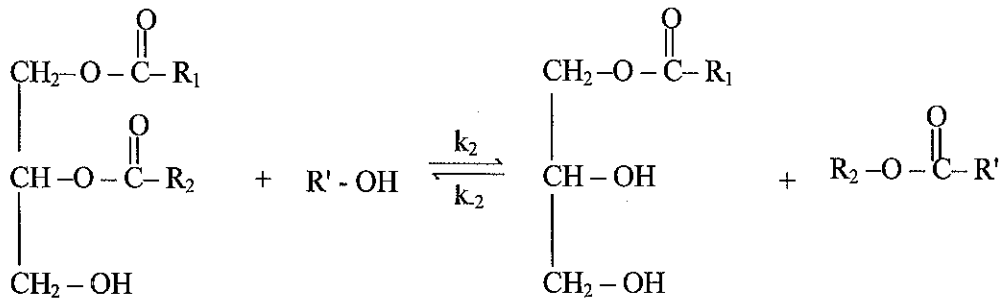
Transesterification is a chemical reaction between triglycerides present in the oils or fats and alcohols to form esters and glycerol in the presence of catalyst or at high pressure and temperature [11]. Methanol is the most preferred alcohol because it is the most cheapest and available alcohol. Methanol can also easily separated from water as compared to other higher alcohols such as ethanol, propanol and butanol such that the excess methanol can easily recovered by conventional distillation for reuse. Other alcohols such as ethanol, propanol, butanol and amyl alcohol can also be used in place of methanol [70]. The molecular weight of ester molecule is about one-third of its parent vegetable oil molecule and has a viscosity approximately twice that of diesel fuel instead of 10 times or more like the case of vegetable oils. The physical characteristics of esters produced by transesterification are very close to those of diesel fuel. Stiochiometrically, one mole of triglycerides reacts with three moles of alcohol to produce three moles of esters and a mole of glycerol. It consists of three consecutive reversible reaction steps [71]. The first step involves formation of diglycerides molecule, the second step involves formation of monoglycerides and the last step is the formation of glycerol. In each step one mole of ester is formed as illustrated in Figure 2.1. Since it is an equilibrium reaction, large excess of alcohol need to be used to shift the equilibrium towards formation of esters and glycerol.

Step one



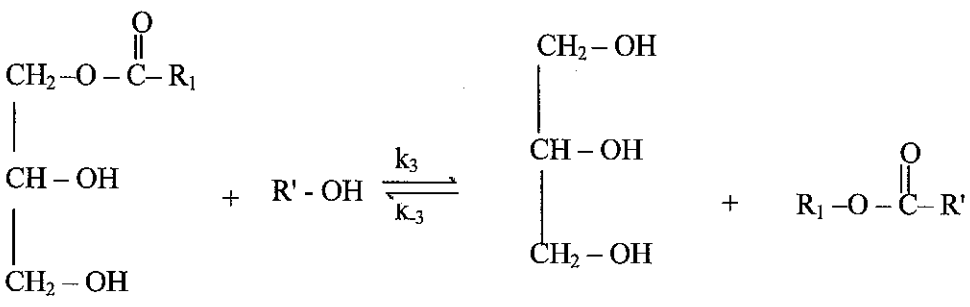
Triglycerides **Alcohol** **Diglycerides** **Esters**

Step two



Diglycerides **Alcohol** **Monoglycerides** **Esters**

Step three



Monoglycerides **Alcohol** **Glycerol** **Esters**

Where: R_1, R_2, R_3 = carbon chain of the fatty acids

R' = alkyl group of the alcohol

Figure 2.1: Stepwise transesterification or alcoholysis of vegetable oils

When transesterification reaction is conducted, it is observed that not all the materials are readily mixed with each other. Two phases of methanol and vegetable oils are observed at the start of the reaction. This is because alcohol is sparingly soluble in oil phase. At the end of the reaction also two phases of glycerol and methyl esters are observed as glycerol and methyl esters are not soluble in each other [15]. The solubility of two compounds in each other depends on the structural features of the compounds such as the existence of the OH groups. Compounds containing OH groups and those not containing OH groups often will not readily mix. Thus, most processes for making biodiesel use catalyst to initiate the transesterification reaction [72-77]. Generally, depending on the technique and types of catalyst used different methods are used to synthesize biodiesel in a transesterification reaction process as:

1. Homogenous alkaline catalyzed transesterification
2. Homogenous acid catalyzed transesterification
3. Homogenous acid and alkaline catalyzed transesterification: a two step process
4. Heterogeneous alkaline and acid catalyzed transesterification
5. Enzyme catalyzed transesterification
6. Non-catalyzed supercritical alcohol transesterification

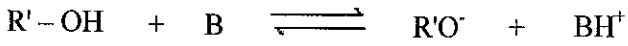
2.4.1 Homogenous Alkali catalyzed transesterification

Alkali catalyzed transesterification reaction of vegetable oil is faster than acid catalyzed reaction and the reaction proceeds at moderate conditions. It is commonly used in the commercial production of biodiesel due to its ability to catalyze the reaction at low temperature and atmospheric pressure, high triglycerides conversion can be achieved in a relatively shorter reaction time, and the cost of the catalyst is relatively cheaper and the catalyst easily is available [71, 78, 79]. Studies indicated that alkali catalyzed transesterification could be 4000 times faster than acid catalyzed transesterification [80]. The commonly used alkali catalysts are sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide ($NaCH_3O$) and potassium

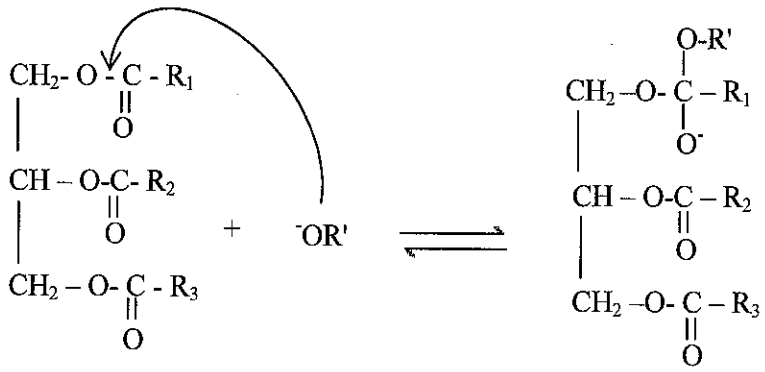
methoxide (KCH_3O) [16, 81, 82]. Alkali catalyzed transesterification is a three step reaction. The first step is the reaction of the base catalyst with the alcohol, producing an alcohol-oxide deprotonating H^+ from the alcohol by the base catalyst (production of the active species RO^-). In the second step, the nucleophilic attack of the alcohol-oxide (RO^-) at the carbonyl group of the triglycerides that generates a tetrahedral intermediate, that is, nucleophilic attack of triglycerides. Then in the third step the alkyl ester and the corresponding anion of diglycerides are formed (intermediate breakdown). In the last step, the later deprotonates the H^+ from catalyst and can react with a second molecule of alcohol and start another catalytic cycle (regeneration of the RO^- active species). Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol [11, 71]. Figure 2.2 illustrates the details mechanisms of the three steps. Several studies were conducted to investigate the catalytic performance of different alkaline catalysts.

Vicente et al. [82] studied the catalytic effect of four different homogenous alkaline catalysts, i.e., NaOH, KOH, $NaCH_3O$ and KCH_3O on transesterification of sunflower oil with methanol. All the reactions were conducted under the same conditions of 65°C with a 6:1 molar ratio of methanol to oil and 1% w/w of catalyst to vegetable oil. After 3 hours of reaction time, they observed that methyl esters concentrations were nearly 100% for all the four catalyst. It was also reported that after product separation and purification, high yields were obtained by using $NaCH_3O$ (99.33% biodiesel yield) and KCH_3O (98.46 % biodiesel yield), respectively. However, when NaOH or KOH were utilized as a catalyst, relatively reduced biodiesel yields of 86.71% and 91.67 % were obtained, respectively. The phenomenon of the yield loss was due to the fact that the hydroxide group in metal hydroxide catalysts could cause more triglycerides saponification. Due to their polarity, the soap dissolved into the glycerol during the separation process. In addition, the dissolved soaps increased the biodiesel solubility in the glycerol leading to a reduction in the product yield. Of the four catalysts used transesterification using NaOH is the fastest.

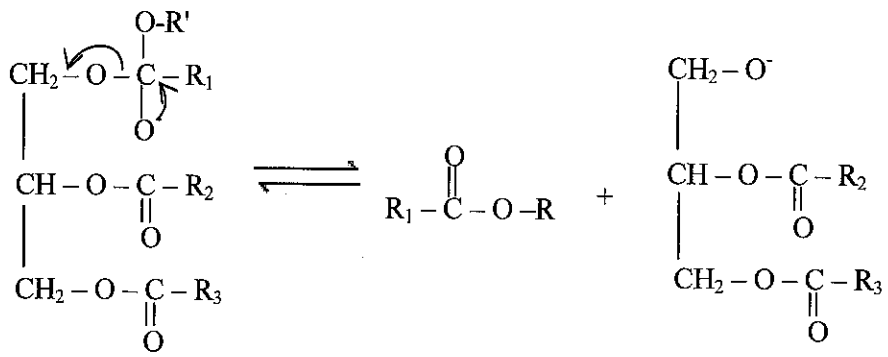
Step one



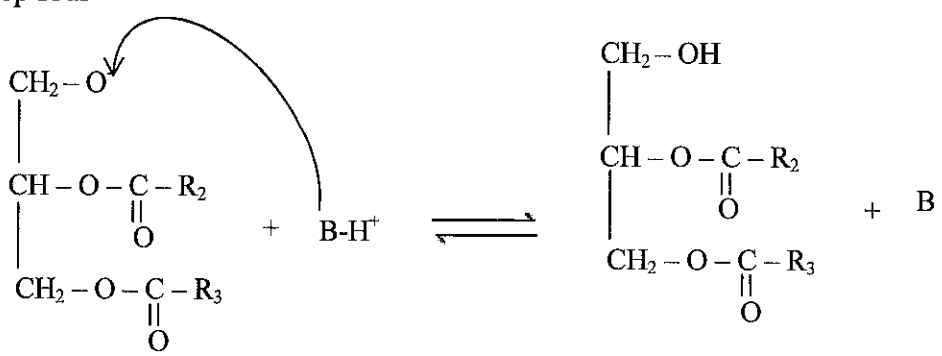
Step two



Step three



Step four



Where: B = base catalyst, R1, R_2, R_3 = carbon chain of the fatty acids and

R' = alkyl group of the alcohol

Figure 2.2: Reaction mechanism of homogenous alkali catalyzed transesterification

Similar investigations were also conducted by Leung and Guo [83] to study the catalytic effects of NaOH, KOH and $NaCH_3O$ on neat and used frying oils. To evaluate the performance of each of these catalysts, they carried out the transesterification of the oils with methanol using individual catalyst under identical molar ratio of methanol to oil (7.5:1), reaction temperature (70°C), reaction time (30 min) and subject to the same degree of mixing. For the maximum esters content of 94.0, 92.5 and 92.8% obtained, the amount of NaOH (1.1% w/w of oil) is less than the amounts of both $NaCH_3O$ (1.3% w/w of oil) and KOH (1.5% w/w of oil), respectively. However, in terms of yield $NaCH_3O$ proved to be a better catalyst than NaOH and KOH; because $NaCH_3O$ easily dissolves and dissociate into CH_3O^- and Na^+ and does not form any water as a side product. On the other hand, NaOH and KOH form sodium or potassium methoxide and water when dissolved in methanol.

Kucek et al. [84] presented ethanolysis of refined soybean oil at 70°C and 12:1 molar ratio of ethanol to oil in order to investigate the effect of NaOH and KOH as alkaline catalyst. They found out that better yields of 97.2% were obtained for NaOH (0.3% w/w) as compared to the maximum yields (95.6%) obtained while using KOH (1% w/w) as alkaline catalyst. Sharma and Singh [43] also developed biodiesel from Karanja oil using NaOH and KOH as a catalyst. They reported better yield with NaOH as a catalyst over KOH while using magnetic stirrer. However, when mechanical stirrer was adopted, the yields were nearly equal by using the same quantity of NaOH and KOH (0.5) catalyst. Rashid et al. [72] reported methanolysis of crude sun flower oil using alkali catalyst. They reported maximum methyl esters of 97.1 at 6:1 molar ratio of methanol to oil, 1% w/w of NaOH and 60°C reaction temperature. A similar investigation was conducted by Bouaid et al. [85], Encinar et al. [86] and Alemu et al. [87] on ethanolysis of vegetable oil (using KOH as a catalyst), used frying oil (using NaOH, KOH, $NaCH_3O$ and KCH_3O as catalysts) and palm kernel oil (using KOH as a catalyst), respectively. Similarly, comparison of the performance of different homogeneous alkaline catalysts during transesterification of waste and virgin oils and evaluation of biodiesel quality were presented by Dias et al. [88]. In the transesterification process the reaction conditions were maintained at 6:1 molar ratio, 60°C, and 1 hour of reaction time with the different catalysts (KOH, NaOH and CH_3ONa). The amounts of catalyst were varied from 0.2% to 1% of oil

weight for virgin oils and 0.4% to 1.2% of oil mass for the waste frying oil. The reaction was conducted under vigorous stirring. They observed that the catalytic performance of KOH was inferior to sodium based catalysts because, using KOH, purity of methyl esters produced was lower than the minimum requirement according to biodiesel standard of EN 14214 for all samples. Considering the studied feedstocks, the optimum conditions which ensured that the final product was in agreement with the European biodiesel standard were 0.6% w/w CH_3ONa for both sunflower and soybean oils, 0.6% w/w and 0.8% w/w NaOH for sunflower oil and soybean oil, respectively. For waste frying oils, the optimum catalyst concentration was 0.8% w/w for both sodium based catalysts. Under optimum conditions, a purity of 99.4% was obtained for sodium based catalysts. Many similar investigations were conducted to study the catalytic performance of different alkaline catalysts.

However, for alkaline catalyzed transesterification, the purity of oil is very important as alkaline catalyzed transesterification is very sensitive to the purity of reactants such as free fatty acid (FFA) and water contents [74, 75, 89]. The application of alkaline catalyst in vegetable oil with high free fatty acid and water content can cause soap formation by neutralizing the free fatty acid in the oil, which can partially consume the catalyst, thus decrease the biodiesel yield [11]. FFA is a key criterion in alkaline catalyzed transesterification design. Studies indicated for oils containing FFA above 5%, the alkali catalyzed transesterification is not suitable for biodiesel production. In order to prevent the formation of soap during transesterification reaction, FFA and water content in the reactant oil must be below 2% and 0.5%, respectively [90-93]. According to these limitations only pure vegetable oils are appropriate for alkaline catalyzed reaction; otherwise extensive pre-treatment is necessary [14].

2.4.2 Homogenous acid catalyzed transesterification reaction

Acid catalysis transesterification is preferred over alkali catalysis for the production of biodiesel from high FFA oil sources [94]. Acid catalysis can directly produce biodiesel from low cost lipid feedstocks associated with greater than 6% FFA such as used waste cooking oil, greases and animal fats. Acid catalyst is insensitive to the

presence of high FFA in the feedstock and can catalyze both esterification and transesterification simultaneously [74, 75, 95]. Lotero et al. [71] reported when the FFA content of the feedstock is high ($\geqslant$6%) acid catalysis transesterification is more economical than alkaline catalysis transesterification a process that requires an extra step to convert the FFA to methyl esters. Acids such as sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), hydrochloric acid (HCl) and organic acids can be used during acid catalyzed transesterification reaction. However, H_2SO_4 and HCl are commonly preferred acids [11, 13].

The mechanism of acid catalyzed transesterification of vegetable oil was investigated by Lotero et al. [71] as presented in Figure 2.3. In the acid catalyzed mechanism, first there is protonation of the carbonyl group of the ester by the acid catalysts promoting formation of carbon-cation followed by the nucleophilic attack of the alcohol producing a tetrahedral intermediates; in the last step there is proton migration and breakdown of the intermediate; this intermediate will eliminate glycerol to form a new ester and regenerate the catalyst for further process as indicated in the Figure 2.3. The process is repeated twice to complete the reaction process.

Several acid catalyzed transesterifications were investigated to address the performance of different acid catalysts. Al-Widyan et al. [96] evaluated the effect of different concentrations of HCl and H_2SO_4 on the transesterification of waste palm oil. It was reported biodiesel with lower specific gravity was obtained at higher catalyst concentration (1.5-2.5% w/w) in a much shorter time than lower concentration of acid catalyst. The authors evaluated the conversion efficiency of the process with respect to the specific gravity of the biodiesel implying lower value mean more complete reaction since more of the heavy glycerol was removed. It was also demonstrated that at 2.5% w/w of the catalyst loaded the reaction is more effective with H_2SO_4 than HCl.

Goff et al. [97] investigated acid catalyzed transesterification of soybean oil using different catalysts such as sulfuric, formic, acetic and nitric acids. A catalyst screening transesterification reaction was conducted at a typical molar ratio of methanol to oil of 9:1, 1% w/w catalyst, 120°C, and 24h reaction time. The report indicated of the

catalyst under screening test, only sulfuric acid was the catalyst that showed significant activity; hydrochloric, formic, acetic, and nitric acids all had conversions less than 0.7%. Nitric and hydrochloric acids darkened the product.

On the other hand, acid catalyzed transesterification process is not commercially well known as alkaline catalyzed processes for biodiesel synthesis due to the slower reaction rate, the requirement of high reaction temperature and pressure, long reaction time, separation of the catalyst through several washing, equipment corrosion and environmental problems posed by the use of acid catalyst [80, 98]

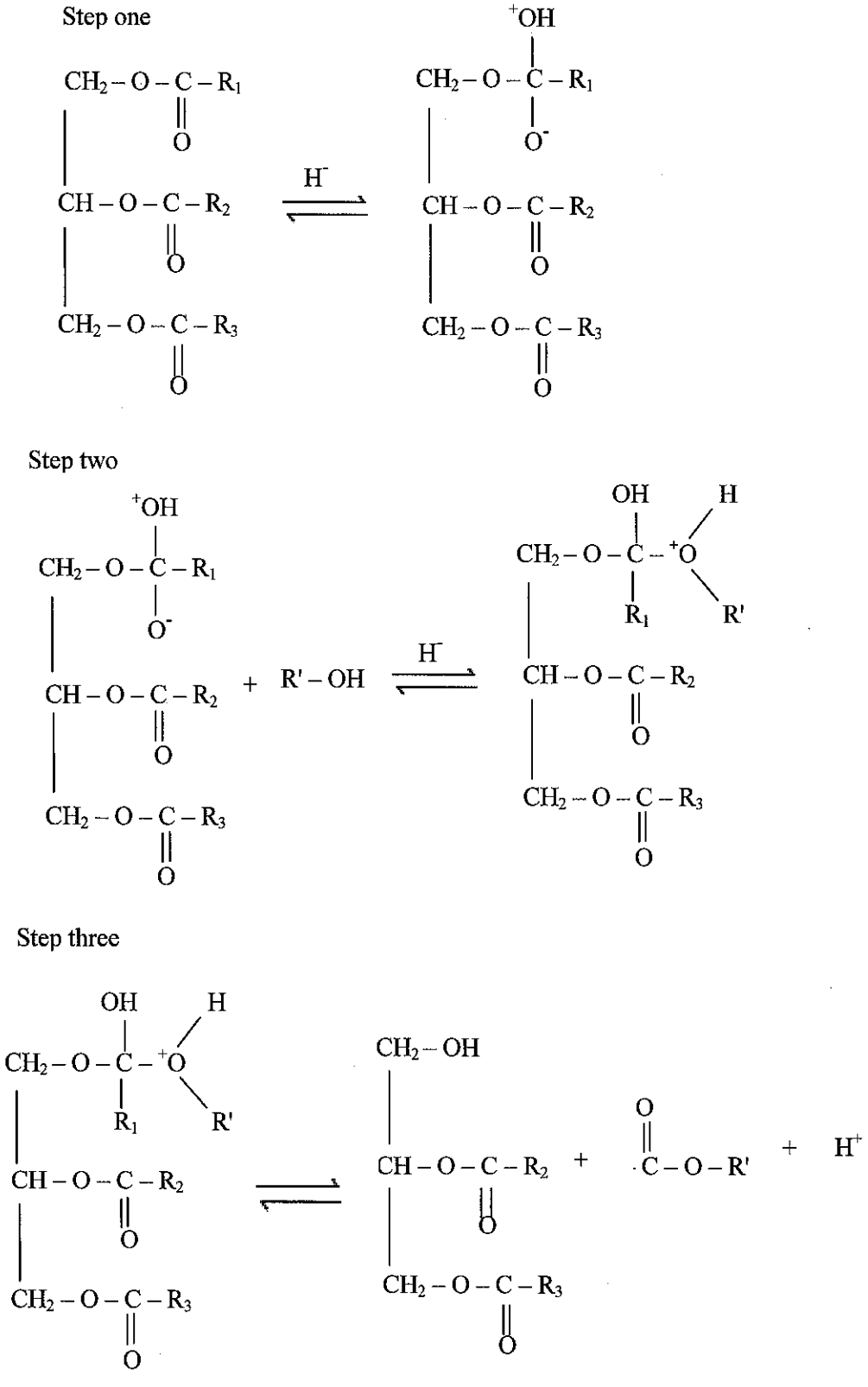


Figure 2.3: Reaction mechanism of homogeneous acid catalyzed transesterification of triglycerides

2.4.3 Homogeneous acid and alkaline catalyzed transesterification: a two step process

Since both alkaline and acid catalysis have their own advantages and disadvantages for transesterification of high free fatty acid feedstocks such as used cooking oils, the two step homogenous acid catalysis followed by alkaline catalysis was designed to overcome their limitation and exploit the advantages they offer. Initially, acid catalysis is used to reduce the high FFA content of the oils through esterification reaction to less than 1%. Then transesterification reaction is conducted using alkaline catalyst [99]. Acid catalysis followed by alkaline catalysis process was patented by Lepper and Friesenhagen [100] in 1986. The investigators first esterified the oil with alcohol in the presence of acid catalysts (sulfuric, sulfonic acids) at a maximum reaction temperature of 120°C and a pressure of 5 bar using glycerol as a liquid entraining agent for the removal of water formed during the acid catalyzed reaction. The reaction product was separated into a glycerol phase containing the acidic catalyst and water of reaction and the treated oil phase. The oil phase was then further reacted with alcohol in the presence of alkaline catalyst for the synthesis of biodiesel. This procedure was reported as economical and efficient for the transesterification of used cooking oil (UCO) with a high content of FFA. Since then different research works were conducted for the two stages transesterification reaction [101-105].

Berchmans and Hirata [106] used a two-step homogeneous catalysis to synthesize biodiesel from jatropha curcas oil with a free fatty acids of 15%. First they conducted the reaction in the presence of 1% w/w H_2SO_4 as an acid catalyst with 0.60% w/w methanol-to-oil ratios at a reaction temperature of 50°C for 1h. Then the reaction mixture was allowed to settle for 2h and the mixture containing methanol and water was separated from the top layer. The treated oil was transesterified using 0.24% w/w methanol to oil and 1.4% w/w NaOH to oil as alkaline catalyst at a reaction temperature of 65°C. At the end of the process 90% methyl esters of fatty acids yield was achieved in 2h of reaction time.

Gandhi and Kumaran [107] conducted the synthesis of biodiesel from jatropha curcas oil with high FFA content of 6.85%. In the first step to reduce the FFA content of the oil, esterification reaction was carried out using H_2SO_4 as acid catalyst at a

concentration of 1% w/w of oil, 60°C and 9:1 methanol to oil molar ratio. In 1h of reaction time, the FFA was reduced to 1.12%. After settling the reaction mixture for 2h and separating the methanol-water mixture from the top layer, they conducted the second step using alkaline catalysis transesterification at methanol to oil molar ratio of 5.41:1 and the catalyst to oil ratio of 0.55% w/w at 60°C. The maximum yield of biodiesel achieved was 95.3% v/v and it was compared with a single step alkaline catalysis which was found to be 80.5% v/v. The investigator concluded that the two steps is better method of reducing the problem of yield reduction caused due to high free fatty acids content of oils during alkaline transesterification.

In spite of several advantages of the two step homogeneous acid catalysis followed by alkaline catalysis, there are still problems associated with this methods as reported by different investigators such as the problem of catalyst removal in both stages, the problem of catalyst removal in the first stage can be avoided by neutralizing the acid catalyst using extra alkaline catalyst in the second stage that, however, needs extra catalyst and excess water for washing. Stoppage of the process to separate water formed during acid catalysis and restarting the reaction increases the overall reaction period. It also requires end-of-pipe treatment to maintain the environment from contamination [99].

2.4.4 Heterogeneous catalysis

Biodiesel is conventionally produced using homogeneous alkaline and acid catalysts such as sodium and potassium hydroxide, sulfuric and hydrochloric acids. Limitations of homogeneous catalysts such as no scope to regenerate and reuse the catalyst, effluent water as a result of catalyst removal through washing that needs treatment step, etc, steered the research work of biodiesel production towards exploring solid catalyst for transesterification reaction [108]. Solid catalysts have advantage over liquid catalysts due to regeneration of catalyst (decrease catalyst cost), utilization of low quality feedstocks for biodiesel production, simplification of separation process and reduction of waste water generated during washing processes [71, 99, 109]. Like homogeneous catalysis, alkaline and acidic prosperities of solid catalyst are important

to enhance transesterification reaction. In heterogeneous catalysis, adsorption of reactants and desorption of products take place on the surface of the solid catalyst for the reaction to progress at the enhanced rate [110]. Wide range of heterogeneous alkaline and acid catalysts transesterification and the catalytic performance of different catalysts were reported in literature. The following subsection presents literature review of major heterogeneous catalysis transesterification reaction.

2.4.4.1 Heterogeneous alkaline transesterification

Commonly used catalysts for heterogeneous catalysis transesterification reaction are alkali earth metal oxides of calcium oxide (CaO), magnesium oxide (MgO) in supported or unsupported form in basic zeolite, anion exchange resin, $Na/NaOH/Al_2O_3$ and K- and Li prompted oxides [108, 111]. The catalytic performances of different heterogeneous alkaline catalysts on the rate of transesterification of vegetable oils and fats were investigated broadly by many researchers.

Kouzu et al. [112] studied using CaO as a heterogeneous catalyst for the transesterification of soybean oil with methanol. The yield of biodiesel obtained was 83% after 1h reaction time at methanol to oil ratio of 12:1. However, the yield of biodiesel was dropped to 66% when waste cooking oil with FFA content of 2.6% was used under the same reaction conditions. The report indicated that the decrease in yield was due to the alkaline catalytic sites of CaO were poisoned by adsorption of FFA on the surface of the catalyst. Consequently, a portion of the catalyst changed into calcium soap by reacting with the FFA adsorbed on the surface of the catalyst. Different studies have shown that for most alkaline metal solid catalysts the soluble substances leached out causing partial homogeneous alkaline catalysts and catalyst deactivation [113]. Thus, an extra purification step is needed such as ion-exchange resin to remove the soluble content in the biodiesel [114].

Taufiq-Yap et al. [115] investigated methanolysis of jatropha curcas oil to biodiesel in the presence of heterogeneous calcium-based mixed oxides catalysts (CaMgO and CaZnO). In their work, the potential of the catalysts for biodiesel

production was evaluated. The catalytic efficiency of both CaMgO and CaZnO were studied and compared with the results of CaO, MgO and ZnO. It was reported that both CaMgO and CaZnO catalysts showed high activity as CaO and were easily separated from the product. Under optimal conditions, i.e., 4% w/w of catalyst loading, 15:1 methanol to oil molar ratio, 65°C reaction temperature and 6h of reaction time a conversion of more than 80% were achieved over both catalysts. After reusing of the catalyst for six runs there appeared to be a slight decrease in its catalytic activity during transesterification of jatropha curcas oil. Of the two catalysts investigated, CaMgO was reported to be more active than CaZnO in its catalytic activity. Heterogeneous catalyst screening, optimization and kinetic studies of jatropha curcas oil transesterification with a variety of catalyst such as resins, zeolites, clays, hydrotalcites, aluminas and niobium were conducted by Zanette et al. [58]. Similarly, Endlew et al. [110] conducted transesterification of jatropha curcas under La_2O_3/ZnO, La_2O_3/Al_2O_3 and $La_{0.1}O_{0.9}/MnO_3$ heterogeneous catalyst. They reported La_2O_3/ ZnO demonstrated higher catalytic activity as compared to the other catalysts under investigation.

2.4.4.2 Heterogeneous acid catalyzed transesterification

Solid acid catalysis transesterification has gained attention over acid catalyst due to its advantage to overcome the limitations posed by acid catalysis transesterification. It is a potential replacement of acid catalysts as it has advantageous as it eliminates the washing steps of biodiesel, allows easy separation from the reaction medium with lower contamination of the product biodiesel, regeneration and recycling of the catalyst [108, 111, 116]. The development and selection of solid acid catalyst depends on interconnection systems of large pores, strong acid sites and hydrophobic surface[11, 94]. There have been several studies on the use of solid acid catalysts for the production of biodiesel.

Chai et al. [117] evaluated the solids catalytic activity of SO_4^{2-}/TiO_2 and $SO4^{2-}/ZrO_2$ for the transesterification of high FFA cotton seed oil. It was reported that the activity of the catalysts were proportional to its specific surface area. With 99.5m^2/g

specific surface area of SO_4^{2-}/TiO_2 and higher reaction temperature of 230°C, 90% of FAME yield was obtained whereas with 91. 5m^2/g specific surface area of SO_4^{2-}/ZrO_2, only 85% of FAME conversion was observed. However at lower reaction temperature of 120°C, the FAME yield obtained was only 40%. A similar work was investigated by Peng et al. [118]. They increased the activity of SO_4^{2-}/TiO_2 by introducing a secondary SiO_2 to produce SO_4^{2-}/TiO_2-SiO_2. The addition of SiO_2 has increased the specific surface area of the catalyst to 258m^2/g. The catalytic effect was evaluated in the transesterification of refined cotton seed oil blended with 50% oleic acid. 90% FAME yield was obtained at optimal conditions of 3% w/w catalyst loading, methanol to oil ratio of 9:1, 200°C reaction temperature and 3h of reaction time. The reaction temperature is high as compared to the alkaline heterogeneous catalysis that needs reaction temperature of less than 60°C.

Furuta et al. [119] studied transesterification of soybean oil with methanol using tungstated zirconia-alumina (WZA) and sulfated zirconia-alumina (SZA) using high temperatures ranging from 200 to 300°C in a fixed bed reactor at atmospheric pressure. The authors evaluated the performance of the two solid acid catalysts and reported WZA has higher catalytic activity than SZA. However, long reaction time (20h) and high temperature (250°C) were needed in order to obtain 90% of biodiesel yield.

The limitations of solid acid catalysts are low reaction rate, i.e., long reaction time, requirement of high reaction temperature and possible undesirable side products. Hence, these limitations affected the industrial scale use of solid acid catalyst in transesterification processes.

2.4.5 Enzymatic catalyzed transesterification

Limitations associated with the biodiesel synthesis using chemical catalysis such as complex removal of catalyst, excessive energy requirements, and recovery of glycerol, undesirable side reactions, material corrosion and the cost of refined feedstocks encouraged the search for alternative methods of biodiesel production. One such option is the use of biological catalysis using enzymes like lipases [14, 120]. The

main advantages of using biological catalysis transesterification is its requirement of mild reaction conditions (20-50°C) and easy recovery of glycerol without purification or chemical waste production along with production of very high purity product [11, 121]. In addition, free fatty acids content in the oil can be completely converted to methyl esters, with no soap formation increasing the biodiesel yield and reducing the costs for fuel purification. This characteristic of biological catalysis allows the usage of materials with high free fatty acids (FFA) or high water content such as non-edible oils, waste cooking oils and industrial waste oil for the production of biodiesel [77].

It was reported that in order to make enzymatic transesterification competitive on industrial scale there are several issues that need to be addressed: solvent engineering, lipases immobilization, selection of acyl acceptor, and selection of the reactor system [11, 122]. Lipases are the most widely used and attractive enzymes as catalyst for transesterification processes. The catalytic performances of different enzymatic lipases catalysts for transesterification of vegetable oils and fats have been investigated and reported elsewhere.

Jegannathan et al. [123] conducted lipase screening using enzymatic transesterification of palm oil with methanol in a solvent free system using five lipases of lipase PS*(Burkhuolderia cepacia)*, lipase AK *(Pseudomonas fluorescens)*, lipase AYS (*Candida rugosa*), lipase AS (*Nagoya, Japan*) and lipase CALBL(*Candida antartica*). Of the five lipases tested, lipase PS (*Burkhuolderia cepacia*) resulted in the highest conversion and it was further investigated in immobilized form by encapsulating with a biopolymer, k-carrageenan. They reported that at optimal conditions of using the immobilized lipase PS as catalyst triglycerides conversion up to 100% was achieved after 72h of reaction time. The immobilized lipase was stable and retained 62% of its catalytic activity. However, the main drawback of this form of immobilized lipase is its long reaction time, the storage and transportation due to its gel forming nature. Similarly, Raita et al. [124] demonstrated bio-catalytic ethanolysis of palm oil using *Aspergillus* strains of *Thermomyces lanuginosus* lipase immobilized in a protein-coated micro-crystals. They investigated the catalytic effect of *Thermomyces lanuginosus* lipase catalyst in the presence of *tert*-butanol as a co-solvent and without *tert*-butanol. The report indicated addition of *tert*-

butanol markedly increased the bio-catalytic activity and stability giving improved product yield. At optimal conditions of 20% w/w protein-coated microcrystal's lipase catalyst loading, 4:1 ethanol to oil molar ratio and 45°C reaction temperature, the fatty acid ethyl yield was 89.9% after 24h of reaction time in the presence of *tert*-butanol at 1:1 molar ratio to triglycerides were reported. Their research work also indicated the addition of *tert*-butanol as a co-solvent improved the recycling of the biocatalyst for at least 8 cycles with only slight reduction in its activity.

Despite numerous advantages, research reports indicated that bio-catalysis transesterification reaction has drawbacks such as low reaction rate, high enzyme cost for industrial scale use in comparison to alkali catalyst, low enzyme stability in the presence of excess methanol, regeneration and reuse of it is limited with a long operating time period, low resistance to excess alcohols and glycerol formed during the reaction.

Shimada et al. [125] studied the production of biodiesel from waste oil using lipase enzyme as a catalyst. They observed that increasing the molar ratio of methanol above 0.5 reduced the catalytic activity of lipase. They recommended the stepwise addition of methanol to avoid the enzyme deactivation problems. Robeles-Medina et al. [120] reported that the glycerol formed during transesterification process had a catalyst inhibiting effect by covering the lipase due to its accumulation in the reaction mixture. A similar investigation was conducted by Royon et al. [126]. They reported the negative effect of methanol and glycerol can be eliminated by the use of *tert*-butanol as a solvent. With the addition of *tert*-butanol as the reaction medium, both methanol and the byproduct glycerol are soluble in oil.

2.4.6 Other additional methods to increase the rate of transesterification reaction

The sparingly solubility of alcohols in oils limits mass transfer between oils and alcohols during in-situ transesterification reaction even in the presence of alkaline catalysis. Hence, transesterification reaction takes long reaction times causing high processing costs. The use of alkaline catalysis is also limited to only refined vegetable oils due to its soap formation for feedstocks with high FFA component. On the other

hand, for feedstocks with high FFA such as waste cooking oil, a two-step transesterification processes of acid catalysis followed by alkaline catalysis transesterification may be required [106, 107]. The two step process, in addition to requiring long reaction time, consumes a lot of process water during washing processes resulting in generation of large quantity of liquid wastes. Similarly, the long reaction time of heterogeneous and enzymatic catalysis deprived these techniques from its industrial scale application. Consequently, different techniques were employed in order to increase the solubility of oils and alcohols so as to enhance transesterification reaction rate. These techniques include non-catalytic supercritical alcohol transesterification reaction [18, 127-129], adding a co-solvent [17, 86, 99], ultrasonic technology [130-132], microwave technology [16, 133, 134] and more recently phase transfer catalysis [135] . The following sections of the literature review present the investigation results of these techniques.

2.4.6.1 Non-catalytic super critical alcohol transesterification reaction

Non-catalytic super critical alcohol transesterification involves the transesterification of vegetable oils and fats at high reaction temperature (>320-350°C) and pressure (19-45MPa). At supercritical alcohol a single phase is formed between oils and alcohols as the two reactants are completely miscible at alcohol supercritical fluid condition [18, 127-129]. In non-catalytic super critical alcohol transesterification reaction, the conversion rate is very high and completed in a relatively shorter time giving high quality yield unlike the catalytic transesterification that need several hours to reach reaction equilibrium [11, 98], Its advantages as compared to catalytic transesterification reaction are that a catalyst is not required so that the end product treatment is much simpler as there is no need of separation of the catalyst and unwanted soap formed during the reaction. Thus, it avoids the acid or alkaline contaminated waste water resulted after purification. Supercritical condition is not affected by the purity of the feedstocks such as high FFA and water; its feedstock flexibility becomes the strong advantage of the biodiesel production with non-catalytic supercritical alcohol transesterification [99, 136]. It is an alternative process to use different types of low cost feedstocks such as waste cooking oils with high FFA

and water. It was reported that the presence of water has a positive impact in non-catalytic supercritical reactions by promoting the mechanisms of reaction [47, 77, 129]. However, non-catalytic supercritical alcohol transesterification reaction has several challenges due its high temperature (320-350°C), pressure (19-45MPa) and high methanol to oil ratio (40:1- 42:1) requirements leading to high temperature and pressure expensive reactor, energy cost, methanol recovery cost and sophisticated safety and energy management to avoid risk of operation. It also requires co-solvents such as carbon dioxide, hexane, propane, and calcium oxide to lower the high operating temperature and pressure that adds up to the production costs associated with co-solvent and its separation [11].

2.4.6.2 Addition of Co-solvent

Co-solvent addition process is a process intended to overcome the slow solubility of alcohol in oils. It was first developed by Boocock et al. [17] which was called a Biox co-solvent process. They reported inert co-solvents such as oxolane (tetrahydrofuran, THF), hexane, etc, could convert the methanol-oil mixture into a single phase and reduces mass transfer problems of transesterification reaction due to limited solubility of oils and alcohol. Similarly, Guan et al. [75] reported co-solvents such as THF, hexane and diethyl ether for their ability to increase the solubility and subsequently increase the mass transfer between methanol and oil phases. Demirbas et al. [137] studied use of THF as a co-solvent and reported that after the completion of the reaction there was a clear separation between the biodiesel and glycerol phase. Similar investigations were conducted by Chai et al. [117], Yang and Xie [138], Pena et al. [139], Furukawa et al. [140] using HTF as a co-solvent and found that THF is a good solvent in order to accelerate biodiesel production within shorter reaction time.

Leung et al. [14] reported that the advantages of co-solvent system uses inert and recyclable co-solvents in a single phase reaction that can be conducted at ambient temperature and pressure and shorter reaction time. However, the main drawbacks associated with the co-solvent process are the requirement of excess methanol and co-solvent, and after the completion of the reaction the co-solvent must be separated

from the final product. Though the separation of the co-solvent from the product is not difficult, simple distillation process, however, the separation of the co-solvent from methanol is a very difficult task as the boiling point of co-solvent such as THF and methanol nearly the same [99].

2.4.6.3 Ultrasonic technology

The application of ultrasound technology is being widely used in chemical and biochemical processes. Ultrasound is a sound frequency beyond the hearing response capacity of human being (16 to 18 kHz), however, the frequency of ultrasound ranges between 20 kHz and 100 kHz [78]. Common laboratory range of ultrasound is generally considered between 20 kHz to 40 kHz. When ultrasound is applied to an aqueous solution or suspension an increase in mixing, shearing and mass transfer is observed. The high frequency sound wave will compress and stretches the molecular spacing of the medium in which it passes through leading to continual vibration and formation of cavities [11, 132]. There is a formation of tiny bubbles due to the sudden expansion and collapse of cavities which burst inwards to produce so called "hotspots" which tend to generate energy for chemical and mechanical effects. In two phase systems the collapse of the cavitations bubbles disrupts the phase boundary and causes emulsification, by ultrasonic jets that impose one liquid on another [131, 141].

The use of ultrasound technology in transesterification reaction was also found to enhance the yield of methyl esters produced by providing efficient mixing and sufficient activation energy to initiate the reaction [81, 142]. Several studies on the transesterification of various vegetable oils with different types of alcohols using low-frequency ultrasound (20 to 40 kHz) mixing have been reported so far. Stavarache et al. [143] concluded that low frequency ultrasound is an efficient, time saving and economically functional method that offers a lot of advantages over the classical procedure. The induced asymmetric navigational bubbles collapse at the oil/alcohol boundary and enhance mass transfer between the phases thus accelerating the reaction. It also presents advantages such as less energy consumption and less molar

ratio of alcohol to oil as compared to conventional mechanical mixing [144, 145]. However, industrial scale application of ultrasonic technology is limited.

2.4.6.4 Microwave technology

Microwave irradiation is a means of rapidly introducing energy into a chemical system in a manner different from the traditional methods of thermal heating. Microwave-assisted organic synthesis has received greater attentions and applications in organic synthesis. During microwave heating, for every cycle of electromagnetic energy, microwave transfers its energy in 10^{-9} seconds, and the kinetic molecular relaxation from its microwave energy is approximately 10^{-5} seconds. This means that energy transfers faster than the molecules can relax giving non-equilibrium conditions and high instantaneous temperature that the kinetics of the system and microwave do not affect the orientation of the collisions [146]. An instantaneous increase in temperature enhances greater movement of molecules which can cause a large number of magnetic collisions. In microwave heating small molecules can be built in a fraction of time required by conventional thermal methods. As a result, it has gained increasing acceptance as an efficient heating medium tool in research of product and process development [147].

Microwave irradiation produces an acceleration of chemical reaction because of selective absorption of microwave energy by polar molecules. Microwave irradiation produces efficient internal heat transfer, resulting in even distribution and heating throughout the sample as compared with the classical heat transfer that occurs when a water/oil bath is applied as an energy source [148]. Investigations on microwave as an efficient heating source for organic reaction was given serious attentions since mid 1980s [149]. Many organic reactions were dramatically enhanced by the use of microwave irradiation. Different studies on microwave heating system indicated that it is an efficient method of heat supply in which the reaction occurs rapidly, safely and with higher product yields. Microwave heating during chemical reaction is characterized by enhanced reaction rates, mild reaction conditions and use of less toxic reagents and solvents which are environmental friendly [150].

a) Fundamentals of microwave heating mechanisms

In the electromagnetic spectrum, the microwave radiation region is located between infrared radiation and radio-wave. Microwaves have frequencies between 0.3 GHz and 300 GHz, corresponding to wavelengths between 1 mm and 1 m, respectively. For its use in laboratory reaction or domestic use, a frequency of 2.45GHz is preferred as this frequency has the right penetration depth for laboratory reaction conditions. Thus, all domestic and commercial equipment uses a frequency of 2.45 GHz (wavelength 12.2 cm) for heating mechanisms [150].

The fundamental mechanisms of microwave heating involve agitation of polar molecules or ions that oscillate under the effect of an oscillating electric or magnetic field. In the presence of oscillating field, particles try to orient themselves or be in phase with the field. The motion of these particles is restricted by resisting forces (inter-particle interaction and electric resistance), which restrict the motion of particle and generate random motion, producing heat [147, 149]. The response of different materials to microwave radiations is different. Based on their response to microwave radiations, materials can be classified as materials that can be transparent to microwaves (example sulfur), materials that reflect microwave (example copper) and materials that absorb microwaves (example water). Materials that absorb microwaves are the only materials used in microwave chemical processes. Microwave heating of these materials can be conducted via dipolar polarization, conduction mechanism or interfacial polarization [151].

Table 2.6: Spectrum of electromagnetic radiation

Region	**Wavelength (Angstroms)**	**Wavelength (centimeters)**	**Frequency (Hz)**	**Energy (eV)**
Radio	$> 10^{9}$	> 10	$< 3 \times 10^{9}$	$< 10^{-5}$
Microwave	$\mathbf{10^{9} - 10^{6}}$	**10 - 0.01**	$\mathbf{3 \times 10^{9} - 3 \times 10^{12}}$	$\mathbf{10^{-5} - 0.01}$
Infrared	10^{6} - 7000	$0.01 - 7 \times 10^{-5}$	$3 \times 10^{12} - 4.3 \times 10^{14}$	0.01 - 2
Visible	7000 - 4000	$7 \times 10^{-5} - 4 \times 10^{-5}$	$4.3 \times 10^{14} - 7.5 \times 10^{14}$	2 - 3
Ultraviolet	4000 – 10	$4 \times 10^{-5} - 10^{-7}$	$7.5 \times 10^{14} - 3 \times 10^{17}$	$3 - 10^{3}$
X-Rays	10 - 0.1	$10^{-7} - 10^{-9}$	$3 \times 10^{17} - 3 \times 10^{19}$	$10^{3} - 10^{5}$
Gamma Rays	< 0.1	$< 10^{-9}$	$> 3 \times 10^{19}$	$> 10^{5}$

Dipolar polarization is a process in which heat is generated in polar molecules on exposure to an oscillating electromagnetic field of appropriate frequency. While exposed to oscillating electromagnetic field, polar molecules try to align themselves in phase with the field, on the other hand, due to the intermolecular forces; polar molecules experience inertia forces and are restricted to follow the field resulting in the random motion of the particles. These random particles interactions generate heat. The frequency ranges of the oscillating field need to be appropriate to allow adequate inter-particles interactions. If the frequency range is very high, inter-molecular force will stop the motion of the polar molecule before it tries to follow the field resulting in inadequate inter-particles interactions. On the other hand, if the frequency range is too low, the polar molecule gets sufficient time to align itself in phase with the field. Hence, no random interaction takes between the adjoining particles [151]. Microwave radiation has the appropriate frequency to oscillate polar particles and enable enough inter-particle interaction. This makes it an ideal choice for heating organic reactants.

Where the irradiated sample is an electrical conductor, the charge carriers (electrons, ions, etc) are moved through the material under the influence of the electric field resulting in polarization. These induced currents will cause heating in the sample due to any electrical resistance. For a very good conductor, complete polarization may be achieved in approximately 10^{-18} seconds, indicating that under the influence of a 2.45GHz microwave, the conducting electrons move precisely in phase with the field. If the sample is too conducting, such as a metal, most of the microwave

energy does not penetrate the surface of the material, but is reflected. However, the colossal surface voltages which may still be induced are responsible for the arcing that is observed from metals under microwave radiation. Thus, if one takes pure water and heats it in a microwave oven, where the polarization mechanism dominates, it can be found that the heating rate is significantly less than when one takes the same volume of water and add salt. In the latter case, both mechanisms occur, and contribute to the heating effect [151].

The interfacial polarization method can be considered as a combination of the conduction and dipolar polarization mechanisms. It is important for heating systems that comprise a conducting material dispersed in a non-conducting material. For example, consider the dispersion of metal particles in sulfur. Sulfur does not respond to microwaves, and metals reflect most of the microwave energy they are exposed to, but combining the two makes them a good microwave-absorbing material.

b) Microwave heating assisted transesterification reaction

Use of microwave irradiation to enhance transesterification reaction rate has recently been used by different investigators. According to different research reports, microwave irradiation heating has a significant effect to increase the rate of reaction and obtain the product yield in very short time as compared to conventional heating system [133, 152]. Microwave irradiation heating processes increases the solubility of oil and alcohol (sufficient mass transfer between oil and alcohol) that results in increased rate of transesterification reaction and conversion of triglycerides. Microwave heating process also offers easy separation of the biodiesel in a very short time [16], [153].

Kumar et al. [133] have investigated the effect of using microwave irradiation as a source of heat during transesterification of pongamia pinnata oil using the alkaline catalysts KOH and NaOH. To investigate the effect of catalyst concentration (0.5%, 1.0% and 1.5% w/w of oil) and reaction time (3, 5, 7 and 10 min), the experiments were carried out at 6:1 molar ratio of alcohol to oil and 60°C reaction temperature (using a programmed microwave to reach 60°C). The result of the study reported that

at a catalyst concentration of 0.5% NaOH and 1.0% KOH the maximum yield of biodiesel (96% and 97%) were achieved, respectively. It was also reported that the reaction time required to obtain the biodiesel that satisfies EN 14214 requirements (at least 96.5% purity) was 5-10 minutes. A similar investigation was carried out by Azcan and Danisman [153] using rapeseed oils in the presence of NaOH and KOH catalyst under microwave irradiation heat. The result showed microwave irradiation heating has effectively increased the biodiesel yield and decreased the reaction time as compared to conventional heating. Generally, investigations conducted by different researchers [16, 134, 154, 155] indicated that biodiesel synthesis under microwave irradiation heat supply is a potential method to increase the rate of reaction and obtain high quality yield.

2.4.6.5 Phase transfer catalysis

Conventional techniques employed to improve the mass transfer rate between immiscible or slightly miscible reactants include increasing the agitation speed [156], use of high temperature and pressure [18] and addition of a co-solvent [17]. However, these efforts are limited due to technique limitations such as side reaction, high energy cost, operational risk at high temperature and pressure, cost of co-solvents, salvation of solvents with reactants, cost of solvent recovery and end-of-pipe treatments [135, 157]. Other methods such as ultrasonication [130, 131] and microwave irradiation [133, 158] have also proven satisfactory results in improving the mass transfer limitation of reacting reagents. Nevertheless, their applications are limited to laboratory scales and certain group of reactants such as those can absorb microwave radiations only.

Therefore, the use of phase transfer catalysis (PTC) appeared as a reasonable and promising approach to such mass transfer limitations during synthesis of organic products. PTC is a phase transfer agent in catalytic amount used to transfer one of the reactants to the location where it can rapidly react with another reactant [159]. The principle of phase transfer catalysis is based on the ability of phase transfer agents to facilitate the transfer of one reagent from one phase into another immiscible phase

where the other reacting agent exists. It makes the reaction possible by bringing the two reacting reagents together which are originally in different phases. During application of PTC, it is also necessary to note that the transferred reagent is in its active state for effective catalytic action [160].

PTC has been used in various types of organic reactions such as oxidation, reduction, polymerization, etc. The major industrial applications of PTC are found in pharmaceuticals, petrochemical, agrochemical and fine chemicals. Currently, its applications are being increasingly used in processes related to environment, energy and in process modifications to eliminate the use of co-solvents and in reactions related to the treatment of poisonous effluents [161]. The most advantage of using PTC technique in organic chemical synthesis are the enhancement of reaction rate, carrying out the reaction at moderate condition, obtaining high selectivity of the desired product, high conversion of the reactant and environment friendly [162]. Reactions such as liquid-liquid, solid-liquid, gas-liquid and liquid-solid-liquid are broadly enhanced by PTC to obtain the desired product [163, 164]. PTC found application in nuclophilic substitution reactions and in reactions in the presence of alkaline, involving the deprotonation of the transferred reagents. Use of PTC has made possible the utilization of cheaper and easily available alternative raw materials in a variety of base mediated reactions especially those involving the deprotonation of weakly acidic organic compounds. Thus, when reactions are carried out in the presence of PTC in two phase systems, bases like NaOH or KOH can be used to increase the selectivity [157, 165].

a) Fundamental mechanism of phase transfer catalysis

The fundamental mechanism of PTC as described above depends on the ability of a phase transfer agent to facilitate the transport of one reagent from one phase into another immiscible or sparingly miscible phase with the previous phase where the other reacting reagent exists. The reaction between the two reagents is made possible by bringing them together which are originally in different phases.

PTC reaction involves several steps taking place in series and parallel such as formation of an ion complex of one of the reagents with the PTC and transfer of this complex from its phase to the second phase where reaction could take place; reaction of the transferred reactant with the non-transferred reactant located in the second phase and transfer of the anion product back into its previous phase where it release the anion product and further proceeds for its next cyclic processes as illustrated in Figure 2.4. The mechanism described in Figure 2.4 is based on Starks extraction mechanism [159]. In PTC catalysis systems, there is also a mechanism known as interfacial mechanism or Brandstrom-Montanari modification of Starks extraction mechanism. In interfacial mechanism, the transfer of the reactant and product anions involves the initial exchange of the species in the presence of the cationic phase transfer agent at the interfacial region of the system followed by the transfer of the product into the organic phase as presented in Figure 2.5 [159]. Since PTC cycle is a multi-step process, factors affecting each step are important. Anion complex transfer and activation are one of the important steps involved in transferring anion from the aqueous or solid phase to the organic phase in a reactive form. The anion transfer includes a number of equilibrium steps and the main reaction of the transferred reactants with the second reactant. Generally, mass transfer resistance (diffusion resistance) can be involved [166].

The PTC system consists of two main cyclic reactions of anion reaction and the main organic reaction steps such as inter-phase and intra-phase mass transfer. The actual type of reaction mechanism and reaction cycle differs according to the type of reaction and phase involved even though the basic principles are similar. In PTC system, factors that cause the reactant anion transfer into the organic phase by the PTC cations (Q^+) and once it is transferred it needed to be in active state in that phase should be clearly understood. It has been reported that the quat cations are used to activate the anions of many organic reagents. It also activates anions by an anion activation agent, that means, it lowers the free activation energy of the displacement reaction by decreasing cation-anion interaction energy [163].

Most industrial reactions employing PTC as a rate enhancement factor uses PTC in the presence of a base such as solutions of NaOH, KOH or solid K_2CO_3 [157, 167].

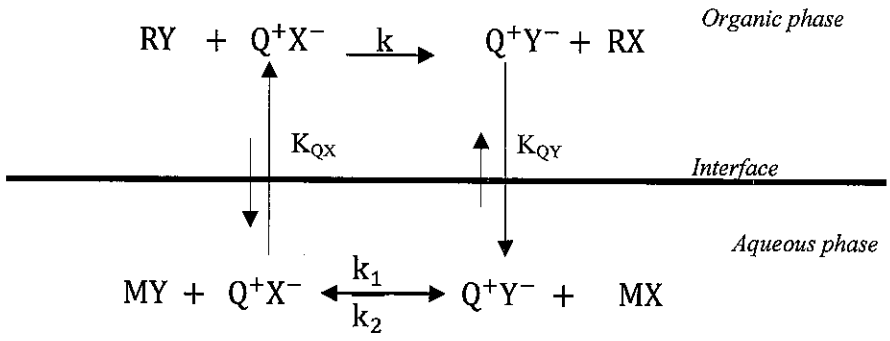


Figure 2.4: Starks Extraction Mechanisms of phase transfer catalysis

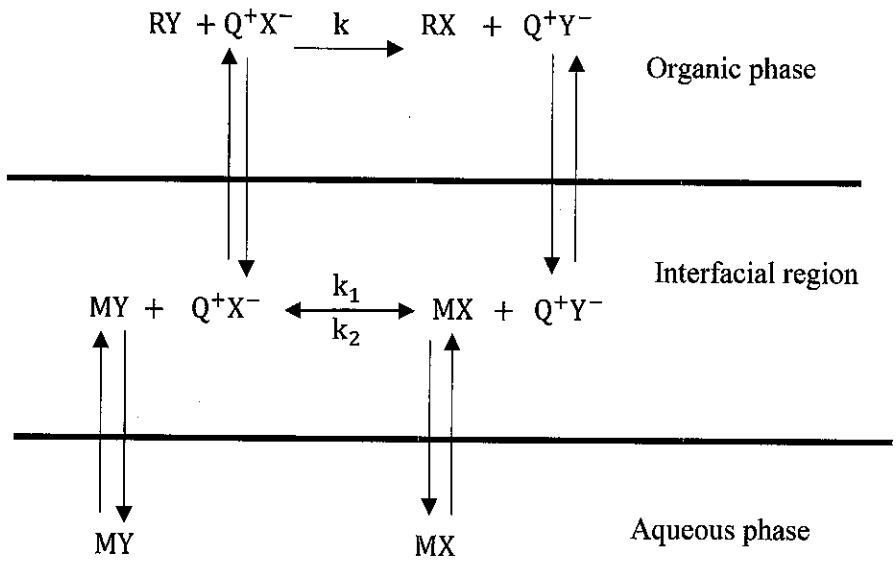


Figure 2.5: Brandstrom-Montanari modifications of Starks Extraction Mechanism

a) PTC assisted transesterification reaction

Even though PTC has been widely applied to enhance the reaction of two or more immiscible or sparingly miscible reactants for the synthesis of many organic chemicals, it has not been exploited as a rate enhancement agent for the synthesis of biodiesel except an investigation conducted by Zhang et al. [135]. Zhang et al. [135] has used different types of phase transfer catalysts to enhance the reaction of transesterification of soybean oil with methanol in the presence of base catalyst as a

deprotonation agent. It was also reported that use of PTC has substantially increased the rate of reaction as compared to the reaction conducted without PTC. However, due to the remarkable ability of PTC to increase the solubility of two insoluble or slightly soluble reactants, it can be used in catalytic amount, its wide availability, environmentally friendly nature [163], the use of PTC to enhance the rate of transesterification reaction needs detail research works to develop appropriate reaction mechanisms and reaction properties.

2.5 Variables affecting transesterification reaction

The rate of transesterification reaction of oils and fats is affected by various process parameters such as the content of free fatty acid and water in the oil, the type of catalyst and their concentration, the ratio of alcohol to oil, reaction temperature, agitation speed and reaction time. Each parameter is equally significant to determine the quality and quantity of biodiesel produced and to achieve high conversion rates [14, 99, 168].

2.5.1 Free fatty acids

The saturated or unsaturated mono-carboxylic acids that occur naturally in fats, oils or greases but are not attached to glycerol backbones are known as free fatty acids (FFAs). The presence of higher amount of FFAs in oil can result in higher amount of acid value of oil. Vegetable oils usually contain a small amount of FFAs. When alkaline catalyst is used to promote the transesterification reaction in oil feedstocks with high FFAs, the FFAs reacts with the alkaline catalyst and soap will be formed as shown in the Figure 2.6. The formation of soap is the undesirable product in transesterification reaction as more catalyst is required to replace the catalyst lost due to soap formation [169, 170]. The presence of soap increases the viscosity (formation of gel) and emulsification resulting in difficulties in separation of biodiesel from glycerol resulting in excessive washing and low yield of biodiesel [134]. For alkaline catalyzed transesterification reaction, the maximum amount of FFAs in the oil needs

to be 5%. However, additional catalyst is required to compensate the catalyst lost due to saponification [12, 91-93].

Figure 2.6: Saponification of FFA during transesterification reaction

Feedstocks with high content of FFAs require special process or pre-treatment to be used in biodiesel production. As discussed earlier, the methods employed are acid catalysed transesterification, acid catalysed followed by alkali catalysed transesterification, enzymatic transesterification or supercritical fluid methods.

The common pre-treatment method is esterification of FFAs with methanol in the presence of acid catalyst (usually sulphuric acid) as shown in Figure 2.7. The catalyst can be homogeneous or heterogeneous acid catalyst. Once the FFAs are reduced to the minimum value, the reaction further proceeds with base catalysed transesterification reaction.

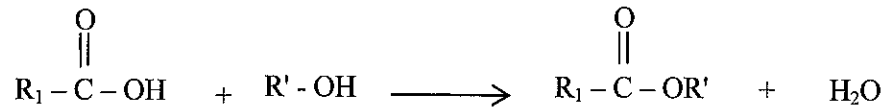


Figure 2.7: Esterification of free fatty acid

2.5.2 Water content

The source of water during transesterification reaction can be water originated from the feedstock oils and fats or water formed during the saponification reaction as shown in Figure 2.6. Water has a negative effect in transesterification reaction. Water retards transesterification reaction through hydrolysis reaction of triglycerides. It hydrolyses the triglycerides to di-glycerides and forms more FFAs which consume

alkali catalyst and form the unwanted soap [83, 89, 171] during transesterification process. The hydrolysis reaction of triglycerides is illustrated in the Figure 2.8.

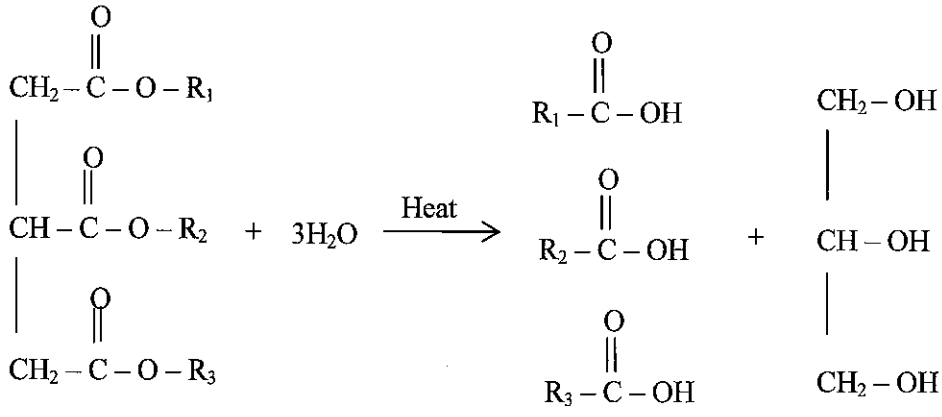


Figure 2.8: Hydrolysis reaction of triglycerides

2.5.3 Catalyst concentration

Catalyst concentration can affect the rate of transesterification reaction and yield of biodiesel. As mentioned in section 2.4, transesterification reaction can be catalyzed by alkaline catalysts, acid catalysts or biological catalysts. The concentration of catalysts has significant effect on the rate of reaction and yields of product. Various studies have been conducted to investigate the effect of catalyst concentration of different types on the rate of transesterification reaction, product separation process, yield and quality of biodiesel.

Patil and Deng [172] studied transesterification of karanja oil and jatropha oil in two-step processes using sulfuric acid and potassium hydroxide as acid and alkaline catalysts, respectively. The catalyst concentration effect of sulfuric acid was investigated by varying its concentration in the range of 0.25–2% w/w for karanja oil and 0.25–1.5% w/w for jatropha oil. When acid catalyst was used, the maximum FAME yield was achieved at the acid catalyst concentration of 1 and 0.5% w/w for karanja oil and jatropha oil, respectively. It was reported that the addition of excess sulfuric acid darkens the color of the product but yield remains the same for karanja oil. The conversion rate in the alkali transesterification step decreases when the

sulfuric acid concentration in the first step increases above 1% w/w. The report indicated for jatropha oil the yield started to decline when the catalyst concentration was increased above 0.5% w/w. In a similar fashion the catalytic effect of an alkali catalyst was studied in the range of 0.3–1% w/w for karanja oil and 0.5–2.5% w/w for jatropha oil using KOH as an alkali catalyst. According to the investigation, the maximum yield was achieved for karanja and jatropha oil at 0.5% w/w and 2% w/w of catalyst loading, respectively. Increasing the catalyst above the maximum value gave rise to the formation of an emulsion, increased the viscosity and led to the formation of gels.

Hoque et al. [91] investigated the effect of process variables of producing biodiesel from low cost feedstocks such as used cooking oil (UCO) and animal fats (AF) using potassium hydroxide as alkaline catalyst. The effect of catalyst concentration was studied by varying the concentration as 0.75%, 1%, 1.25%, 1.5% and 1.75% while keeping the rest of the variables constant. The highest yields of 82.1%, 88.7% and 85.7% were obtained for beef fat, chicken fat and UCO at a catalyst concentration of 1.25% w/w. Meanwhile, increasing the concentration of the catalyst greater than 1.25% w/w caused significant reduction in the yield of FAME. It was reported the decrease in yield was due to the formation of fatty acid salts (soap) at higher concentration of KOH favoring saponification reaction.

Keera et al., [73] also reported their experimental data on the production of fatty acid methyl esters from vegetable oils (soybean and cotton seed oils) using NaOH as alkaline catalyst. The variables investigated were reaction time (1–3 h), catalyst concentration (0.5–1.5), and oil-to-methanol molar ratio (1:3–1:9). From the reported results, the best yield was obtained using methanol/oil molar ratio of 6:1, sodium hydroxide as catalyst (1%) and 60 ± 1°C temperature for 1 h. Similarly, Keera et al. [73] studied alkaline transesterification of vegetable oil for preparation of biodiesel in order to determine the optimum transesterification conditions. NaOH was employed as a catalyst and the optimum reaction conditions investigated by the researcher was 1% w/w of NaOH, 6:1 molar ratio of methanol to oil, 60°C and 1 h of reaction time. Similar investigations were conducted for the transesterification of jatropha oil using

KOH and NaOH as alkaline catalysts by Lu et al. [173], Berchmans et al. [106], Georgogianni et al. [174], Saydut and Ozturk [169] and Ginting et al. [39].

2.5.4 Alcohol type and molar ratio of alcohol to oil

The amount of alcohol is one of the main factors that affect the rate of transesterification reaction and yield of biodiesel. Even if stiochiometrically three mole of alcohol reacts with one mole of triglycerides to yield three moles of fatty acid alkyl ester and one mole of glycerol, since transesterification reaction is an equilibrium reaction, excess alcohol is required to ensure all oils or fats will be converted to the desired product. High alcohol to oil ratio increases solubility and contact between oil and alcohol leading to high conversion in relatively short reaction time [47, 78, 172, 175]. The excess amount of alcohol depends on the type of catalyst used in the reaction [11]. Commonly for alkaline catalysed reactions 100% excess alcohol is used, that is, 6 mole of alcohol per mole of triglycerides; for acids catalysed reaction, mostly 30 moles of alcohol is used per mole of triglycerides. However, further increasing the amount of alcohol beyond the optimum value does not increase the yield but it increases the solubility of fatty acid ethyl esters in alcohol and complicated the ester recovery resulting in high cost of alcohol recovery and reduction in the product fatty acid ester [134].

Sahoo and Das [176] carried out an investigation aimed at optimizing the process variables of biodiesel production from non-edible oils sources of jatropha, karanja and polanga oils. After the pretreatment of oils to decrease the FFA content to less than 2%, transesterification reactions were conducted to determine the optimum quantity of the ratio of alcohol to oil on volume basis. The maximum FAME yields of 93%, 91% and 85% were achieved for oil to methanol volumetric ratio of 11:1, 11.5:1 and 12:1 for jatropha, karanja and polanga oil, respectively. With further increase in volumetric ratio there is no improvement in the conversion efficiency. Also, it has been reported the reduction in viscosity increases with increase in volume of methanol in the mixture.

Miao et al. [76] varied the molar ratio of methanol to oil as 5:1,10:1, 20:1, 30:1, 40:1, 50:1 and 60:1 to investigate the effect of methanol on transesterification reaction of refined soybean oil using trifluoro-acetic acid catalysis while keeping other conditions constant at 2% w/w of catalyst concentration, 120°C and 5 h of reaction time. At methanol to oil molar ratio of 20:1, the maximum FAME yield of 98.5% with specific gravity of 0.878 was reported. Further increase of molar ratio did not significantly increase the amount of FAME content. A similar investigation was made by Soriano et al. [74] using lewis acids ($AlCl_3$ or $ZnCl_2$) as a catalyst. In their work the effect of molar ratio of methanol to oil was investigated at 6:1, 12:1, 24:1, 42:1 and 60:1. The yield of FAME increased while increasing the molar ratio of methanol to oil up to 24:1 at 110°C for 18h of reaction time in the presence of CFC as a co-solvent in $AlCl_3$ catalyzed reaction. The maximum FAME exchange rate of 98% was achieved at this condition. Further increase to molar ratio of 42:1 or 60:1 had a negative effect on the conversion due to solubility of FAME in alcohol.

2.5.5 Effect of reaction temperature

Reaction temperature influences the rate of reaction and yield of biodiesel. Increasing reaction temperature can decrease the viscosity of oil and increase reaction rate. In alkaline catalysis reaction, the reaction temperature needs to be below or near the boiling point of alcohol because at higher temperature saponification reaction is favoured. Thus, higher temperature must be avoided in alkaline transesterification reaction. In alkaline transesterification reaction the temperature ranges from room temperature up to 65°C. However, in acid catalyzed reaction higher temperature (up to 120°C) is employed to increase the solubility of alcohol in oil so as to enhance the mass transfer rate and reaction between the two reactants. In supercritical alcohol transesterification reactions the reaction temperature can reach up to 400°C. Different research works were reported on the effect of temperature during transesterification reaction at various reaction conditions and catalyst type.

Kafuku and Mbarawa [177] studied the effect of reaction temperature on transesterification of croton megalocarpus oil by varying the reaction temperature

from 30 to 60°C at the interval of 10°C while keeping other parameters constant. The maximum yield of FAME was attained at 50°C reaction temperature. At 60°C the yield declined slightly due to saponification of oil. Hoque et al. [91] also conducted transesterification of used cooking oil , chicken fat and beef fat at various temperatures of 55, 60 and 65°C. High conversion (87.4 and 87.6%) were obtained for waste cooking oil and beef fat at 65°C, however, a maximum yield of 89% was obtained for chicken fat at 60°C. It was reported that the increase in temperature to 65°C had no influence on the yield of chicken fat.

Crabbe et al. [178] also conducted transesterification of crude palm oil at 5% sulfuric acid catalyst and 40:1 methanol to oil molar ratio. The effect of different reaction temperature was studied by varying the reaction temperature from 70°C, 80°C, and 95°C at various reaction times. They reported reaction rate was increased by increasing the reaction temperature and about 99.7% conversion efficiency was obtained in 9 h at the reaction temperature of 95°C. However, when the reaction temperature was reduced to 80°C a similar conversion was obtained after 24 h of reaction time. At 70°C reaction temperature the yield obtained was very low even after 24h of reaction time. Several similar research works were also reported elsewhere in literature [74, 75, 179].

2.5.6 Reaction time

The conversion of triglycerides to biodiesel increases with increasing reaction time. At the start of the reaction the rate is very slow due to the limited solubility of oils and alcohol [135]. However, after sometimes due to mixing and dispersion of alcohol and oil the reaction proceeds faster until the equilibrium is reached. For alkaline catalyzed transesterification reaction, maximum conversion is reached in a relatively shorter time (1-3h) as compared to acid catalysis transesterification reaction which may take 18 to 24h to reach maximum conversion [12, 13, 47, 71, 80]. Transesterification reaction using biological catalysis is also slow reaction rate; the reaction can take up to 72h to reach completion. However, during non-catalyzed super critical methanol condition (300-400°C), the conversion rate is very high and the product can be

obtained in a very short reaction time as compared to both base and acid catalyzed reactions. However, the problem associated with this method is high equipment and energy cost and risk of operation[11, 14].

In summary, reaction parameters such as alcohol to oil molar ratio, catalyst type and concentration, reaction temperature, mixing rate and reaction time are the main variables which affect the conversion of oils and fats into esters. These parameters need to be carefully considered during design of transesterification experiments.

2.6 In-situ transesterification reaction

Conventionally biodiesel is produced by transesterification of oils extracted and purified from oil bearing plant sources such as soybean, rapeseed, sunflower, palm, jatropha, castor, etc. Recovery of oil from oil bearing seeds can be accomplished through chemical method (extraction using hexane) or mechanical method such as extrusion as presented in section 2.3. Generally, oil extraction and purification steps for transesterification process constitute more than 70% of total production costs [35, 36, 180].

It is necessary to reduce or eliminate oil extraction and purification steps to make biodiesel cost competitive enough to make it attractive. Harrington and D'Arcy-Evans [37] developed a method of biodiesel production that cuts out the expensive intermediary with a process known as in-situ transesterification. In-situ transesterification is a biodiesel production method that utilizes the original agricultural component as the source of triglycerides for direct transesterification eliminating the costly hexane extraction process and works with any lipid-bearing material. Moreover, in-situ transesterification utilizes oils that could be lost through imperfect hull-kernel during oil extraction as whole seeds are subjected to transesterification processes resulting in increase of the overall yield of biodiesel. This process was further investigated by different researchers [3, 32, 36, 38, 171, 181-183] using seeds of edible oils. They observed that in-situ transesterification is more efficient than the conventional transesterification.

Kildiran et al. [3] have investigated the parametric effects and type of alcohol on the in-situ transesterification of soybean oil using sulfuric acid catalyst. It was reported that the oil which was dissolved in the methanol was approximately 20% of the total oil in the seeds and the amount of methyl esters was only 42%. However, when ethanol was used the oil extracted and dissolved into ethyl esters was 80.9%. It was concluded that methanol is a poor solvent since the oil dissolved in it is less than those of other types of alcohols such as ethanol, n-propanol and n-butanol. They also reported that the solubility of triglycerides increases in alcohol with increasing the alcohol chain-length. The particle size of the seed is also one of the factors that affect the amount of esters obtained by in-situ transesterification methods. The experiments conducted by Siler-Marinkovic and Tomasevic [38] to investigate the effect of molar ratio of alcohol to oil, the amount of catalyst, reaction time and temperature on the in-situ transesterification of sunflower oil using acid catalyst indicated the yield of methyl esters obtained by in-situ transesterification process was higher than the conventional transesterification process. The highest yield of methyl esters was obtained when 300:1 molar ratio of alcohol to oil was employed at 64.5°C and 4 h reaction temperature and time, respectively.

The feasibility of in-situ alkaline transesterification of vegetable oils was investigated by Hass et al. [32]. In their investigation highest yield of fatty acid methyl esters was obtained at methanol: oil concentration of 226:1 and 1.6 NaOH catalyst, 60°C and 8 h of reaction time. In their study, it was also reported that the yield of fatty acid methyl esters was higher when the reaction was conducted at room temperature (23°C) than 60°C reaction time; however, the molar ratio of methanol to oil was increased to 543:1 and the catalyst concentration to 2% w/w. They also conducted a similar study on in-situ transesterification of distillers dried grains with soluble (DDGS) which is the co-product of the production of alcohol from corn and meat and bone meal (MBM), a product of animal rendering with alkaline methanol. In-situ transesterification for both DDGS and MBM were successfully achieved at 35°C demonstrating any lipid bearing materials can be potentially used to produce biodiesel using in-situ transesterification process [181].

Geargogianni et al. [182] studied in-situ transesterification of sunflower seeds oil and compared with conventional transesterification using mechanical agitation and ultrasonication technology. A high yield of biodiesel (95%) was obtained in both ultrasonication (24 kHz) and mechanical stirring (600 rpm) during conventional transesterification. A similar result was also reported (95% yield) during in-situ transesterification process in both ultrasonication and mechanical stirring. On the other hand, when ethanol is used instead of methanol higher yields (98%) of ethyl esters was achieved using ultrasonication mixing as compared to 88% yields of ethyl esters produced by mechanical stirring. Another study conducted on the in-situ transesterification of sunflower oil with methanol assisted by diethoxymethane (DEM) was demonstrated by Zeng et al. [36]. In their study DEM was used as both extraction solvent and reaction promoters. In their work the effect of each reaction parameters were investigated and optimal conditions were set. 97.7% FAME yield was achieved at optimal conditions (molar ratios of catalyst to oil of 0.5:1, molar ratio of methanol to oil of 101.39:1, molar ratio of DEM to oil of 57.85:1, mixing speed of 150 rpm and reaction temperature of 20°C in 13 minutes of reaction time). However, the use of large quantity of co-solvent could be a limitation as it increases the cost of production due to the high cost of solvent and solvent recovery cost.

The feasibility of in-situ transesterification of biodiesel production was further studied using non-edible oil sources such as cotton seed, municipal primary and secondary sledges, microalgae lipids, jatropha curcas and castor seed [31, 56, 156, 174, 184-186]. Quin et al. [186] conducted in-situ alkaline transesterification of cotton seed oil for the production of biodiesel. In their work, they examined the amount of cotton seed oil dissolved in methanol was nearly 99% of the total oil in the cotton seeds. 98% conversion of the dissolved oil into biodiesel was achieved under the reaction condition of 0.3-0.335 mm particles size, less than 2% moisture content of seeds, 0.1 molar ratio of NaOH to methanol, 135:1 molar ratio of methanol to oil, 40°C and 3 h of reaction time. In this study, the effect of moisture content of seeds was also investigated. When the moisture content of the seeds was decreased from 8.7 to 1.9%, the amount of oil extracted in the methanol increased from 92.2 to 99.7%. Accordingly, its conversion was increased from 80 to 99%. However, further decreasing the moisture content below 1.9% had little effect on the amount of oil

extracted and conversion. A similar investigation was reported by Hass et al. [181]. They reported increasing the reaction temperature has no significant effect on the in-situ transesterification of cotton seeds and the optimum temperature found was 40°C. Ginting [31] has also studied in-situ transesterification of jatropha curcas in alkaline methanol and ethanol in order to investigate its feasibility. It was reported that in-situ transesterification of jatropha curcas with methanol was unsuccessful as only 45% w/w yields of FAME were obtained even after 24 h of reaction time; however, the use of ethanol instead of methanol was successful as 89.7% w/w FAEE yield was obtained in 4 h of reaction time.

The feasibility of reactive and in-situ esterification of jatropha curcas was also studied by Shuit et al. [35]. The study reported that the size of the particles and the reaction time had significant effect on the yield of FAME. Decreasing the size of the particle to about 0.335 mm coupled with n-hexane as a co-solvent resulted in the oil extraction efficiency and FAME yield of 91.2% and 99.8%, respectively at the following reaction conditions: 60°C reaction temperature, 24 h reaction time, and 7.5 ml/g of methanol to oil ratio and 1.5% of H_2SO_4 catalyst concentration. It was observed that the reaction time was too long (24 h) and additional cost of co-solvent and co-solvent recovery indicated that its feasibility for commercial scale needs further investigation. Lim et al. [18] have also studied the feasibility of biodiesel production from jatropha curcas seeds oil using supercritical reactive extraction method. The particle size of the seeds (0.5-2 mm) and reaction temperature (200-300°C) are the two important factors studied in this research work. High extraction efficiency (105.3%) and yield (103.5%) were achieved at reaction temperature of 300°C, 240 MPa operating pressure, 10ml/g methanol to solid ratio, 2.5% ml/g of n-hexane to seed ratio and total operating time of 45-80 minutes as compared to the values achieved based on hexane extraction. Though high yields of biodiesel was achieved in a relatively shorter time, the high pressure and temperature of the reaction condition will incur high energy cost and risk of operation, moreover, the use of co-solvent will increase the cost of production, solvent recovery and downstream treatment of the effluent.

Though in-situ transesterification is a cost effective approach to reduce the cost of biodiesel processing as compared to conventional transesterification, continuous research and development is necessary to increase simultaneous reaction and extraction rate of oil during transesterification and reducing the reaction time while increasing the product both quantitatively and qualitatively.

2.7 Quality and standards of biodiesel

Biodiesel standards have been developed to facilitate its commercialization and bring credibility to consumers. Even though many countries have developed their own standards, the most significant and internationally accepted standards are ASTM D6751 (in USA) which was published as a full biodiesel standard in 2002 and DIN EN 14214 (in Europe) which was published in 2003. Transesterification reaction of vegetable oil does not go to 100% completion; it reaches equilibrium state at a certain point. The resulting product of transesterification reaction contains fatty acid esters, monoglycerides (MG), diglycerides (DG) and triglycerides (TG) and other minor impurities. The biodiesel standards limit components of biodiesel such as glycerol, mono, di and triglycerides, FFA (by limiting the acid number), residual alcohol (by limiting flash point) and moisture contents. However, from all of these quality parameters, the glycerol content, that is, the free glycerol, MG, DG, TG and acid value are the most important. Thus, the ASTM D6751 limits the free glycerol to 0.02%, the total glycerol to 0.24% and the acid value to 0.5 mgKOH/g as shown in Table 2.12. The total glycerol and chemically bound glycerol in the system can be determined using the relation

$$Gl_T = Gl + .025 * MG + 0.15 * DG + 0.10 * TG \quad (2.1)$$

Where: Gl is free glycerol, MG, DG and TG represents mono, di and triglycerides and multiplied by the corresponding glycerol moiety which together is called chemically bound glycerol.

High amount of free glycerol in the biodiesel indicates there is incomplete separation of biodiesel from its byproducts after reaction. High level of free and

bound glycerol can cause incomplete combustion resulting in carbon deposits in the combustion engine. To keep the level of the impurities well below the level of both ASTM D6751 and DIN EN 14214, the transesterification reaction needs to be carefully designed for the reaction to approach to completion. The separation of biodiesel is also key factor to keep the quality of biodiesel within the limits of the international standards.

Table 2.7: ASTM D6751 and DIN EN 14214 biodiesel standards

Property	Unit	Standard limit		Test method	
		ASTM D6751	**DIN EN 14214**	**ASTM D6751**	**DIN EN 14214**
K.Viscosity at 40°C	mm^2/s	1.9–6.0	3.5–5.0	D445	EN ISO 3104
Density at 15°C	kg/m^3	-	860–900	–	EN SIO 3675 EN SIO 2185
Flash point	°C	130.0 min	101.0 min	D93	ISO CD3679e
Acid value	mg KOH/g	0.80 max	0.5 max	D664	pr EN 14104
Free glycerol	% (m/m)	0.020 max		D6584	EN 14106
Monoglycerides	% (m/m	–	0.8 max	–	pr EN 14105m
Diglycerides	% (m/m)	–	0.2 max	–	pr EN 14105m
Triglycerides	% (m/m)	–	0.2 max	–	pr EN 14105m
Total glycerol	% (m/m)	0.240 max	0.25 max	D6584	pr EN 14105m
Methanol	% (m/m)	–	0.2 max	–	pr EN 141101
Cloud point	°C	–	–	D2500	–
Distillation T90AET	°C	360 max	–	D1160	
Iodine value	–	–	120 max	–	pr EN 14111
Water and sediment	%vol	0.050 max	–	D2709	–
Water content	mg/kg	–	500 max	–	EN ISO 12937
Cetane number	–	47 min	51 min	D613	EN ISO 5165
Sulphated ash	% (m/m)	0.020 max		D874	ISO 3987
Carbon residue	% (m/m)	0.050 max	0.3 max	D4530	EN ISO 10370
Sulfur (S 15 Grade)	ppm	0.0015 max	–	D5453	–
Sulfur (S500 Grade)	ppm	0.05 max	–	D5453	-
Oxidation stability at 110°C	h	–	6	–	pr EN 14112

2.8 Summary

Currently, more than 95% of biodiesel is produced from edible oil sources affecting both the price of biodiesel and food industry. High cost of edible vegetable oil is the main limitation for biodiesel to compete as alternative fuel to petroleum based diesel fuel. Use of non-edible oil sources such as jatropha curcas can reduce the high cost of edible oil sources.

Vegetable oil can be processed into biodiesel using transesterification in the presence of catalyst or using non- catalysis process. The catalysts can be alkaline homogenous and heterogeneous catalysts, acid homogenous and heterogeneous catalysts or biological (enzyme) catalysts. Currently, homogeneous alkaline catalysis transesterification is used at industrial scale of biodiesel processing as homogeneous alkaline catalysis transesterification is much faster than acid and enzyme catalysis and the catalysts are relatively cheaper.

In addition to catalytic transesterification reaction, other techniques are used to increase the rate of transesterification. These include non-catalysis supercritical condition, addition of co-solvents, use of ultrasonication technology and use of microwave irradiation energy. Transesterification reaction variables such as alcohol to oil ratio, catalyst concentration, reaction temperature, speed of agitation and reaction time can also affect the rate of reaction and yield of biodiesel qualitatively and quantitatively. During transesterification process these variables need to be considered and optimized for the achievement of maximum yield.

In-situ transesterification is a process that uses the original agricultural component as the source of triglycerides for direct transesterification eliminating the costly hexane extraction process and works with any lipid-bearing material. This method also utilizes the oils that could be lost through imperfect hull-kernel during separation as whole seeds are subjected to transesterification processes, thus, it increases the overall yield of biodiesel.

Phase transfer catalysis is processes that use a phase transfer agent in catalytic amount to transfer one of the reactants to the other phase where it is immiscible or

sparingly miscible to enhance the reaction with another reactant [152]. Phase transfer catalysis technique is increasingly applied at industrial level to processes related to environment, energy and in process modifications to eliminate the use of co-solvents and in reactions related to the treatment of poisonous effluents for a reaction involving liquid-liquid, solid-liquid, gas-liquid and liquid-solid-liquid[154], [156, 157]. Its main advantages are the enhancement of reaction rate, carrying out the reaction at moderate condition, obtaining high selectivity of the desired product, high conversion of the reactant and environment friendly [155].

3.2 Materials and Chemicals

Jatropha curcas seeds produced in Malaysia was purchased from Agro Innaz Resources, Malaysia, a local jatropha seeds and oil trading company. The seeds were stored in an oven adjusted at 30°C to avoid any moisture contamination. Chemicals used for transesterification reaction, pro-analysis chemicals, alkaline catalyst, and phase transfer catalysts and standard chemicals for biodiesel analysis in gas chromatograph are presented in Table 3.1.

Table 3.1: Chemicals used in the present research work

Description	Purity	Supplier
Alcohol		
Methanol	≥ 99.7%	Merck chemicals
Ethanol	≥ 99.7%	
Catalyst		
Sodium hydroxide (alkaline catalyst)	≥ 99%	Merck chemical
Cetyltrimethylammonium bromide (PTC)	≥ 99%	Sigma Aldrich
Benzyltrimethylammonium hydroxide (PTC)	40% methanol	
Crown ether (PTC)	≥ 99%	
Pro-analysis chemicals		
Iso-propanol	>99.8%	Merck chemicals
N-hexane	≥ 99%	
N-heptanes	≥ 99.5%	
Potassium hydroxide	0.1 N	
Iodine	≥ 99.99%	
Sodium sulphate	≥ 99%	
α-Naphtholphthalein	≥ 99%	
Starch solution as indicator		
Iodochloride in glacial acetic acid	1.5% in acetic acid	
Sodium thiosulphate	≥ 99%	
Chloroform	99.9%	
Acetic acid	Reagent grade	
Diethyl ether	Reagent grade	

Reference standards for GC		
1,2,4 butanetriol	GC grade	Sigma Aldrich
Tricaprin	GC grade	
Glycerin	GC grade	
Monoolein	GC grade	
Diolein	GC grade	
Triolein	GC grade	
Methyl laurate	≥99%	
Methyl myristate	≥99%	
Methyl palmitate	≥99%	
Methyl stearate	≥99%	
Methyl oleat	≥99%	
Methyl linoleat	≥99%	
Ethyl laurate	≥98%	
Ethyl myristate	≥98%	
Ethyl palmitate	≥95%	
Ethyl stearate	≥98%	
Ethyl oleat	≥99%	
Ethyl linoleat	≥99%	
N-Methyl-N-trimethylsilyltriflouroacetamide (MSTFA)	GC grade	
Pyridine	≥99%	

3.3 Experimental approach of jatropha curcas seed preparation and oil characterization

In this section preparation of jatropha seed particles from seeds (section 3.3.1), oil extraction to estimate oil content of seed particles (section 3.3.2) and characterization of the properties of extracted oil (section 3.3.3) are presented.

3.3.1 Jatropha curcas seeds preparation and pretreatment

In order to increase the extractability of oil from jatropha seeds, the jatropha seeds need to be dried and dehulled to recover oil kernel. The kernel was ground to small size particles using Panasonic MX-799S blender-grinder and dried. These crushed seeds of jatropha curcas seeds were separated by sieving and a three particles size range of seeds, that is, 300 to 500, 500 to 850 and greater than 850μm were obtained. However, due to the sticky nature of the oil seed particles, collecting particle sizes less than 300μm were almost impossible. Preliminary experiments were conducted using the three ranges of particle sizes (300 to 500, 500 to 850 and greater than 850μm) to select particle sizes range that can help to achieve maximum extraction of oil from the seeds using both Soxhlet extractor and in-situ transesterification experiment in a relatively shorter time. It was observed that particle sizes in the range of 300 to 500μm were yield better result during oil extraction in Soxhlet extraction and in-situ transesterification in a relatively shorter time. Thus, particles in the size range of 300 to 500μm were then collected by sieving for the in-situ transesterification experiments throughout the present work. The graded particles were further dried to avoid hydrolysis of oil to free fatty acids (FFA) which can lead to formation of unwanted soap during alkali catalyzed transesterification reactions. The moisture content was monitored using Mettler Toledo moisture analyzer (RH73). A sample of 20 g particles was loaded into the moisture analyzer set to operate at 100°C with 3 minutes ramp time. The moisture content was monitored till it reached the equilibrium moisture content. The prepared seed particles were kept in amber-colored air tight bottles to eliminate any moisture contact and prevent photo oxidation of the seed particles.

3.3.2 Jatropha curcas oil extraction

Soxhlet extraction unit was used to measure original oil content present in the jatropha curcas seeds by hexane solvent extraction. The Soxhlet extraction unit consists of a round bottom flask sitting over a heating mantle, Soxhlet extractor and a vapour condenser for reflux. A sample of jatropha seed particles (20 g) was placed in

the thimble made of thick filter paper in the Soxhlet extractor and the solvent was loaded in the round bottom flask. On heating the vapors of the solvent flow into the condenser through vapor flow arm and warm condensate drips into the Soxhlet extractor thimble to extract oil from the sample; as the thimble gets filled the condensate siphons back to round bottom flask through liquid flow arm. Oil in the sample gets extracted with time till extraction was complete. After extraction, the solvent was evaporated using a rotary evaporator to estimate oil yield. Extractions were carried out for five ratios of 4.5, 6, 7.5, 9 and 10.5 ml of hexane per gram of oil seed particles each for periods of 1, 2, 3 and 4 h to investigate the optimum amount of hexane needed per gram of oil seed particles and extraction period for complete oil extraction.

3.3.3 Characterization of Jatropha Curcas Oil

Vegetable oils contain free fatty acids (FFA), saturated and unsaturated fatty acid glycerides. Acid Value provides a measure of FFA. Saponification Value provides a measure of fatty acid glycerides and Iodine Value gives a measure of level of unsaturation. Calorific value of the oil is an indicator of its fuel value; viscosity and density of the oil provides an indication of its usability as a fuel. Methods used to measure these properties are presented in the following sections.

a) Determination of Acid Value and Acid Number

Acid value is the measure of the free fatty acid (FFA) present in the oil. According to ASTM D 974-06 [187], acid number is defined as the quantity of base expressed in milligrams of potassium hydroxide per gram of sample to a specified end point. FFA percentage of oil is one of the important factors to design transesterification reaction experiments. The acid value of biodiesel fuel also affects the quality of the biodiesel as fuel. Thus, determination of the acid value of the oil prior to transesterification reaction as well as the acid value of biodiesel is very essential to produce a biodiesel fuel that satisfies international requirements of biodiesel as a fuel. The acid number of jatropha curcas oil and the corresponding biodiesel produced were determined using

titration method of American Oil Chemists Society, AOCS Official Methods cd 3d-63, revised 2003 [188]. The details of the experimental procedures and laboratory set up are shown in Appendix A. According to AOCS Official Methods cd 3d-63, revised 2003, the acid number is calculated as;

$$Acid\ value, mgKOH/g = (A-B)*\frac{N*56.1}{w} \quad (3.1)$$

Where: A = *KOH solution required for titration of the sample, ml*

B = *KOH solution required for titration of the blank, ml*

N = *Normality of standard alkali KOH solution (mol/l)*

w = *the amount of sample used, g*

The acid percentage due to FFA in a sample is assumed to be due to the contribution of presence of oleic, lauric and palmitic FFA acid components. The FFA percentage due to each of these components may be estimated by dividing the acid value by 1.99, 2.81 and 2.56, respectively [188]. For a mixture of known composition acid value may be estimated as;

$$FFA\,\% = \frac{Acid\ value}{K} \quad (3.2)$$

Where:

$$K = (0.0199 * Oleicacid) + (0.0281 * Lauricacid) + (0.0251 * Palmiticacid)$$

b) Determination of Saponification Value

Saponification value is the amount of alkali, in milligrams of potassium hydroxide, necessary to convert 1 gram of oil into soap. After transesterification is complete, the left over catalyst and some soap formed tend to concentrate in the glycerol phase. However, some soap may be left in the biodiesel phase. During design of transesterification reaction experiment, it is important to know the amount of soap formed when alkaline catalyst is used and how effective the washing process is in removing soap formed and left over catalyst. In the present work, AOCS Cd 3b-76 titration procedure [189] was used to estimate the saponification value of both

jatropha oil and biodiesel. The details of the experimental procedures and laboratory set up are shown in Appendix A. Mathematically, it is expressed as;

$$Saponification\ value = (A - B) * \frac{N * 56}{w} \quad (3.3)$$

Where: w = *weight of sample taken, g*

A = *volume of KOH required for blank titration, ml*

B = *volume of KOH required for sample titration, ml*

N = *normality of KOH solution, mol/l*

c) Determination of Iodine Value

Iodine value or iodine number is the measure of the total amount of unsaturated fatty acids in the oil. It is the measure of the number of grams of iodine which will combine with 100 grams of the oil. The method specified by AOCS official method 993.20 [190] was used in order to determine the iodine value. The details of the experimental procedures and laboratory set up are shown in Appendix A. Then the iodine value (I.V) is determined by the expression;

$$Iodine\ value = (A - B) * \frac{N * 12.69}{W} \quad (3.4)$$

Where: N = *Normality of sodium thiosulphate* ($Na_2S_2O_3$) *used; mol/l*

A = *Volume of sodium thiosulphate used for blank; ml*

B = *Volume of sodium thiosulphate used for determination, ml*

W = *weight of the sample, g*

d) Determination of viscosity, specific gravity and calorific value

The viscosity, density and calorific value of jatropha oil and the corresponding alkyl esters synthesized were measured using BROOKFIELD (model cap 2000+, USA) programmable digital viscometer, a calibrated pycnometer (Jayteck, UK) and bomb calorimeter, respectively.

3.4 In-situ transesterification reaction experimental approach

A two neck round bottom flask reactor equipped with a reflux condenser (to prevent loss of alcohol), a magnetic stirrer and a thermometer was used. Twenty grams of conditioned jatropha curcas seed particles were prepared and placed in the round bottom flask reactor. Required amount of alkaline alcohol (methanol or ethanol) mixed with (or without) the desired amount of PTC was prepared in a separate flask, preheated to the reaction temperature and then added to the round bottom flask reactor to start the reaction. The flask was immersed in a silicon oil bath thermostat immediately to maintain the reaction temperature. The reactor assembly is shown in Figure 3.2.

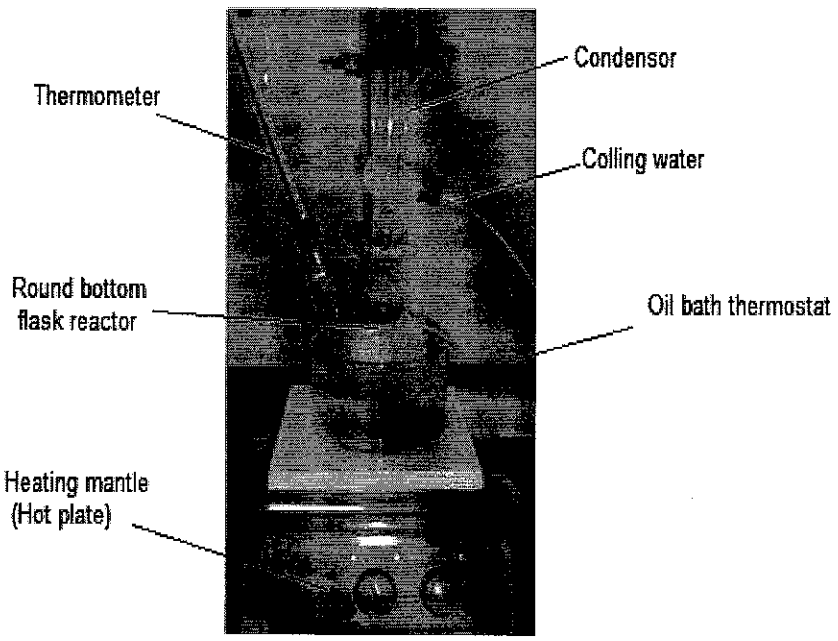


Figure 3.2: Batch reactor for in-situ transesterification of jatropha curcas

After a specified reaction time, the reactor was withdrawn from the thermostat. The reaction mixture was filtered using a vacuum Buchner funnel to separate solid residue from the liquid mixture. The solid residue was further washed with 20 ml methanol/ethanol to recover the remaining liquid in the solid residue. The liquid mixtures were transferred to a separation funnel and diluted with distilled water to arrest further reactions. The resulting liquid was in the form of an emulsion. N-hexane was added to extract alkyl esters and enhance the clarification of the mixture into two

phases. The separation processes requires several hours to form a clear phase separation between the top layer that contains mixture of alkyl ester and n-hexane mixture while the bottom layer containing glycerol, methanol (or ethanol), sodium hydroxide, PTC, water and unspent oil.

The top layer was recovered and then washed with warm (50 - 60°C) water several times to remove contaminants; traces of moisture in the washed top layer (containing hexane and alkyl esters) were removed by passing the mixture through an adsorption column of sodium sulphate particles. Alkyl ester produced was recovered by evaporating n-hexane from the mixture using a rotary vacuum evaporator operating at a temperature of 70°C, 200 mmHg and a rotational speed of 20 rpm. The recovered alkyl ester was weighed and stored in a screw capped bottle for further analysis. Figure 3.3 shows the flow process of in-situ transesterification of jatropha curcas of the present work.

This procedure was used in all the experiments to investigate yields of methyl and ethyl esters with or without PTC (cetyltrimethylammonium bromide (CTMAB), benzyltrimethylammonium hydroxide (BTMAOH) or crown ether (CE)). Optimal operating conditions were evaluated for better PTC with or without microwave pretreatment of seed particles by statistical tool of response surface methodology (RSM). The details of the experimental methods are presented in the following sections.

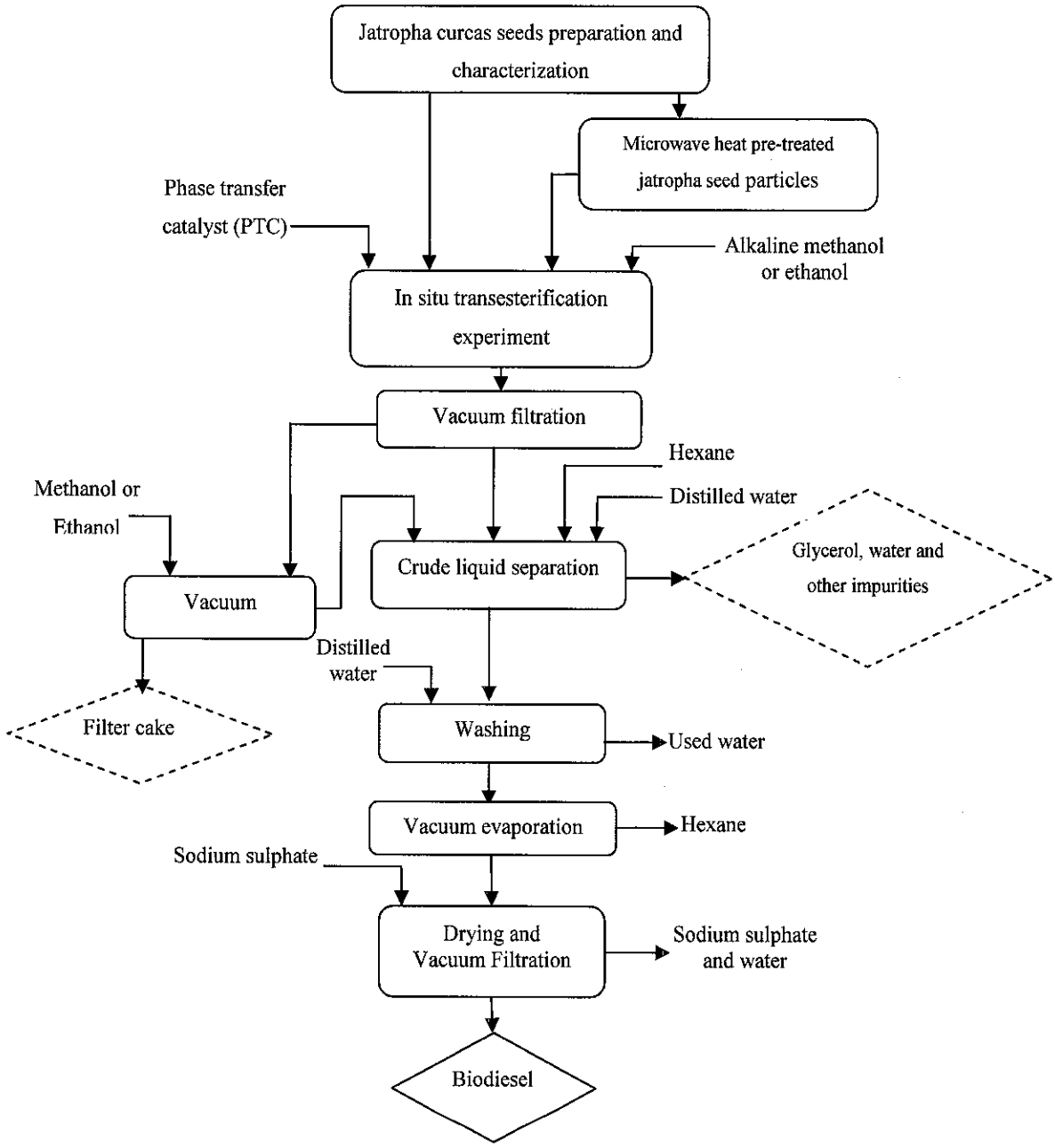


Figure 3.3: Process flow of in-situ transesterification of jatropha curcas of the present study

3.4.1 Experiments using cethyltrimethylammonium bromide as a phase transfer catalyst

In-situ transesterification is affected by reaction variables such as cethyltrimethylammonium bromide (CTMAB) concentration, sodium hydroxide (NaOH) concentration, methanol or ethanol to jatropha curcas seed particles ratio, reaction temperature, agitation speed and reaction time. Experimental plan to

investigate the effect of each reaction variable in the presence and absence of CTMAB as a PTC is presented in Table 3.2. Effect of each reaction variable was investigated by keeping the rest of the variables constant to identify the best value that produced maximum yield. Each experiment was conducted in duplicate to observe its reproducibility.

Table 3.2: In-situ transesterification reaction matrix using CTMAB as a PTC

No	Process Parameters	Unit	Test variables
1	Jatropha curcas seeds	g	20
2	CTMAB/NaOH	mol/mol	0, 0.5, 1, 1.5, 2, and 2.5
3	NaOH to Jatropha curcas seeds	% w/w	0.068, 0.338, 0.675, 1.013, 1.35 and 1.68
4	Methanol (or Ethanol) to Jatropha curcas seeds	ml/g	3, 4.5, 6, 7.5, 9, 10.5 and 12
5	Reaction temperature	°C	30, 40, 50, 60 and 70
6	Agitation speed	rpm	100, 200, 300, 400, 500, 600 and 700
7	Reaction time	minutes	30, 60, 90, 120, 150, 180, 210 and 240

3.4.2 Experiments using different Phase Transfer Catalysts

In-situ transesterification reaction experiments were conducted using different PTCs such as cetyltrimethylammonium bromide, benzyltrimethylammonium hydroxide and crown ether to identify (select) a phase transfer catalyst with better catalytic performance. The experiments were conducted using PTC without alkaline catalyst and using (combining) both PTC and alkaline catalyst to evaluate the catalytic performance of PTC in each conditions.

3.4.3 In-situ transesterification experiment using microwave irradiation heat pre-treated jatropha seed particles

In-situ transesterification experiments were conducted using microwave irradiation heat pre-treated jatropha curcas seed particles. The seed particles were treated with microwave irradiation heat. Methanol (or ethanol) was used as a reactive-extraction reagent. Microwave pre-treated jatropha curcas seed particles in-situ transesterification experiments were conducted using NaOH as a catalyst to investigate the effect of microwave pre-treatment of seed particles. The experiment was also repeated with microwave untreated seed particles. The reaction condition matrix is shown in Table 3.3. Further experiments were conducted in order to investigate the combined effect of microwave irradiation pretreatment of seed particles and use of BTMAOH as a PTC on alkaline in-situ transesterification reaction rate and yield of biodiesel. The experiment was also conducted with untreated seed particles for comparison. Experiments were conducted according to reaction variables matrix shown in Table 3.3. Each experiment was conducted in duplicate to observe its reproducibility.

Table 3.3: Reaction conditions of in-situ transesterification of microwave heat treated jatropha seeds

No	Process Parameters	Unit	Test variables	
			With NaOH	With NaOH + BTMAOH
1	Jatropha curcas seeds	g	20	20
2	Microwave power	watt	70	70
3	Microwave heating time	minutes	4.5	4.5
4	BTMAOH/NaOH	mol/mol	-	1.25
5	NaOH to Jatropha seeds	% w/w	0.675	0.675
6	Alcohol to Jatropha seeds	ml/g	7.5	7.5
7	Reaction temperature	°C	30	30
8	Agitation speed	rpm	400	400
9	Reaction time	minutes	15, 30, 60, 90, 120, 150 180, 210	15, 30, 60, 90, 120, 150

3.4.4 Statistical Experimental Design for investigating the individual and cross effects of reaction variables to determine optimum operating conditions

Identification of optimum operating condition using conventional method was near impossible due to cross influence of different variables. The use of statistical methods can be advantageous in understanding interactions among process variables with minimum number of experiments that need to be performed and find optimal condition [191-193]. Response surface methodology (RSM) is one such widely applied statistical tool for experimental design and identification of optimal condition [194, 195]. In the present study central composite design (CCD) technique of RSM was used for experimental design to investigate the individual and interaction effects of reaction variables and determine the optimum reaction condition for microwave untreated jatropha curcas seeds as well as microwave heat pretreated jatropha curcas seeds in-situ transesterification in the presence of alkaline PTC .

The experimental results were fitted using a polynomial quadratic equation in order to correlate the response variables. The general form of the polynomial quadratic equation shown in equation (3.5) was used to develop a model that predicts (estimates) the yield of alkyl esters (FAME and FAEE) at designed reaction variable combination.

$$Y_i = \beta_o + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j \qquad (3.5)$$

Where: Y_i is the predicted response and X_i is the input variables for BTMAOH concentration, NaOH concentration, and volume of alcohol, reaction temperature and time. The term β_o is the offset term (intercept), β_i is the linear terms, β_{ii} is the squared terms and β_{ij} is the interaction terms and X_j is the cross term to represent two-parameter interactions.

The variable X_i was coded according to equation (3.6).

$$x_i = \frac{X_i - X_i^*}{\Delta X_i} \qquad (3.6)$$

Where: x_i is the coded value of the i^{th} variable, X_i is the natural value of the i^{th} variable, X_i^* is the central value of X_i in the investigated area, and ΔX_i is the step size.

The statistical significance of the mathematical model equation was tested using analysis of variance (ANOVA) with 95% confidence intervals.

3.5 Analysis of biodiesel samples

Biodiesel standards were established to maintain the quality of biodiesel as a fuel and bring credibility to biodiesel consumers. ASTM D6751 and EN 14214 are two well established standards for testing the quality of biodiesel as a motor fuel. The standards define the quality of biodiesel in terms of physical and chemical properties of biodiesel such as glycerides (G), monoglycerides (MG), diglycerides (DG) and triglycerides (TG), acid numbers, viscosity, specific gravity, flash point, etc. Quality of biodiesel produced in the present study was ascertained in terms of the physical and chemical properties to verify its quality with the international requirements. The test methods used during the analysis are described in the following sections.

3.5.1 Gas chromatographic analysis

In the present research work, Gas chromatography (QP 5000 series, Shimadzu Japan, 2010) was used to determine the quality of biodiesel. The GC used was equipped with an on column injection and flame ionization detector (FID), HT 5 column with 0.32mm, 0.1μm and 30m of diameter, flame thickness and length, respectively. The operating temperature of the column was set at initial temperature of 50°C for 1 minute, and then increased to 150°C at a rate of 15°C per minute and the rate decreased to 7°C/minutes until it reached to 230°C and again the rate increased to 30°C/min until it reached 380°C. It was maintained at this temperature for 10 minutes. Helium was used as a carrier gas with a flow rate of 3ml/min in which the flame ionization detector (FID) was set at a temperature of 380°C.

i) Calibration and standardization of the chromatographic analysis

The chemicals (glycerin, monoolein, diolein, triolein, butanetriol and tricaprin) needed for GC analyses of biodiesel were procured from Sigma Aldrich, Malaysia. Standard stock solutions were prepared and used to prepare standard solutions for calibration of chromatograph as explained in section (a). The chromatograph is calibrated and standardized using standard solution.

a) Standard solution preparation

Stock solutions (glycerin, monoolein, diolein, triolein, butanetriol and tricaprin) needed as per ASTM D 6584-00 for GC analysis [196] were weighed into the volumetric flasks and diluted by pyridine to the mark in the volumetric flasks as per Table 3.4. These were stored in a refrigerator at 4-5°C when not in use.

Table 3.4: Stock Solutions

Compound	Approximate Mass (g)	Volumetric Flask Size (ml)
Glycerin, (reference standard)	25	50
1-Mono [cis-9-octadecenoyl]-racglycerol (monoolein),(reference standard)	50	10
1,3-Di [cis-octadecenoyl]glycerol (diolein), (reference standard)	50	10
1,2,3-Tri [cis-octadecenoyl]glycerol (triolein), (reference standard)	50	10
1,2,4-Butanetriol - (Internal Standard 1)	25	25
1,2,3-Tridecanolylglycerol (tricaprin) - (Internal Standard 2)	80	10

Using the stock solutions, five standard solutions were prepared by transferring the specified volumes by means of micro-liter syringes to 10ml septa vials as presented in Table 3.5. 100µl of N-Methyl-N-trimethylsilytrifluoroacitamide (MSTFA) was added to each of the five standard solutions. The vial was screw caped, shaken gently and stored for 20minutes at room temperature. Then, approximately 8ml of n-heptanes was added to the vial with shaking. An aliquot of the solution of

the sample was then transferred into a glass GC auto sampler 2ml vial and sealed with a TFE-fluorocarbonlined cap [196].

Table 3.5: Standard Solutions

Standard Solution Number	**1**	**2**	**3**	**4**	**5**
µL of glycerin stock solution	10	30	50	70	100
µL of monoolein stock solution	20	50	100	150	200
µL of diolein stock solution	10	20	40	70	100
µL of triolein stock solution	10	20	40	70	100
µL of butanetriol stock solution	100	100	100	100	100
µL of tricaprin stock solution	100	100	100	100	100

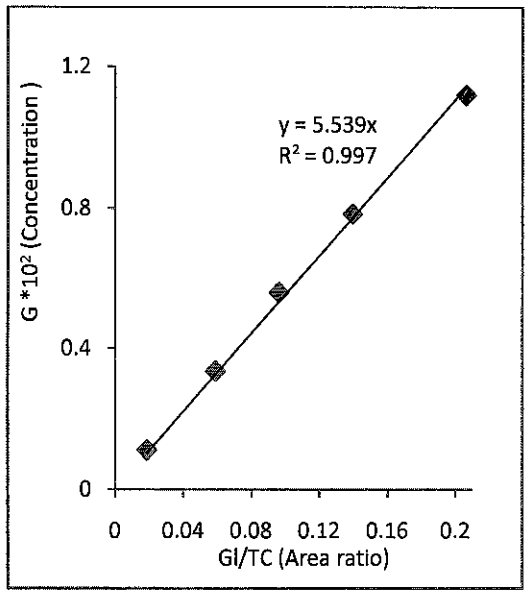
b) Biodiesel sample derivatization for GC

Glycerin, monoglycerin, diglycerin and triglycerin are not volatile to be detected through the GC column; therefore it is very important to derivatize the samples prior to GC analysis; 100mg of sample was weighed to the nearest 0.1mg directly into a 10ml septa vial; exactly 100µl of each internal standard and N-Methyl-N-trimethylsilytrifluoroacitamide (MSTFA) were added to the vial using micro-liter syringes, screw capped and well shaken to mix. The vials were allowed to stand for 20minutes at room temperature and then approximately 8ml of reagent grade n-heptanes was added to the vial and well shaken to mix. An aliquot of the solution of the sample was then transferred into a glass GC auto sampler 2ml vial and sealed with a TFE-fluorocarbonlined cap.

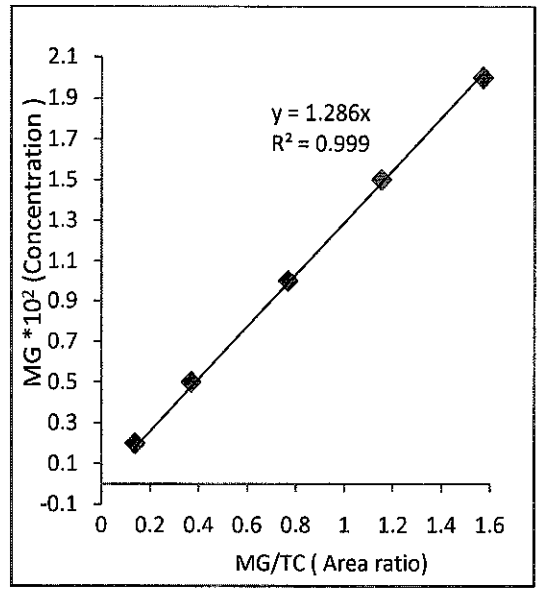
c) Calibration curve

For measuring the glycerol and glycerides (MG, DG and TG), the prepared internal standard samples of standard solutions were analyzed in the GC to obtain peak integration report. The concentration of the standards versus the corresponding peak areas ratios were used to obtain the calibration curve for each of the components of glycerin, monoolein, diolein, triolein, butanetriol and tricaprin. The best fit curves

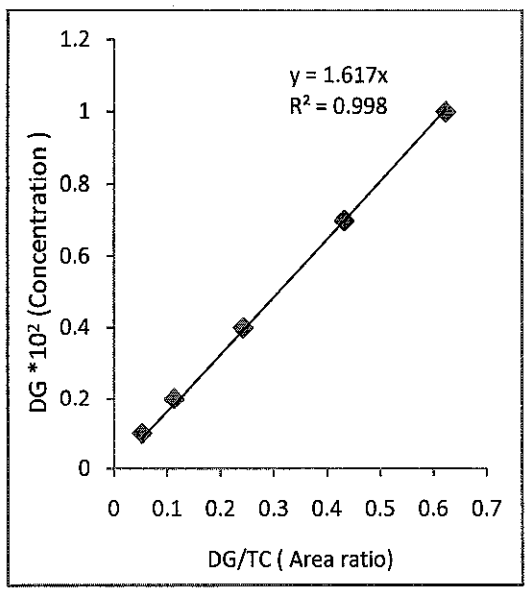
with a correlation coefficient R^2 value of 0.99 or greater for each reference component [196] were chosen for converting the detected peak signals to weight percent of the required product during kinetics study sampling. Typical calibration plots are presented in Figure 3.4.



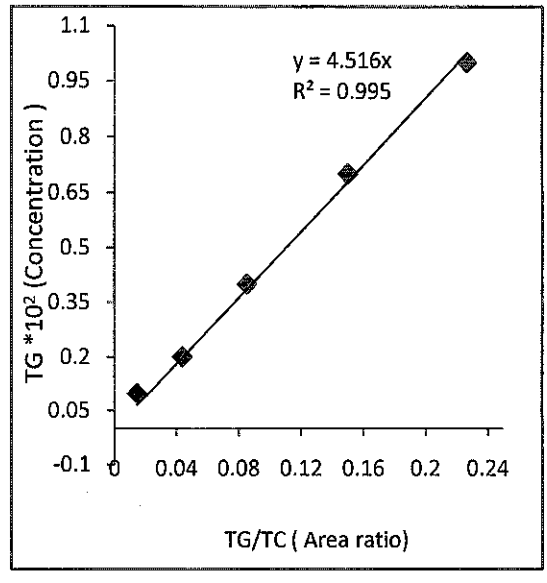
a) Response factor for glycerides



b) Response factor for MG



c) Response factor for DG



d) Response factor for TG

Figure 3.4: The effectiveness plot of the calibration curve for the reference standards of (a) G, (b) MG, (c) DG and (d) TG (gas chomatograph (GC) calibration curve)

The slops, the y-intercepts and the correlation coefficients R^2 of the calibration plots are presented in Table 3.6. The detector response factor (RF) for the reference standards were calculated from the calibration plot.

Table 3.6: Response factor for the reference standards

Standards	Slopes	Y-intercepts	R^2
Glycerin	5.38	0.022	0.998
Monoolein	1.258	0.032	0.999
Diolein	1.754	0.019	1
Triolein	4.332	0.029	0.998

ii) Determination of Glycerides in biodiesel: Peak Identification and Calculation

The major fatty acid components of jatropha curcas oil of the present study are 12.9% palmitic acid (16:0), 6.2% stearic acid (18:0), 46.7% oleic acid (18:1) and 33.4% linoleic acid (18:2). In GC analysis, glycerides peaks are primarily separated according to carbon number. Figure 3.5 shows the gas chromatogram of the standard solution. The GC retention time for reference standards are also presented in Table 3.7. Peaks are identified by comparison of retention times to the standards.

Table 3.7: Retention time for the reference standards.

Standards	Retention time (min.)
Glycerine (Gl)	4.122
Monoolein (MG)	16.023
Diolein (DG)	20.701
Triolein (TG)	23.299
Tricaprin(TC)	19.361

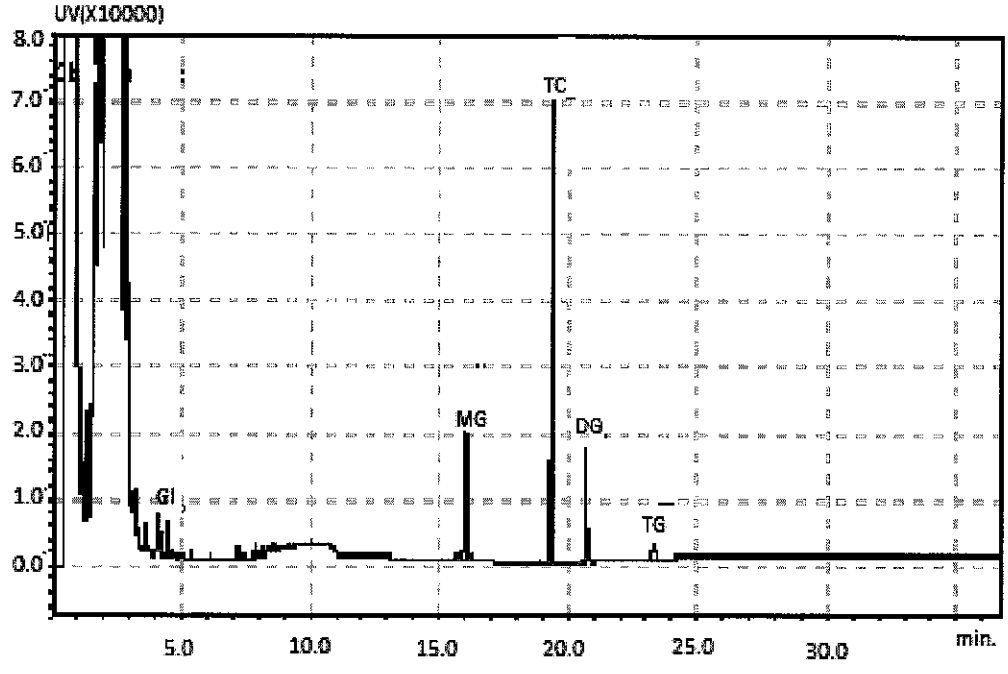


Figure 3.5: Chromatogram of standard solution

After identifying the peaks, the areas of the peaks identified as glycerin, monoglycerides, diglycerides and triglycerides were measured. Using the slope and y-intercept of the calibration functions, the mass of each component was calculated using equations (3.7) to (3.9) as presented below:

a) Glycerin

$$Gl = a_g * \left(\frac{A_g}{A_{iS_1}} + b_g \right) * \frac{w_{iS_1}}{w} * 100 \qquad (3.7)$$

Where:

Gl = mass percentage of glycerin in sample,

A_g *= peak area of glycerin,*

A_{is1} *= peak area of Internal Standard 1,*

W_{is1} *= weight of Internal Standard 1, mg,*

W = weight of sample, mg,

a_g *= slope of the calibration function,*

b_g *= intercept of the calibration function.*

b) Individual Glycerides

$$Gl_i = \left(a_{ol} + \frac{A_{gl\,i}}{A_{iS_2}} + b_{ol} \right) * \frac{w_{iS_2}}{w} * 100 \quad (3.8)$$

Where:

Gl_i = *mass percentage of individual glycerides in sample,*

A_{gli} = *peak area of individual glycerides,*

A_{is2} = *peak area of Internal Standard 2,*

Wi_{s2} = *weight of Internal Standard 2 , mg,*

W = *weight of sample, mg,*

a_{ol} = *slope of the calibration function for mono, di-, or triolein, and*

b_{ol} = *intercept of the calibration function for mono, di, or triolein.*

c) Total Glycerin

$$Total\ glyc\ erin = free\ glyce\ rin + bound\ glyc\ erine \quad (3.9)$$

where:

Free glycerin = glycerin determined in Equation 3.6, and

Bound glycerides = ∑(GlM, GlD, GlT)

where:

Gl_M = *0.2591 * Σ (monoglycerides, mass % determined in equation 3.7,*

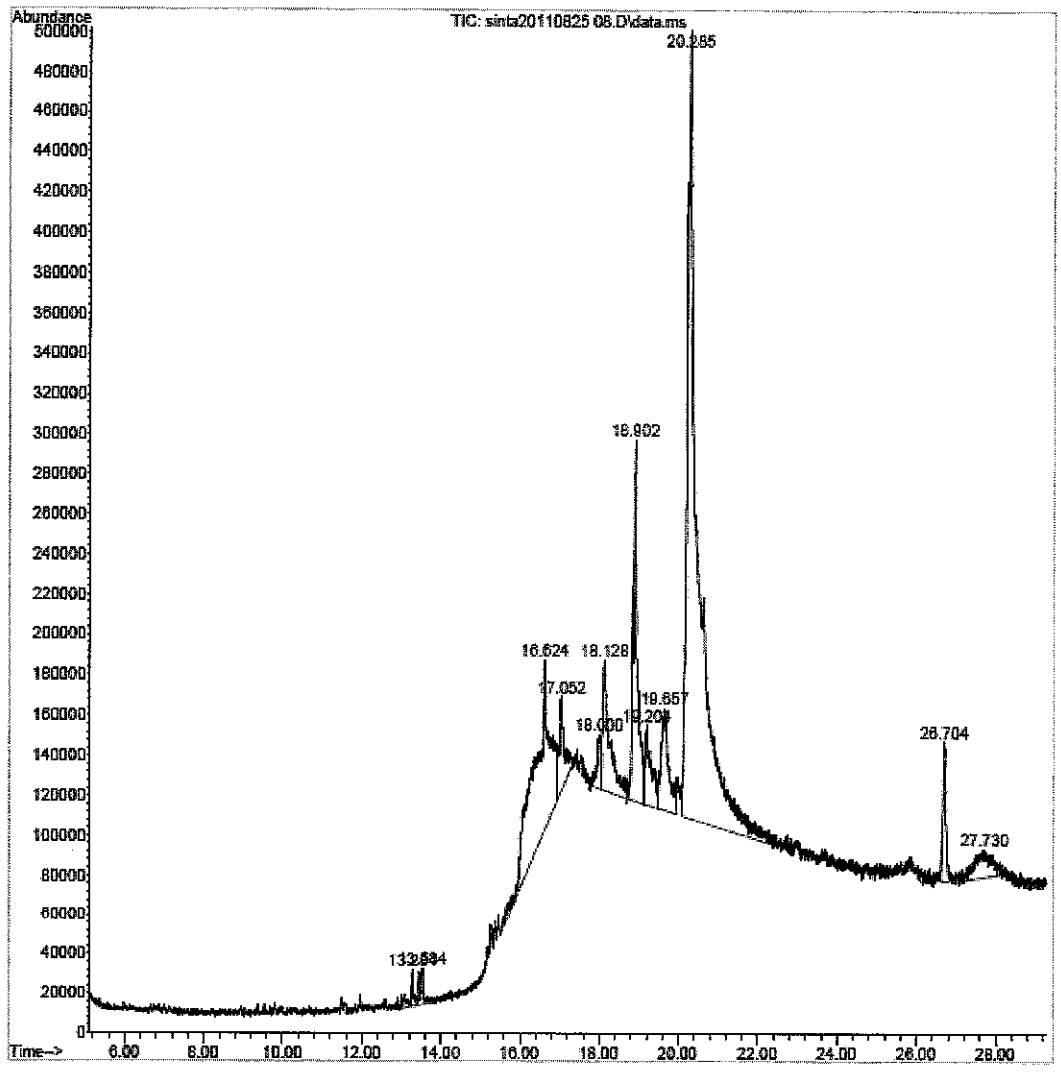
*GlD = 0.1488 * Σ (diglycerides, mass % determined in equation 3.7, and*

*GlT = 0.1044 * Σ (triglycerides, mass % determined in equation 3.7.*

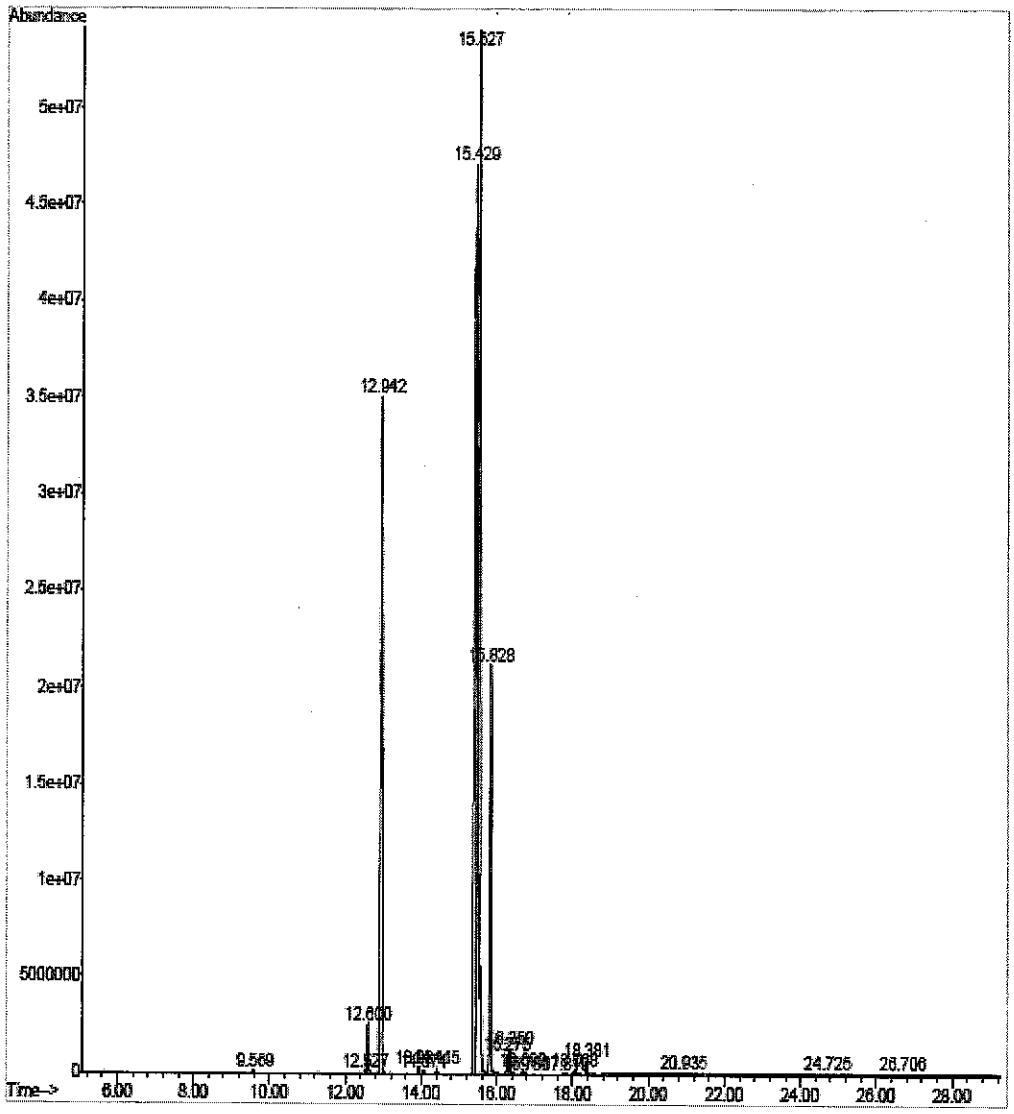
3.5.2 Gas chromatograph-mass spectrometry (GC-MS)

In the present research work, GC-MS analysis was performed using electronic impact ionization mode using GC-MS QP 5000 series, Shimadzu Japan, 2010. A 60m length, 0.25mm internal diameter and 0.25μm thickness capillary tube was used for the separation of esters. 3 minutes of equilibrate time was set to rise the temperature to 150°C and it is maintained at this temperature for 5minutes, then the temperature is increased to 250°C at the rate of 7°C/minute and maintained at this temperature for

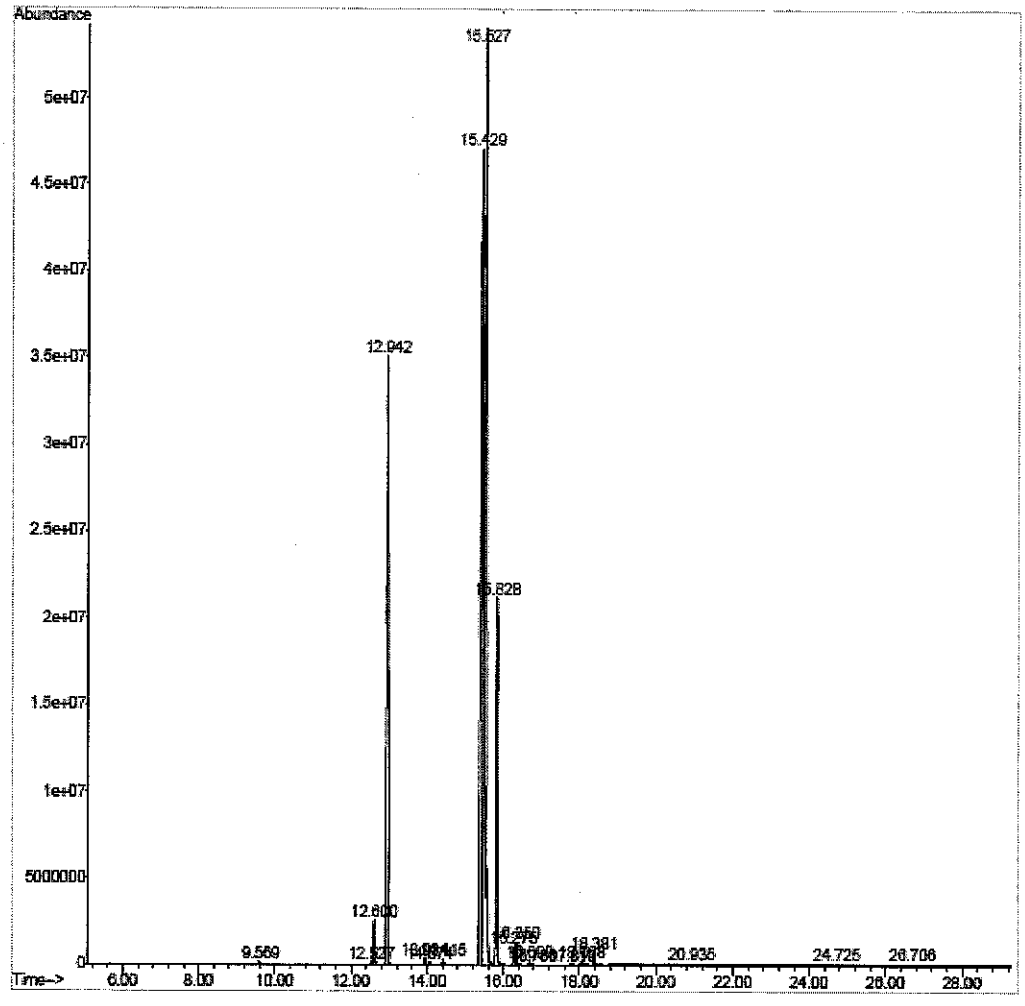
10minutes. An ionization voltage of 70Ev over the mass scanning range of 45-750 atomic mass units was used to fragment the components. 1µl helium was used as carrier gas. Other operating conditions were injector temperature of 250°C, interface temperature of 240°C, and ion source temperature of 200°C. Figure 3.6 represents the typical GC-MS peak identification results of the compositions of jatropha curcas oil, fatty acid methyl esters (FAME) and fatty acid ethyl esters (FAEE) of the present study, respectively.



a) Jatropha curcas oil fatty acids profile using GC-MS



b) Fatty acid methyl esters (FAME) fatty acids profile obtained by GC-MS



c) Fatty acid ethyl esters (FAEE) fatty acids profile obtained by GC-MS

Figure 3.6: Fatty acids profile of Jatropha oil and typical Fatty acid methyl esters (FAME) and Fatty acid ethyl esters (FAEE)

3.5.3 Analysis of physical and chemical properties of alkyl esters

Properties of biodiesel such as viscosity, specific gravity, calorific value and flash point were also determined to test the quality of biodiesel fuel. A calibrated pycnometer (Jayteck, UK) was utilized for density measurement. Brookfield (model cap 2000þ, USA) viscometer was employed to determine its viscosity. The flash point was measured using Penske Martens automatic flash point analyzer (FP93 5G2, ISL, France). Bomb calorimeter is used to investigate the heating value of biodiesel.

3.6 Quantification methodology of experimental results

The quantification of the experimental results is necessary for the investigation of each process variables, conduct discussion and draw appropriate conclusion. The following relations were used to calculate the molecular weight of jatropha curcas seeds, amount of triglycerides present in the oil, the conversion of triglycerides and yield of fatty acid methyl and ethyl esters.

The molecular weight of triglycerides present in the jatropha curcas oil was determined from the fatty acid composition of jatropha oil using the relation that three moles of fatty acid reacts with each mole of glycerol to produce one mole of TG and three moles of water [31].

$$3FA + Gl \longleftrightarrow TG + 3H_2O \tag{3.10}$$

The average molecular weight of triglycerides is therefore; three times the weighted average molecular weight of fatty acids present added to the molecular mass of glycerides less three water molecules.

$$AMW_{TG} = 3AMW_{FA} + MW_{Gl} - MW_{H_2O} \tag{3.11}$$

The average molecular weight of fatty acid in the oil was calculated by multiplying the molecular weight of each individual fatty acid present in the oil by its mole percentage and divide by 100% as shown below;

$$AMW_{FA} = \frac{(FA_1) * (MWFA_1) + (FA_2) * (MWFA_2) + \ldots + (FA_n) * (MWFA_n)}{100} \tag{3.12}$$

Where: FA_1 is first fatty acid present in the oil sample

FA_2 is second fatty acid present in the oil sample

FA_n is n^{th} fatty acid present in the oil sample

$MWFA_1$ is molecular weight of first fatty acid present in the oil sample

$MWFA_{2\,is}$ molecular weight of second fatty acid present in the oil sample

$MWFA_n$ is molecular weight of n^{th} fatty acid present in the oil sample

The total amount of triglycerides present in the feedstock (jatropha curcas oil seed) is determined as;

$$Moles\ of\ TG\ in\ the\ oil \quad = \quad \frac{amount\ of\ TG\ in\ the\ oil}{AMW_{TG}} \tag{3.13}$$

The conversion of triglycerides during in-situ transesterification reaction was calculated as;

$$\%\ conversion\ (X_{TG}) = \frac{(mole\ of\ TG\ in\ the\ oil) - (moles\ of\ TG\ in\ the\ \ esters)}{moles\ of\ TG\ in\ the\ oil} * 100 \tag{3.14}$$

The yield of fatty acid obtained by in-situ transesterification is calculated as

$$\%\ yield\ FAE = \frac{(Weight\ of\ biodiesel\ produced) * (total\ \%\ weight\ of\ FAME\ /\ FAEE)}{Total\ \ weight\ of\ oil} \tag{3.15}$$

Cetane number of FAME and FAEE produced in the present work can be estimated using the equation (3.15) [197, 198]

$$CN = 46.3 + \frac{5458}{SN} - 0.225 * IV \tag{3.16}$$

Where: CN = cetane number, SN = Saponification number and IV = Iodine value.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents effect of phase transfer catalysis and microwave irradiation pre-treatment of jatropha curcas seed particles on the in-situ transesterification of jatropha curcas seed particles. Section 4.2 describes the characteristics of jatropha curcas seed particles and the properties of the extracted oils. Section 4.3 presents experimental investigations on in-situ transesterification of jatropha curcas seed particles in presence of phase transfer catalysts and results of response surface methodology technique used to identify optimal operating parameters for the best PTC. Section 4.4 describes the effect of microwave irradiation pre-treatment of jatropha seed particles on the in-situ transesterification reaction rate. Response surface methodology techniques was used to identify optimal operating parameters for microwave irradiation pre-treated seed particles. Section 4.5 compares the quality of biodiesel produced at optimal operating condition with international standards while section 4.6 summarizes the experimental results and discussions.

4.2 Jatropha curcas oil seed characterization and oil properties

To establish the reaction conditions needed to achieve the maximum product yield of in-situ transesterification reaction, oil seed particles preparation and treatment, quantification of oils present in the oil seed particles, investigation of physical and chemical properties of oils such as free fatty acids content, fatty acid composition, saponification value, iodine value, viscosity, density and heating value need to be conducted.

i. Particle preparation and oil content of jatropha curcas seeds

The ground and graded jatropha curcas seed particles in the size range of 300 to 500μm (with an average particle size of 400μm) were dried to reduce the moisture content to the extent possible. The moisture content of the dried seed particles was found to be 1.3±0.17% w/w. The oil content of jatropha curcas seeds was investigated using hexane as an extraction solvent in soxhlet apparatus. Amount of oil extracted depended on the extraction time as well as volume of hexane used per gram of oil seed particles. Observations on the amount of oil extracted with time for five ratios of hexane to weight of oil seed particles in ml/g are shown in Figure 4.1. Oil extraction experiments were done in duplicate for every data point to observe its reputability. Maximum amount of oil was extracted in 2 h for hexane to oil seed particles ratio greater or equal to 7.5 ml/g. The average oil content in the jatropha curcas seed particles was found to be 52.8±0.16% w/w. The oil content investigated in the present study was in the range of the values of the oil content of jatropha curcas seeds reported elsewhere ranging from 35 to 60% [31, 35, 53, 199].

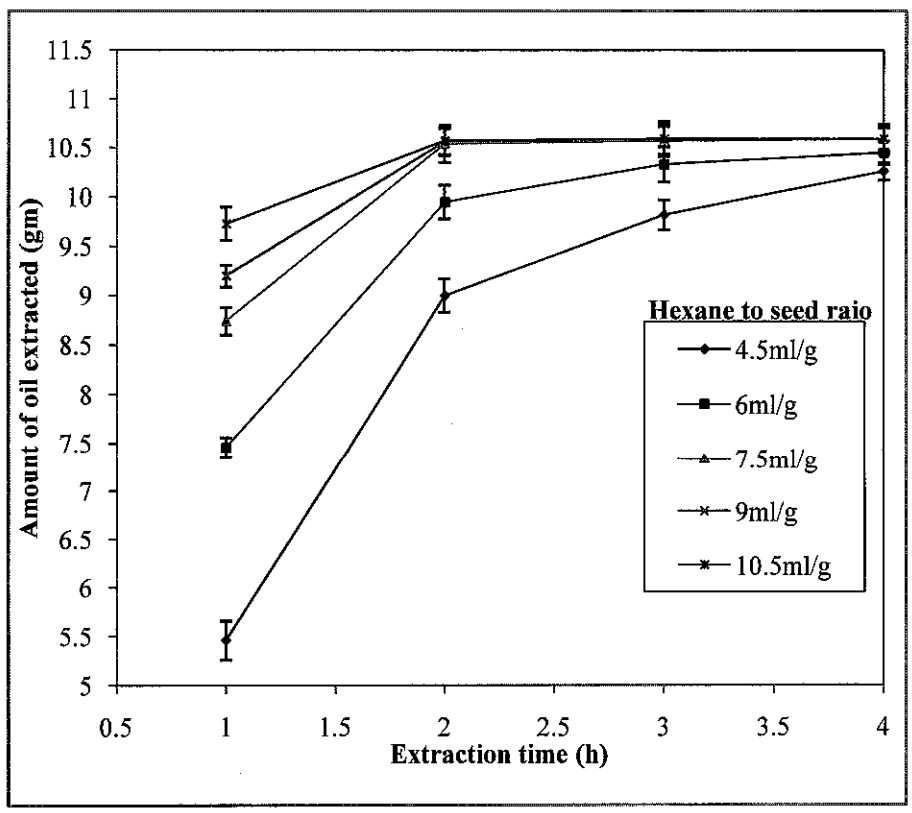


Figure 4.1: Oil extracted from 20 g of jatropha curcas particles as a function of time at different hexane to seed ratio

ii. Oil Characteristics

The physical and chemical properties of jatropha curcas oil were evaluated prior to in-situ transesterification reaction as presented in Table 4.1. The acid value was found to be 1.67 ± 0.03 mg KOH/g and the corresponding free fatty acid percentage of the oil was 0.67%. The acid value was within the range (1.391 to 3.8 mg KOH/g) reported in the literature [31, 53, 199]. The FFA content of jatropha curcas oil of the present study was low as compared to the FFA content of jatropha curcas oil commercially available after extraction and purification of oils from the seeds. The reason is that majority of the fatty acid content of jatropha oil is unsaturated oleic acid (47 %) and linoleic acid (33.4 %) which can easily oxides and converted to FFA during oil extraction purification and storage upon exposure to light and moisture resulting in high FFA of jatropha oil. In the present work, in order to avoid such unwanted FFA formation, jatropha curcas oil seeds were stored in amber color bottle to avoid photo-oxidation and the seeds were used directly for transesterification such that the possibility of formation of FFA by photo-oxidation was minimized. The low FFA percentage of jatropha oil of this study (0.67%) which was less than 2% demonstrates alkaline catalysts such as NaOH can be used to catalyze the reaction [11, 14, 98]. Thus, in the present work, NaOH was employed as alkaline catalyst. Table 4.1 presents the physical and chemical properties of jatropha curcas oil of the present work.

Table 4.1: Physicochemical properties of jatropha curcas oil

Property	**Unit**	**Quantity**
Acid value	mg KOH/g	1.67
Free fatty acid	%	0.67
Saponification Value	mg KOH/g	201.82
Iodine value	mg I_2/g Oil	101
Kinematic viscosity at 40°C	mm^2/s	29.13
Specific gravity at 25°C	-	0.91
Calorific Value	cal/g	9297

a) Fatty acid compositions

The fatty acid profile of jatropha curcas oils used in the present work was investigated. Table 4.2 presents composition of jatropha curcas oil in terms of fatty acid type, its molecular formula, systematic name, structure and compositions. Present observations on composition of jatropha oil compare well with the observations of other investigators [31, 56-59] as shown in Table 4.3. Jatropha oil contains mostly unsaturated fatty acids [oleic acid (46.7%) and linolenic acid (33.4%)] and hence is a good candidate for biodiesel production [61].

Table 4.2: Fatty acid composition of jatropha curcas oil of the present study

Fatty acid	Formula	Systematic Name	Structure	% Amount
Mystric acid	$CH_3(CH_2)_{12}COOH$	Tetradecanoic Acid	C14:0	0.14
Palmitic acid	$CH_3(CH_2)_{14}COOH$	Hexadecanoic acid	C16:0	12.9
Stearic acid	$CH_3(CH_2)_{16}COOH$	Octadecanoic acid	C18:0	6.2
Oleic acid	$CH_3(CH_2)_7–CH_5CH = (CH_2)_7COOH$	Cis9-Octadecanoic acid	C18:1	46.7
Linoleic acid	$CH_3(CH_2)_4$ CH=CH–CH_2–CH=CH–$(CH_2)_7COOH$	cis-9- cis-12-Octadecadeneoic acid	C18:2	33.4
Linolenic acid	$CH_3(CH_2)_4CH=CH–CH_2–CH=CH–CH_2–CH=CH–(CH_2)_4COOH$	cis-6-cis-9-cis-12 Octadecatrienoic acid	C18:3	0.2
Arachidice acid	$CH_3–(CH_2)_{18}COOH$	Eicosanoic acid	C20:0	0.2

Table 4.3: Fatty acid compositions of jatropha oils as compared to investigated by different researchers

Fatty acid	structure	Formula	Molecular weight	% mass*	% mass[31]	% mass[56]	% mass[57]	% mass[58]	% mass[59]
Myristic acid	14 : 0	$C_{14}H_{28}O_2$	228.38	0.14	0.12	-	-	-	-
Palmitic acid	16 : 0	$C_{16}H_{32}O_2$	256.43	12.9	19.5	17.4	14.1	13.73	15.18
Palmitolic acid	16:1	$C_{16}H_{30}O_2$	258.25	-	-	-	-	-	0.99
Stearic acid	18 : 0	$C_{18}H_{36}O_2$	284.48	6.2	6.8	6.0	6.7	5.79	
Oleic acid	18 : 1	$C_{18}H_{34}O_2$	282.47	46.7	41.3	50.3	47	42.37	41.17
Linoleic acid	18 : 2	$C_{18}H_{32}O_2$	280.45	33.4	31.4	23.2	31.6	37.52	31.25
Linolenic acid	18 : 3	$C_{18}H_{30}O_2$	278.43	0.2	0.2	-	-	0.59	0.08
Arachidic acid	20:0	$C_{20}H_{40}O2$	312.14	0.2	0.12	-	-	0.09	-

* Fatty acid composition of jatropha curcas oil of the present work

4.3 In-situ transesterification reaction using phase transfer catalysis

In-situ transesterification of jatropha seed particles with alkaline (NaOH) methanol to fatty acid methyl esters (FAME) and in-situ transesterification of jatropha seed particles with alkaline (NaOH) ethanol to produce fatty acid ethyl esters (FAEE) were investigated as presented in section 4.3.1. Catalytic performances of cetyltrimethylammonium bromide (CTMAB), benzyltrimethylammonium hydroxide (BTMAOH) and crown ether (CE) as phase transfer catalyst were compared in section 4.3.2 to identify the better one of these for in-situ transesterification of jatropha seed particles to produce FAME/FAEE. Response surface methodology technique was used to identify optimum reaction conditions of alkaline in-situ transesterification to produce FAME or FAEE in presence of better PTC identified in section 4.3.2 and the results were presented and discussed in section 4.3.3.

4.3.1 In-situ transesterification using cetyltrimethylammonium bromide as a phase transfer catalyst

As solubility of vegetable oils in methyl or ethyl alcohols is very limited, application of a phase transfer catalyst such as cetyltrimethylammonium bromide (CTMAB) may help to increase reaction rates [200]. The transesterification reaction is affected by process variables such as

- Ratio of catalyst concentrations (CTMAB/ NaOH),
- Amount of alcohols (methanol or ethanol) per gram of seed particles,
- Reaction temperature, agitation speed and reaction time.

Effect of each of these variables was studied while keeping the rest of the variables constant to identify the best values that gave maximum yield for both in-situ methanolysis and in-situ ethanolysis reaction. The results are presented in the following sections:

4.3.1.1 Effect of molar ratio of CTMAB to alkaline catalyst (NaOH)

The catalytic effect of CTMAB was investigated by varying the molar ratio of CTMAB to NaOH while keeping alcohol (methanol/ethanol) to jatropha curcas seed particles ratio, NaOH to jatropha curcas seed ratio, reaction temperature, stirrer speed and reaction time constant as presented in table 4.4.

Table 4.4: Reaction condition of in-situ methanolysis and in-situ ethanolysis of jatropha curcas seed particles at different CTMAB to NaOH molar ratio.

Reaction Variables	**Unit**	**Quantity**
CTMAB/NaOH	mol/mol	0:1, 0.5:1, 1:1, 1.5:1, 2:1 and 2.5:1
NaOH/Jatropha Seed Particles	%w/w	0.675
Alcohol/Jatropha seed	ml/g	7.5:1
Reaction Temperature	^{o}C	30
Mixing Speed	rpm	300
Reaction time	min	150

Figure 4.2 shows the effect of CTMAB on the yield of FAME and FAEE. For in-situ methanolysis, the yield of FAME increased from 47.2 to 88.2% w/w when the molar ratio of CTMAB to NaOH increases from 0:1 to 1.5:1. Further increasing the concentration of CTMAB beyond 1.5:1 has no significant effect on the yield of FAME. Similarly, for in-situ ethanolysis reaction, in the absence of CTMAB, the extraction of oil and its conversion to FAEE was the lowest as shown in the Figure 4.2. However, addition of CTMAB increased the yield of FAEE significantly and the yield increased with increasing the concentration of CTMAB. Thus, it was noted that in the absence of CTMAB, the maximum yield of FAEE achieved was 88.2% w/w; however, a maximum FAEE yield of 99.2% w/w was produced at 1 molar ratio of CTMAB to NaOH. Further increasing the concentration of CTMAB beyond 2mol/mole of NaOH slightly reduced the yield. It was also observed that as compared to in-situ methanolysis, better yield of esters were obtained by in-situ ethanolysis due to better solubility of ethanol as compared to the solubility of methanol in oil.

Increase in the yield of FAME and FAEE were due to the effect of CTMAB acting as catalyst to deprotonate hydrogen ion to produce a reactive state alcohol-oxide ions and also acting as a phase transfer catalyst to transfer the alcoho-oxide ion from the alcohol phase to the oil phase where it can easily reacts with triglycerides in the oil phase. Thus, the cation of CTMAB ($C_{19}H_{42}N^+$, abbreviated as Q^+) is helping as an intermediate carrier agent to facilitate the transfer of anions of alcohol-oxide (CH_3O^- and $C_2H_5O^-$) from polar methanol/glycerol phase into the non-polar oil phase in the seed where reactive-extraction takes place between transferred reactant anions (CH_3O^- and $C_2H_5O^-$) and TG followed by transfer of diglycerides anions ($CH_2COOR_3CHCOOR_2CH_2O^-$, abbreviated as DG^-) to the bulk alcohol/glycerol phase with the PTC cations as carrier agent (the detail mechanisms and reaction kinetics of PTC assisted in-situ transesterification reaction is described in chapter five).

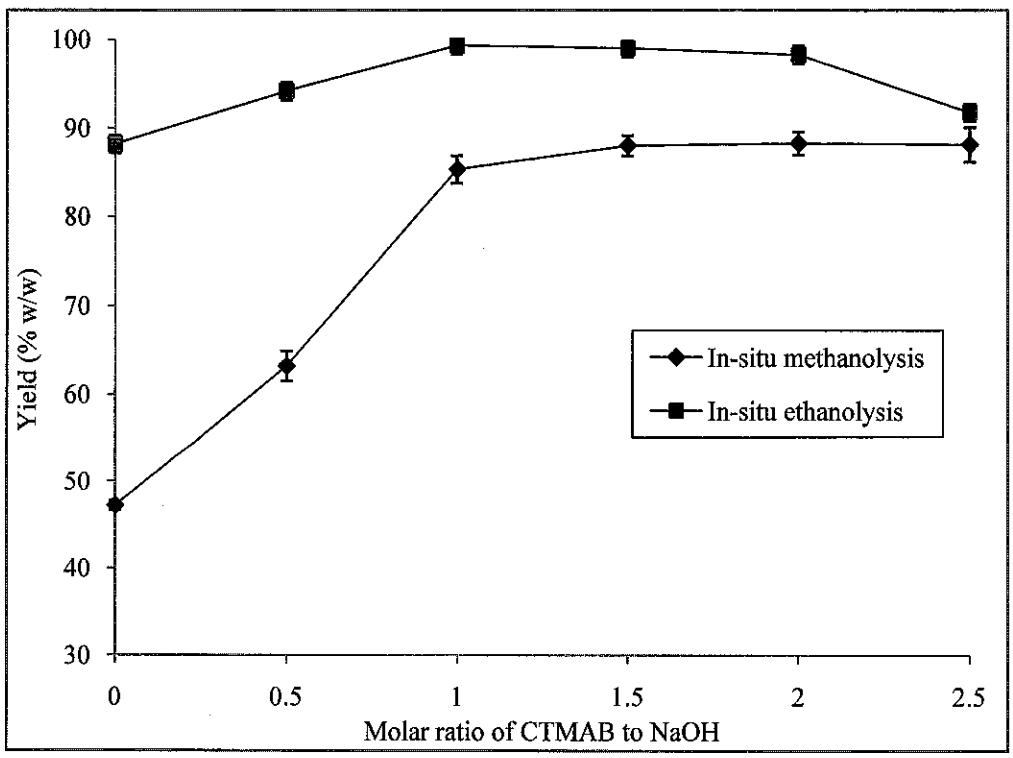


Figure 4.2: Effect of molar ratio of CTMAB to NaOH on FAME and FAEE yields

4.3.1.2 Effect of ratio of NaOH to jatropha curcas seed particles

In the present study, NaOH was used as alkaline catalyst and its catalytic contribution was investigated while it was used with PTC to enhance the rate of reaction. The reaction was carried out by varying the concentration of NaOH to jatropha curcas seed particles (% w/w) while keeping constant other operating condition as shown in Table 4.5.

Table 4.5: Reaction condition of in-situ methanolysis and in-situ ethanolysis of jatropha curcas seed particles at different NaOH to jatropha curcas seeds weight ratio.

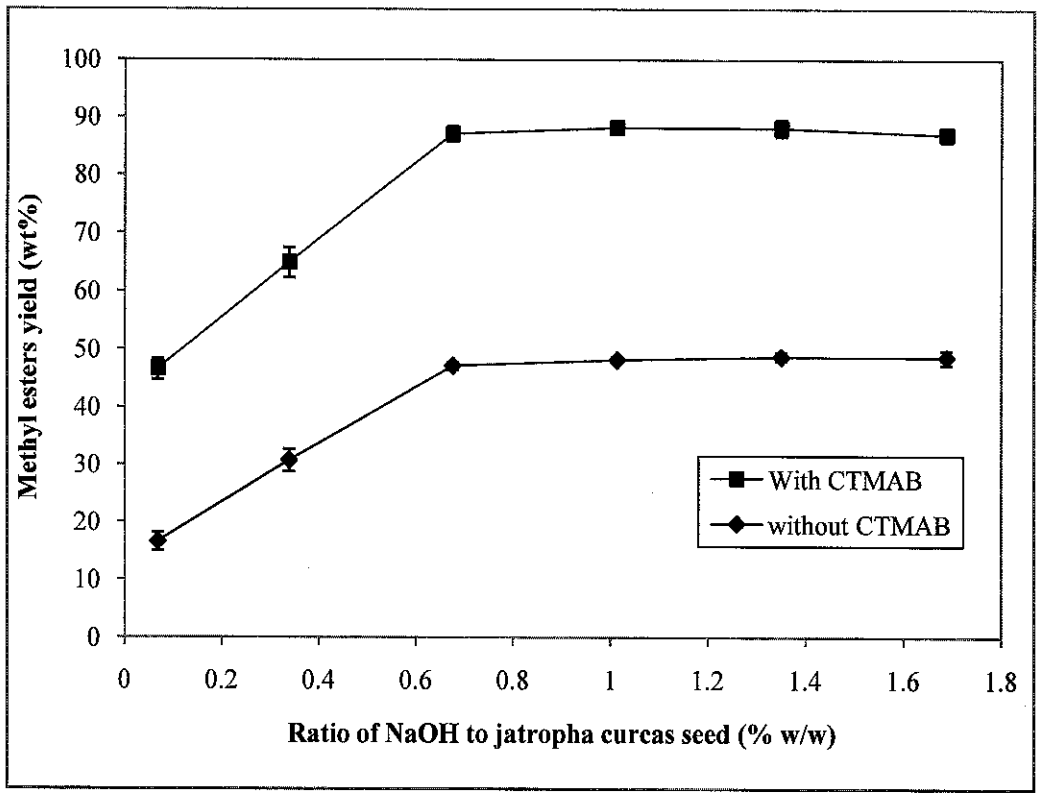
Reaction Variables	**Unit**	**Quantity**
CTMAB/NaOH	mol/mol	1.5:1
NaOH/Jatropha Seed	% w/w	0.068, 0.334, 0.675, 1.013, 1.334 and 1.68
Alcohol/Jatropha seed	ml/g	7.5:1
Reaction Temperature	°C	30
Mixing speed	rpm	300
Reaction time	min	150

The yields of FAME and FAEE as a function of the concentration of NaOH are shown in Figure 4.3 (a) and (b), respectively. For comparison, the effect of ratio of NaOH to jatropha curcas seed (% w/w) in the absence of CTMAB on the yield of FAME and FAEE are also shown in the respective figures.

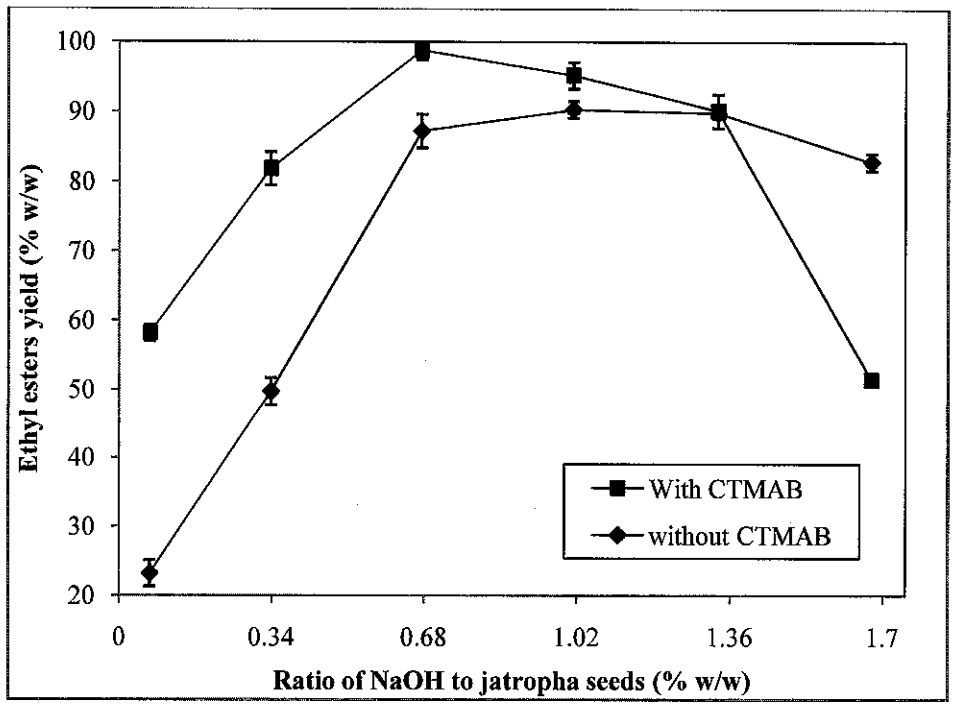
In the absence of CTMAB, the highest yield of FAME obtained was 48.2% w/w at NaOH concentration of 1.334% w/w where as in presence of CTMAB, highest yield of FAME achieved was 88.5% w/w at a NaOH concentration of 1.013% w/w. The result demonstrated that reactions assisted by CTMAB gave advantage of 40.3% w/w increments in yield of FAME and at the same time use of CTMAB reduced the consumption of NaOH by 24.3% w/w. Similarly for in-situ ethanolysis (Figure 4.3 (b)), the yield of FAEE increased with increasing the concentration of NaOH from 0.068 up 0.675% w/w for a reaction assisted by CTMAB. Further increasing the concentration of NaOH to 1.034, 1.334 and 1.68% w/w has a slight negative impact since saponification reaction is favored at high concentration of NaOH. For a reaction

conducted only using alkaline catalyst NaOH, the yield of FAEE increased by increasing the concentration of NaOH up to 1.013% w/w. While comparing the yield of FAEE at the two conditions, in the absence of CTMAB, highest yield of FAEE was 89.1% w/w at a NaOH concentration of 1.013% w/w where as in the presence of CTMAB, highest yield of FAEE produced was 98.8% w/w at NaOH concentration of 0.675% w/w. Hence, reactions assisted by CTMAB gave advantage of 9.7% w/w increment in yield and at the same time use of CTMAB reduced the consumption of NaOH by 33.3% w/w.

Further increasing the concentration of NaOH beyond 1.013% w/w for a reaction in the presence of CTMAB and 1.334% w/w for a reaction without CTMAB did not have significant impact on FAME yield and a slight decrease in yield was observed due to the formation of emulsion. At higher concentration of NaOH saponification reaction could be favored resulting in formation of soap the undesirable product that could increase the viscosity of the reaction components in the reactor causing difficulties during separation processes and lose of biodiesel. During the present experiment at high concentration of NaOH, formation of soap was observed causing the formation of emulations in the reaction mixture while affecting the separation processes. Large amount of water was consumed in order to wash the product several times to remove traces of soap and other impurities.



a) In-situ methanolysis



b) In-situ ethanolysis

Figure 4.3: Effect of ratio of NaOH to jatropha curcas seed (% w/w) on FAME and FAEE yields

4.3.1.3 Effect of ratio of methanol to jatropha curcas seed

Transesterification reaction is a reversible reaction; excess amount of alcohol is required to drive the reaction in the forward direction. In-situ transesterification proceeds through dissolution and alcoholysis of oil whereby sufficient amount of alcohol is required for effectively extracting the oil and shift the reaction in the forward direction. During in-situ transesterification reaction, more alcohol is required than conventional transesterification reaction as alcohol acts both as extraction solvent and reaction reagent [186]. In the present study, effect of volume of methanol and ethanol were investigated by varying the ratio of methanol (ethanol) to jatropha curcas seed particles (ml/g) as 3:1, 4.5:1, 6:1, 7.5:1, 9:1 and 10.5:1 while keeping all other reaction variables constant as presented in Table 4.6.

Table 4.6: Reaction condition of in-situ methanolysis and in-situ ethanolysis of jatropha curcas seed particles at different volume of methanol to weight of jatropha curcas seeds

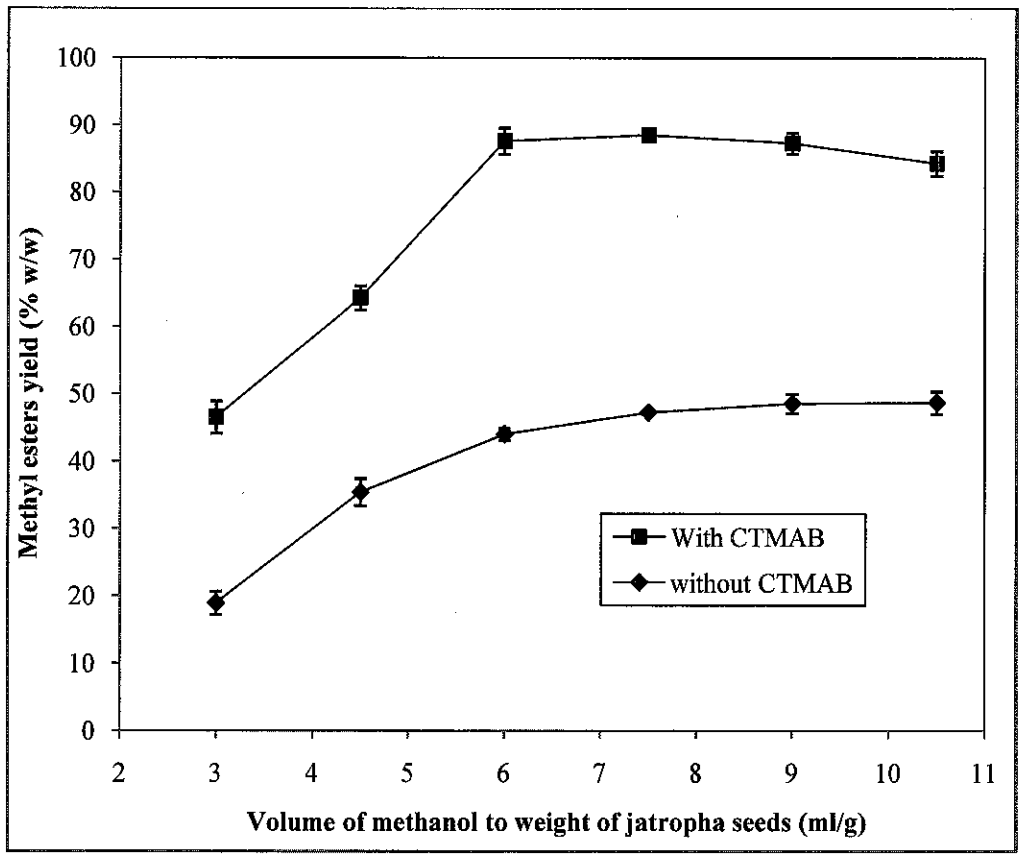
Reaction Variables	**Unit**	**Quantity**
CTMAB/NaOH	mol/mol	1.5:1
NaOH/Jatropha Seed Particles	% w/w	1.013
Alcohol/Jatropha seed	ml/g	3:1, 4.5:1, 6:1, 7.5:1, 9:1 and 10.5:1
Reaction Temperature	^{o}C	30
Mixing speed	rpm	300
Reaction time	min	150

Figure 4.4 (a) and (b) present the effect of ratio of methanol to jatropha curcas seed particles on the yield of FAME and FAEE in the presence of CTMAB, respectively. For comparison, the effects of ratio of volume of methanol and ethanol to weight of jatropha curcas seed particles on the yield of FAME and FAEE in the absence of CTMAB are also shown in the respective Figures. For in-situ methanolysis reaction (Figure 4.4 (a)), at lower volume of methanol to jatropha seed weight ratio, low yield of FAME was observed both in the presence of CTMAB and in the absence of CTMAB. The reason may be the solvent quantity is inadequate to extract the oil and conduct transesterification reaction. Increasing the amount of methanol in the

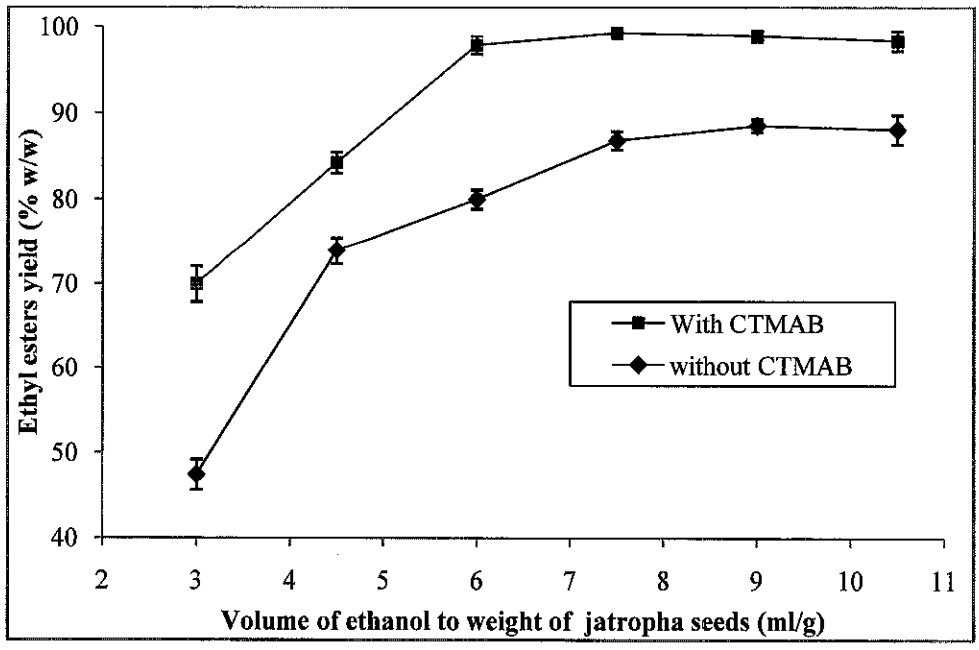
reaction mixture increases the yield of FAME; in the absence of CTMAB, highest FAME yield of 48.6% w/w was obtained at ratio of methanol to jatropha seed particles of 9ml/g. In the presence of CTMAB, highest yield of FAME of 88.5% w/w was achieved at methanol to jatropha curcas seed particles ratio of 7.5ml/g. The comparison of the two conditions showed that reactions assisted by CTMAB gave 39.9% w/w additional yield of FAME and reduced the consumption of methanol by 16.7%.

Similarly for in-situ ethanolysis (Figure 4.4 (b)), the yield of FAEE increased with increasing the volume of ethanol and the maximum FAEE yield of 88.5% w/w was synthesized in the absence of CTMAB at ratio of ethanol to jatropha curcas seed of 9ml/g. Similarly, in the presence of CTMAB, the yield increases with increasing the volume of ethanol and reaches a maximum yield of 99.3% w/w at a ratio of ethanol to jatropha seed particles of 7.5ml/g. In both conditions further addition of ethanol beyond the maximum value slightly decreased the yield due to solubility and catalyst dilution. It was observed that use of CTMAB as a PTC gave 10.8% w/w additional yield of FAEE and reduced the consumption of ethanol by 16.7%.

Further overloading of methanol in the reaction mixture has slightly reduced the yield of FAME. This was occurred presumably due to the decreases in the concentration of catalyst at large volume of methanol, increases the solubility of FAME into the glycerol phase that could affect the separation processes as observed during the experiment. At excessive volume of alcohol, loss of the biodiesel with the glycerol and ultimately reducing the yield of FAME was observed.



a) In-situ methanolysis



b) In-situ ethanolysis

Figure 4.4: Effect of ratio of methanol (ethanol) to jatropha curcas seed particles (ml/g) on FAME/FAEE yields

4.3.1.4 Effect of reaction temperature

Reaction temperature is one of significant variable that influence the rate of reaction. Five different temperatures (30, 40, 50, 60 and 70°C) were used in the experiment to study the influence of reaction temperature during in-situ methanolysis and in-situ ethanolysis of jatropha curcas seed particles using CTMAB as a PTC together with NaOH as alkaline catalyst. The experiments were also conducted with only NaOH at the same reaction conditions for comparison while keeping all other reaction parameters constant as shown in Table 4.7.

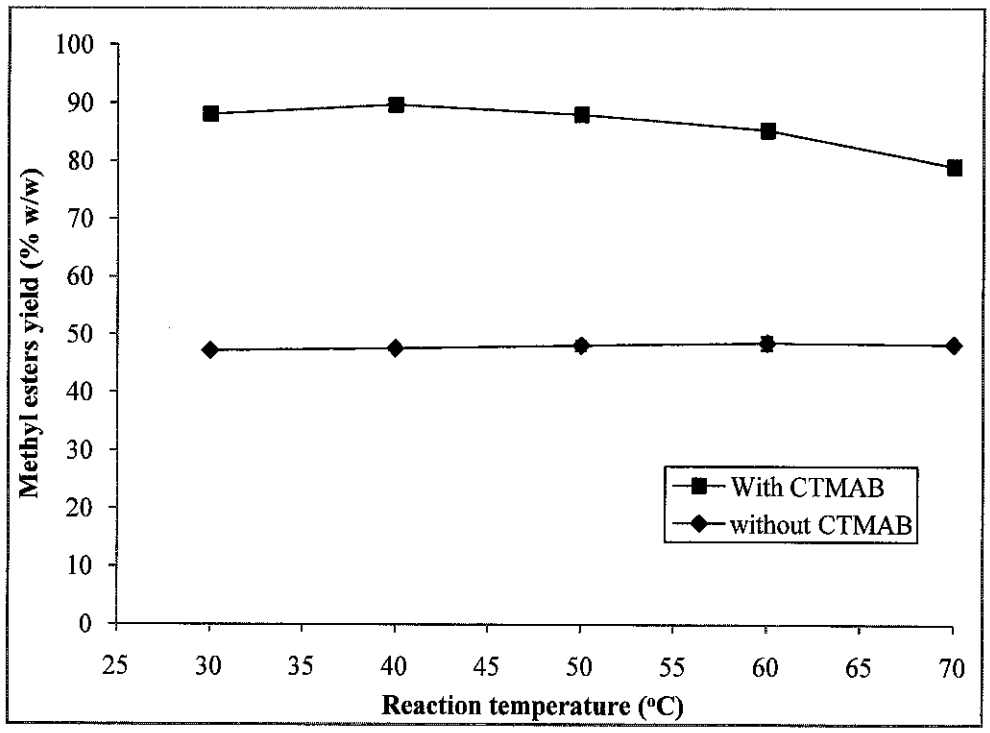
Table 4.7: Reaction condition of in-situ methanolysis and in-situ ethanolysis of jatropha curcas seed particles at different reaction temperature

Reaction Variables	**Unit**	**Quantity**
CTMAB/NaOH	mol/mol	1.5:1
NaOH/Jatropha Seed Particles	% w/w	1.013
Alcohol/Jatropha seed	ml/g	7.5:1
Reaction Temperature	°C	30, 40, 50, 60 and 70
Mixing speed	rpm	300
Reaction time	min	150

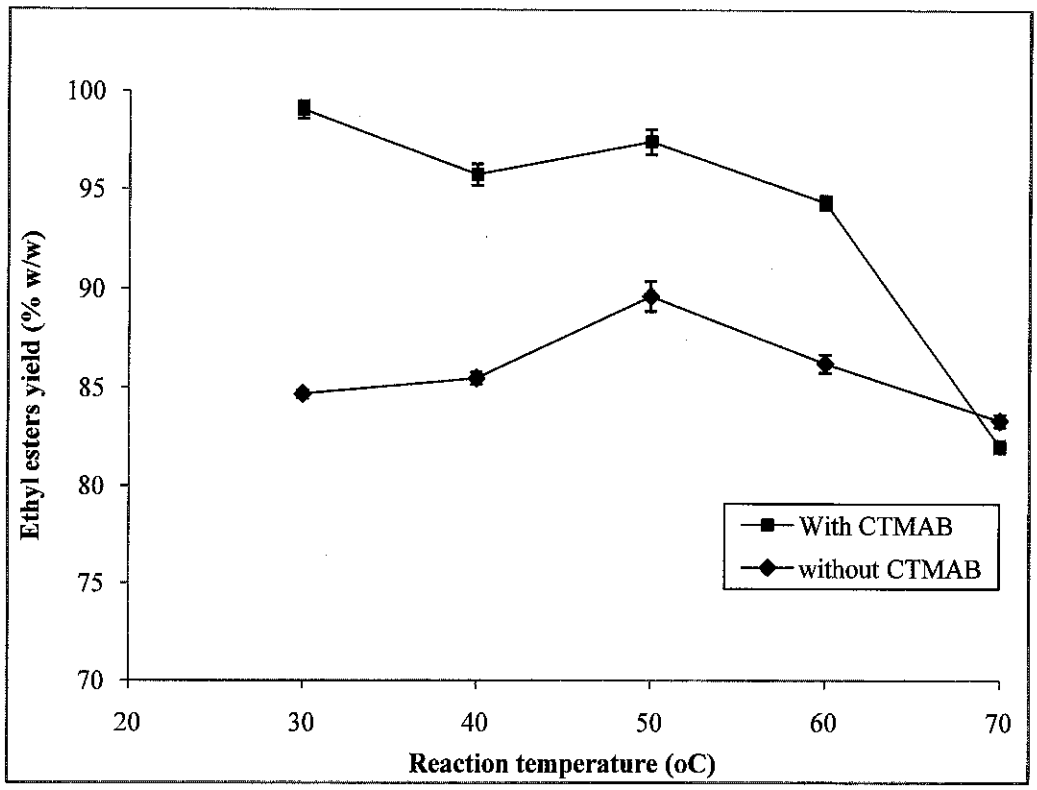
The effect of reaction temperature on the yield of FAME and FAEE in the presence and absence of CTMAB are shown in Figure 4.5 (a) and (b), respectively. As depicted in the Figure 4.5 (a) for in-situ methanolysis, reaction temperature has little influence on the extraction and conversion of triglycerides present in the jatropha curcas seed particles assisted by both CTMAB as a PTC and alkaline catalyst NaOH. Highest FAME yield of 88.8% w/w was achieved at a reaction temperature of 40°C. Increasing the reaction temperature to 50, 60 and 70°C slightly decreased the yield of FAME. On the other hand for a reaction conducted only with the help of alkaline catalyst (NaOH) the effect of temperature was relatively significant; the yield of FAME was increased with increasing the reaction temperature from 30 to 60°C. 49% w/w FAME yield was obtained at a reaction temperature of 60°C. Further increasing the reaction temperature to 70°C does not have significant effect on the yield of FAME. The results of the investigation (Figure 4.5 (a)) showed

as compared to in-situ methanolysis without CTMAB, reactions assisted by CTMAB gave 39.8% w/w additional yield of FAME and reduced the reaction temperature to 40°C.

Similarly for in-situ ethanolysis (Figure 4.5 (b)), maximum FAEE yield of 99.4% w/w was achieved at a reaction temperature of 30°C. Further increasing the reaction temperature slightly reduced the yield of FAEE. On the other hand for a reaction conducted only with the help of alkaline catalyst, the yield of FAEE increased with increasing the reaction temperature from 30 to 50°C and a maximum FAEE yield of 89.7% w/w was achieved at a reaction temperature of 50°C. It was observed that reactions assisted by CTMAB gave 11.3% w/w additional yield of FAEE and reduced the reaction temperature to room temperature. Hence, conducting a reaction at room temperature has an added advantage as it eliminates extra energy cost and the process operation at ambient temperature eliminates the risk of high temperature operation. The decrease in yield can be due to at higher temperature saponification of glycerides by the alkali catalyst is much faster than the methanolysis reaction[172].



a) In-situ methanolysis



b) In-situ methanolysis

Figure 4.5: Effect of reaction temperature (°C) on FAME and FAEE yields

4.3.1.5 Effect of mixing speed

To ascertain the effect of mixing rate on the mass transfer resistances between methanol and jatropha curcas oil, the speed of agitations was varied from 200rpm to 700rpm at an interval of 100rpm. During the experiment, all the rest of the reaction variables were kept constant as presented in Table 4.8.

Table 4.8: Reaction condition of in-situ methanolysis and in-situ ethanolysis of jatropha curcas seed particles at different agitation speed

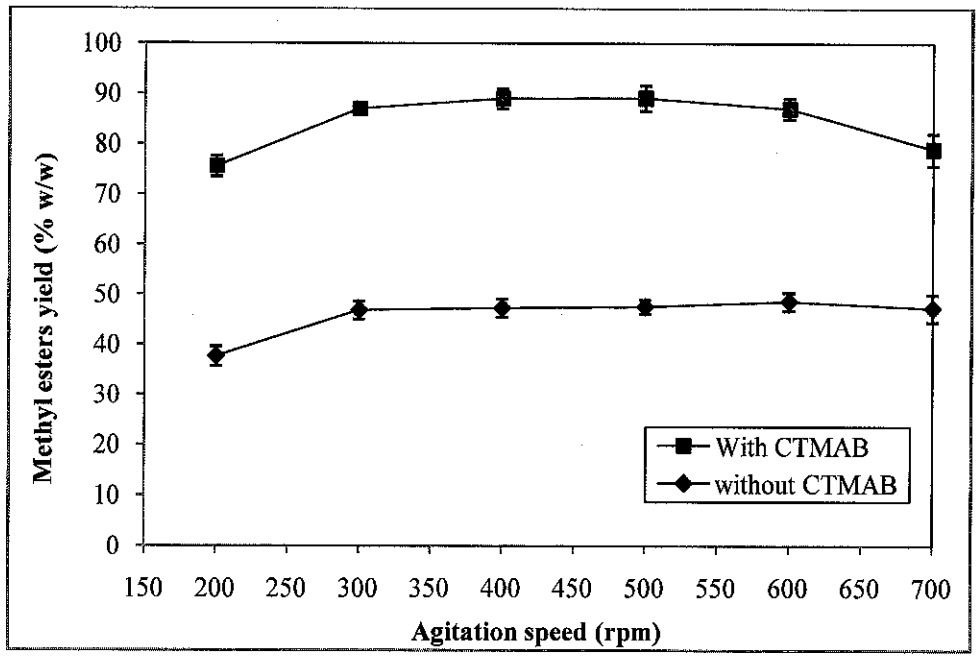
Reaction Variables	**Unit**	**Quantity**
CTMAB/NaOH	mol/mol	1.5:1
NaOH/Jatropha Seed Particles	% w/w	1.013
Alcohol/Jatropha seed	ml/g	7.5:1
Reaction Temperature	°C	40 (for in-situ methanolysis) and 30 (for in-situ ethanolysis)
Mixing speed	rpm	200, 300, 400, 500, 600 and 700
Reaction time	min	150

Figure 4.6 (a) and (b) presents the effect of mixing speed on the yield of FAME and FAEE in the presence of CTMAB and absence of CTMAB while using NaOH as alkaline catalyst, respectively. At lower mixing rate, there was lower formation of FAME and FAEE; for both in-situ methanolysis and in-situ ethanolysis, yields increased with increasing the mixing speed. For in-situ methanolysis (Figure 4.6 (a)), in the absence of CTMAB, highest yield of FAME achieved was 49.2% w/w at a mixing speed of 600rpm. In the presence of CTMAB, highest yield of FAME observed was 89% w/w at a mixing speed of 400rpm. Hence, reactions assisted by CTMAB gave 39.8% w/w additional yield of FAME and reduced the mixing speed by 200rpm.

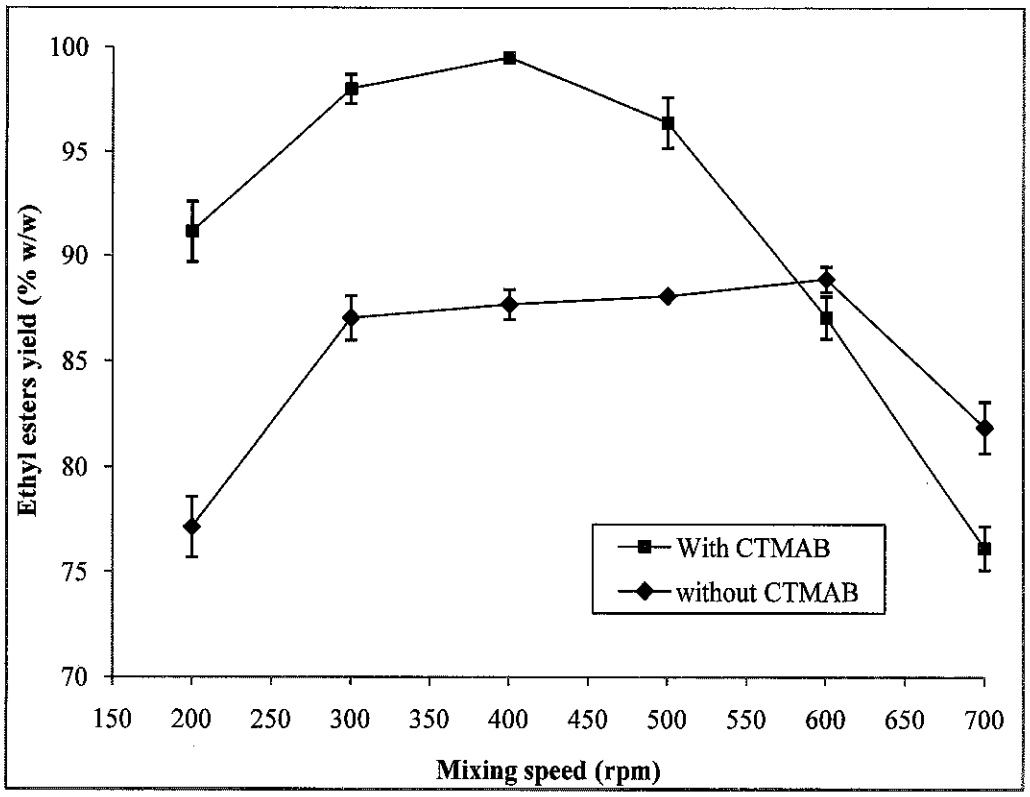
Similarly for in-situ ethanolysis (Figure 4.6 (b)), in the presence of CTMAB, highest yield of FAEE of 99.5% w/w was attained at a mixing speed of 400 rpm. However, increasing the mixing rate beyond 400 rpm has a negative response on the

yield of FAEE and the yield declined unexpectedly. In the absence of CTMAB, highest yield of FAEE achieved was 88.4% w/w at a mixing speed of 600rpm. Similarly, for a reaction assisted by only NaOH, increasing the mixing speed greater than 600rpm has shown a decline in the yield of FAEE.

While comparing the effect of CTMAB as a PTC on the agitation speed of transesterification, reactions assisted by CTMAB gave 11.1% w/w additional yield and reduced the mixing speed by 200rpm. It might be said that the mass transfer can be a controlling step up to 600rpm for a reaction without CTMAP and 400rpm for a reaction with CTMAB. Beyond 600rpm (without CTMAM) and 400rpm (with CTMAM), reaction kinetics might be the controlling step as mass transfer limitation can be minimized. The results of the experiment also indicated high mixing rate requires shorter reaction time.



a) In-situ methanolysis



b) In-situ ethanolysis

Figure 4.6: Effect of mixing speed (rpm) on FAME and FAEE yields

4.3.1.6 Effect of reaction time

The reaction time has significant effect on the conversion of triglycerides and yields of FAME and FAEE. Generally sufficient reaction time must be provided to ensure the reaction completion and better formation of FAME and FAEE yields during reactive-extraction process. Lower reaction time do not promote sufficient interaction of the reacting mixture as the methanol needs to be dispersed into the oil seed particles to carry out effective extraction and reaction mechanism. Thus, in the present study, the effect of reaction time was investigated by varying the reaction time from 30 to 240 minutes with an increment of 30 minutes. Other reaction parameters were kept constant as presented in Table 4.9. The reactions were repeated using only NaOH as alkaline catalyst for comparison of the effect of CTMAB on the speed of reaction.

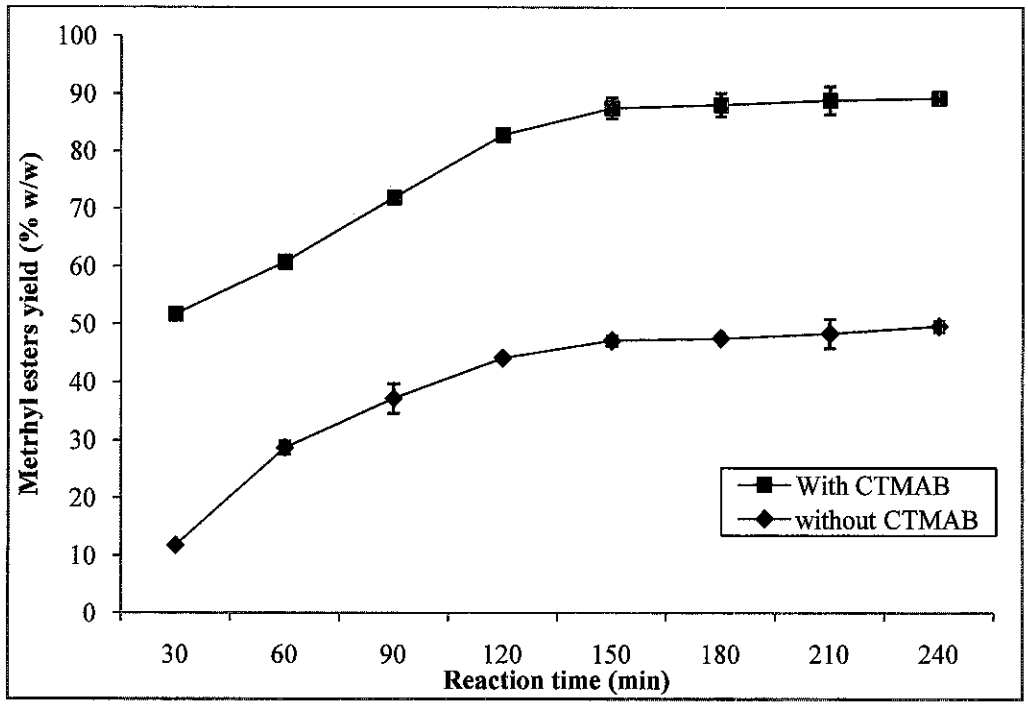
Table 4.9: Reaction condition of in-situ methanolysis and in-situ ethanolysis of jatropha curcas seed particles at different reaction times

Reaction Variables	**Unit**	**Quantity**
CTMAB/NaOH	mol/mol	1.5:1
NaOH/Jatropha Seed	% w/w	1.013
Alcohol/Jatropha seed	ml/g	7.5:1
Reaction Temperature	°C	40
Mixing speed	rpm	400
Reaction time	min	30, 60, 90, 120, 150, 180, 210 and 240

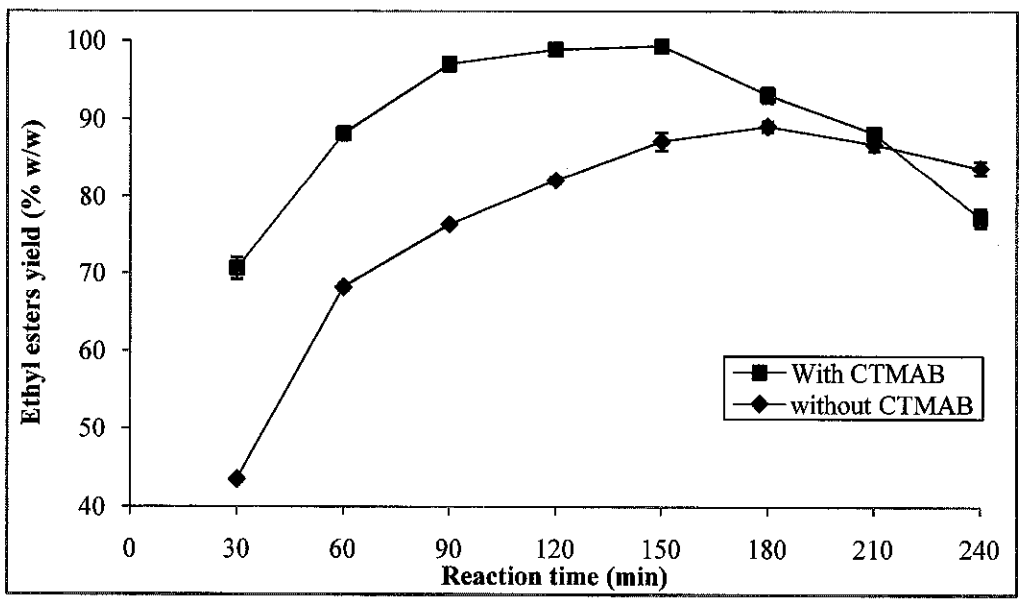
The plots of FAME and FAEE yields versus reaction time in the presence of CTMAB as a PTC and NaOH as alkaline catalyst as well as the yields of FAME and FAEE with a reaction assisted by only NaOH as alkaline catalyst are shown in Figure 4.7 (a) and (b) for comparison of the two conditions, respectively. In the range of reaction time under study, for in-situ methanolysis (Figure 4.7 (a)), increasing the reaction time increased the formation of FAME. In the absence of CTMAB, highest yield of FAME was 49.7% w/w at a reaction time of 240 minutes. In the presence of CTMAB, highest yield of FAME was 89.2% w/w at a reaction time of 180 minutes. Further increasing the reaction time does not have significant effect on the yield of FAME. Hence, reactions assisted by CTMAB gave 40.5% w/w additional yield of FAME and reduced the reaction time. Thus, for in-situ transesterification without CTMAB substantial amount of oil is either not extracted or transesterified, however use of CTMAB as a PTC has helped to extract about 90% of the oil from the seed with simultaneously transesterifying triglycerides to produce FAME.

Similarly, in-situ ethanolysis of jatropha curcas demonstrated, in the absence of CTMAB, highest yield of FAEE achieved was 89.2% w/w at a reaction time of 180 minutes. However, in the presence of CTMAB, highest yield of FAEE observed was 99.5% w/w at a reaction time of 150 minutes. The result exhibited reactions assisted by CTMAB gave 10.3% w/w additional yield of FAEE and reduced the reaction time by 30 minutes. As observed in the Figure 4.7 (b), further increasing of the reaction time has a negative impact resulting in a slight reduction in the yield of FAEE due to

side product formation caused by overheating of the mixture for extended long reaction period. It also resulted in loss of solvent and energy when the reaction time was extended beyond the optimum value.



a) In-situ methanolysis



b) In-situ methanolysis

Figure 4.7: Effect of the reaction time (minutes) on FAME yield

In summary, when the reaction is catalyzed using alkaline (NaOH) catalyst alone, the extraction of triglycerides and its conversion to FAME was very low. The maximum FAME yield produced while using alkaline catalyst was around 50% w/w. The result indicates that there was a substantial amount of oil either not extracted or not converted to biodiesel. However, when CTMAB was used as a PTC together with alkaline catalyst NaOH, high yield of FAME (about 90% w/w) was achieved at a reduced consumption of methanol, concentration of NaOH and reaction time. This demonstrated that the use of CTMAB as a PTC in conjunction with alkaline catalyst is a good approach for biodiesel synthesis using in-situ methanolysis method.

Unlike in-situ methanolysis, during in-situ ethanolysis in the absence of CTMAB as a PTC high yield of FAEE (about 90% w/w) was produced using only NaOH as alkaline catalyst as compared to about 50% w/w of FAME yield produced when the reaction was catalyzed by NaOH alone. This is due to the relatively high solubility of ethanol in oil as compared to the low solubility of methanol. A similar investigation was reported by Kildiran et al [3] on the in-situ transesterification of soybean oil using sulfuric acid catalyst and different type of alcohols such as methanol and ethanol. It was reported that during in-situ transesterification the maximum amount of methyl esters synthesized from the extracted oil was only 42% when methanol was used as a reactive extraction agent. On the other hand, they reported that when ethanol was used the oil extracted and produced ethyl esters were 80.9%. They concluded methanol is poor solvent of oil since the oil dissolved in it is less than those of others types of alcohols such as ethanol, n-propanol and n-butanol. Thus, the solubility of triglycerides increases in alcohol with increasing the alcohol chain-length and higher biodiesel would be obtained when long chain alcohol is used during in-situ transesterification reaction. A similar investigations were also reported by Georgiani et al [182] and Ginting [31]. In the present investigation, ethanol is identified as a better reactive-extraction agent as compared to methanol.

However use of CTMAB as a PTC has significantly increased reactive-extraction of jatropha curcas oil both during in-situ methanolysis and in-situ ethanolysis reaction by increasing the yield of FAME from about 50% w/w to about 90% w/w and the

yield of FAEE from about 90% w/w to about 99.5% w/w, respectively. Use of CTMAB has also reduced the concentration of NaOH (by 33.3%), volume of alcohol (16.7%) and mixing speed (by 200rpm) while conducting the reaction at room temperature in a reduced reaction time.

4.3.2 Catalytic effect of different PTCs in comparison with alkaline catalyst

Encouraged by the promising results of cetyltrimethylammonium bromide (CTMAB) as a PTC to enhance in-situ transesterification reaction, benzyltrimethylammonium hydroxide (BTMAOH) and crown ether (CE) were investigated as possible contender of phase transfer catalysts for in-situ transesterification of jatropha curcas oil with methanol and ethanol. To evaluate if PTC alone can catalyze transesterification reaction or need to be used in conjunction with NaOH, the reaction was performed using PTC (CTMAB, BTMAOH and CE) without NaOH at different reaction time while keeping other reaction conditions constant as presented in Table 4.10. The reaction was also conducted using only NaOH as alkaline catalyst for comparison of its effect with the catalytic performance of different PTCs.

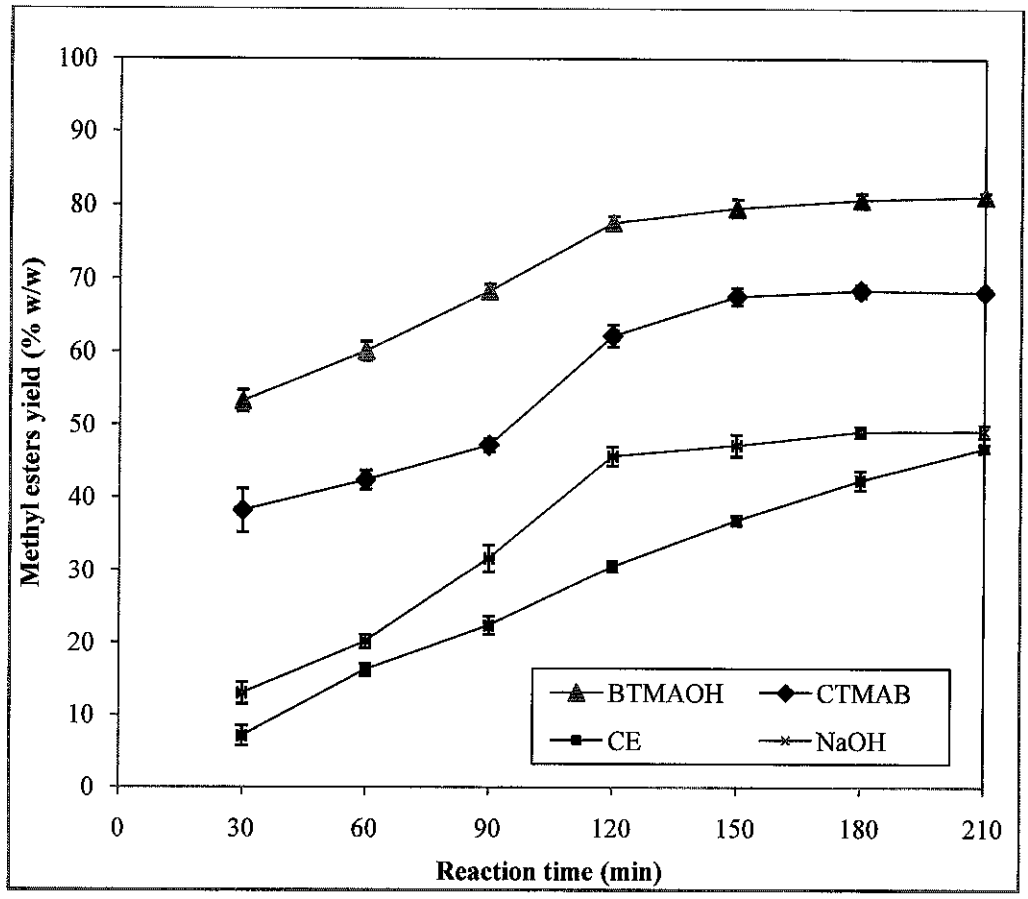
Table 4.10: Reaction condition of in-situ methanolysis and ethanolysis of jatropha curcas particles with different PTCs

Reaction Variables	Unit	Quantity	
		In-situ methanolysis	**In-situ ethanolysis**
PTC/Jatropha Seed	% w/w	1.5	1
NaOH/Jatropha Seed	% w/w	1.013	1.013
Methanol(Ethanol)/ Jatropha seed	ml/g	7.5	7.5
Reaction Temperature	°C	40	30
Mixing speed	rpm	400	400
Reaction time	min	30, 60, 90, 120, 150, 180 and 210	30, 60, 90, 120, 150, 180 and 210

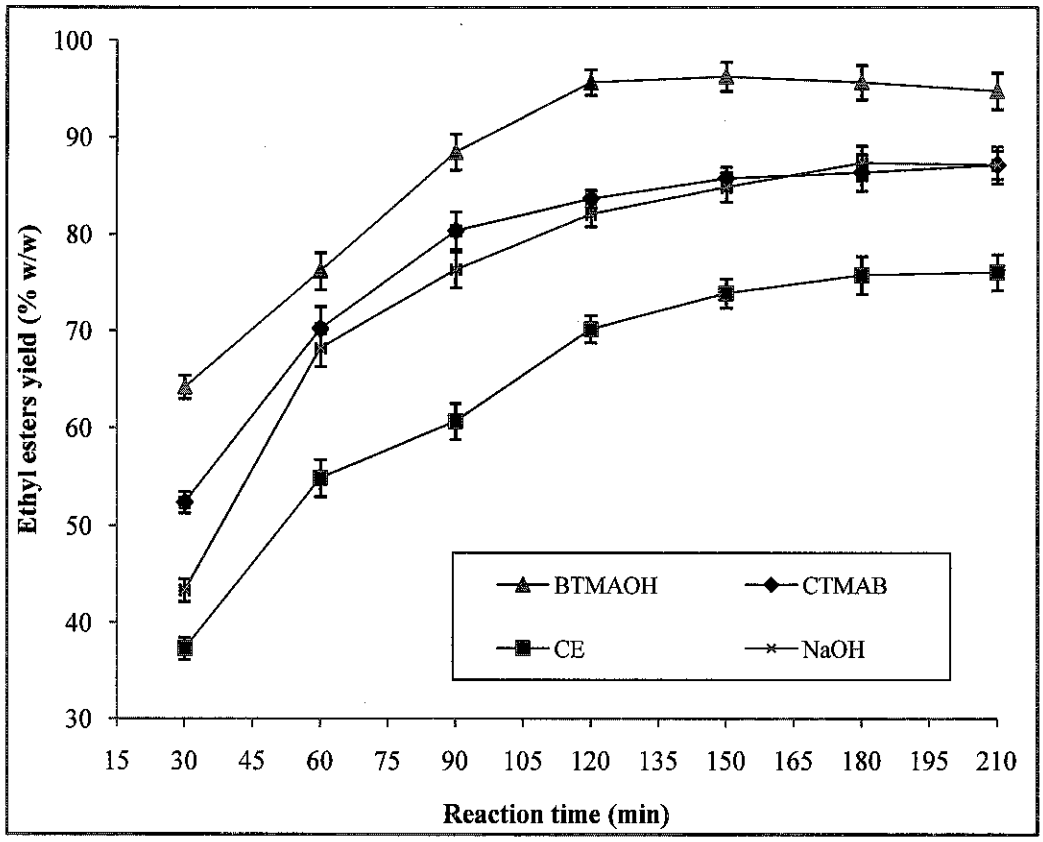
Note: PTC used were CTMAB, BTMAOH and CE

Figure 4.8 (a) and (b) shows the yield of FAME and FAEE as a function of reaction time for in-situ methanolysis and in-situ ethanolysis reactions with stand

alone chemicals (CTMAB, BTMAOH and CE) as phase transfer catalyst. The yield of FAME and FAEE produced using only base catalyst NaOH was also plotted in the same Figures for comparison. It can be seen from Figure 4.8 (a) that the yield of FAME increased with increasing the reaction time. The result demonstrates BTMAOH and CTMAB showed better catalytic performance compared to NaOH while the performance of crown ether was inferior to NaOH. Performance of BTMAOH was better than CTMAB with a maximum yield of 79.6% in about 150 minutes. Increasing the reaction time further has slight change on the yield of FAME. Similarly, from Figure 4.8 (b) for in-situ ethanolysis reaction, it can be seen that yield of FAEE was better with the use of BTMAOH compared to CTMAB, NaOH and CE. The maximum FAEE yield with BTMAOH was 95.7% w/w in 120 minutes of reaction time. The result shows better FAEE yield was obtained during in-situ ethanolysis as compared to in-situ methanolysis.



a) In-situ methanolysis



b) In-situ ethanolysis

Figure 4.8: The yield of FAME and FAEE as a function of reaction time using different PTCs (CTMAB, BTMAOH and CE) and NaOH as a catalyst

4.3.3 Catalytic effect of different PTCs mixed with alkaline catalyst

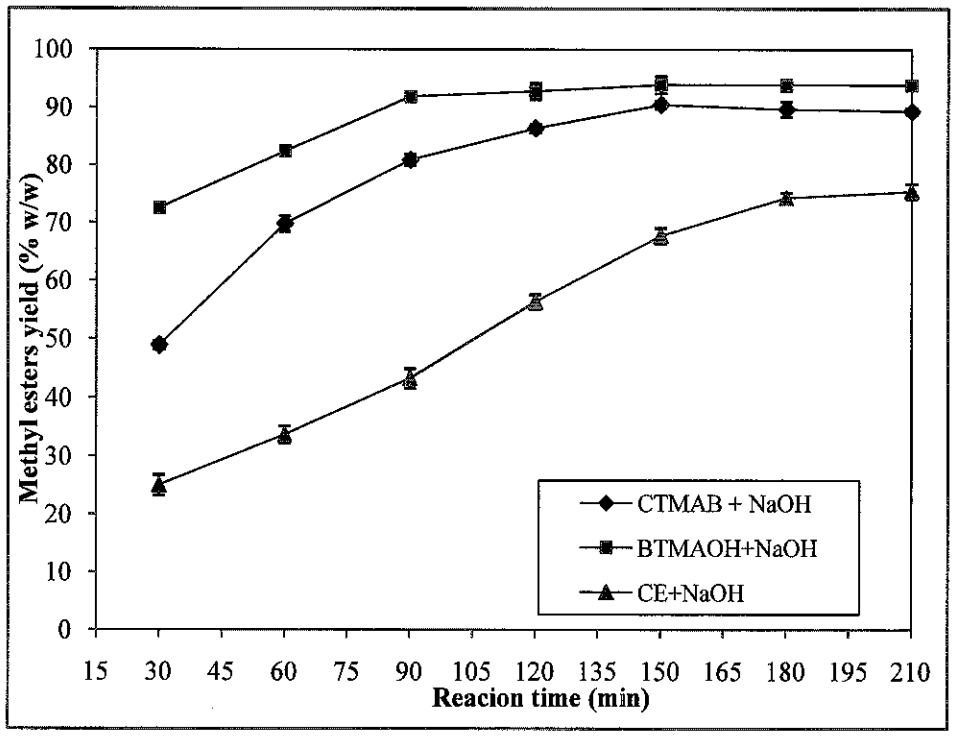
The catalytic performance of PTC was further investigated by combining PTC and NaOH for both in-situ methanolysis and in-situ ethanolysis reaction as shown in Figure 4.9 (a) and (b). The reaction conditions are summarized in table 4.11.

Table 4.11: Reaction condition of in-situ methanolysis and ethanolysis of jatropha curcas particles with different PTCs combined with NaOH.

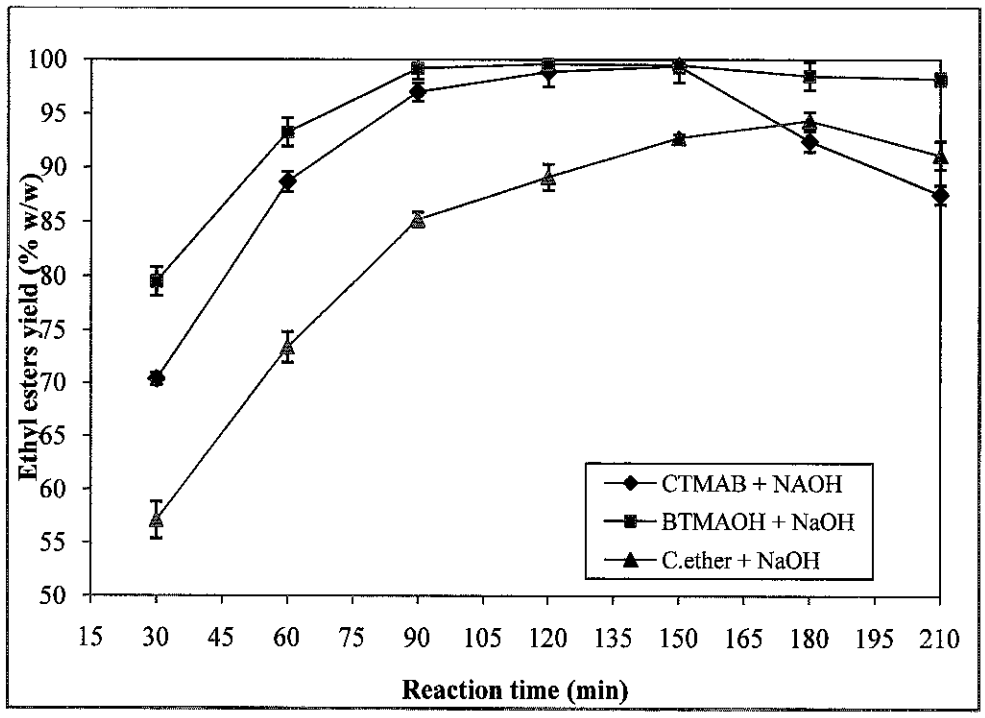
Reaction Variables	Unit	Quantity	
		In-situ methanolysis	**In-situ ethanolysis**
PTC/NaOH	mol/mol	1.5:1	1:1
NaOH/Jatropha Seed	% w/w	1.013	1.013
Methanol(Ethanol)/ Jatropha seed	ml/g	7.5	7.5
Reaction Temperature	°C	40	30
Mixing speed	rpm	400	400
Reaction time	min	30, 60, 90, 120, 150, 180 and 210	30, 60, 90, 120, 150, 180 and 210

Note: PTC used were CTMAB, BTMAOH and Crown Ether

For both in-situ methanolysis and in-situ ethanolysis yield of FAME and FAEE were higher when PTC was used in combination with NaOH to catalyze the reaction (Figure 4.9) as compared to use of PTC alone as a catalyst (Figure 4.8). Maximum FAME yield of 91.2% w/w was achieved when BTMAOH was used together with NaOH to catalyze the reaction in 90 minutes of reaction time (Figure 4.9 (a)) as compared to 79.6% w/w maximum yield of FAME obtained when the reaction was conducted in the presence of only BTMAOH as a PTC (Figure 4.8 (a)) for in-situ methanolysis reaction. Similarly, for in-situ ethanolysis reaction, 99.6% w/w maximum yield of FAEE was obtained when the reaction was conducted in the presence of both BTMAOH as a PTC and NaOH as alkaline catalyst 90 in minutes of reaction time (Figure 4.9 (b)) as compared to 95.7% w/w maximum yield of FAEE achieved when the reaction was conducted in the presence of only BTMAOH as a PTC in 120 minutes of reaction time (Figure 4.8 (b)). However, when CTMAB and CE were used the yields of FAME/FAEE were less than the corresponding yield of FAME/FAEE achieved when BTMAOH was used as a PTC.



a) In-situ methanolysis



b) In-situ ethanolysis

Figure 4.9: The yield of FAME and FAEE as a function of reaction time using different PTCs (CTMAB, BTMAOH and CE) combined with NaOH

Observation of FAME and FAEE yields achieved at different PTCs and NaOH combination to enhance transesterification reaction (Figure 4.9) indicate that BTMOH is a good phase transfer catalyst for alkaline in-situ transesterification of jatropha seed particles. Understanding the individual and cross effect of process variables is a key to optimize the reaction conditions to achieve the desired product qualitatively and quantitatively. Response surface methodology (RSM) technique was used for further investigations to identify optimum operating conditions to achieve higher yields in shorter reaction time.

4.3.4 Parametric study and optimization of in-situ transesterification of jatropha curcas in the presence of alkaline BTMAOH

Preliminary experiments in sections 4.3.1 and 4.3.2 indicated that yield of biodiesel produced by in-situ transesterification, Y, depends mainly on the five independent variables: - PTC concentration (X_1), NaOH concentration (X_2), volume of alcohol per weight of oil seed (X_3), reaction temperature(X_4) and reaction time(X_5). In all the experiment, jatropha curcas particle sizes range of 300-500 μm and stirrer speed of 400 rpm were kept constant. The individual and interaction effect of process variables and the optimal conditions needed to achieve maximum yield were investigated using central composite design (CCD) technique of response surface methodology (RSM) for in-situ methanolysis and in-situ ethanolysis reaction assisted by BTMAOH as a PTC and NaOH as alkaline catalyst. According to RSM experimental design technique, it was considered that each reaction variable can take five different levels from low (-2), (-1), (0), (1) and to high (2). For the 5 independent variables at 5 levels using CCD method requires 32 (= 2^5) experiments. Out of these, 6 experiments were replicated at center points to evaluate the error. Based on a set of experiments in section 4.3.2 and 4.3.3, range of the variables, step size and the central value were chosen as shown in Table 4.12.

Table 4.12: Experimental range and level of the independent variables

Variables	Coded symbol	Unit	Range and levels				
			-2	-1	0	1	2
BTMaOH	X_1	mol/mol	0.25	0.75	1.25	1.75	2.25
NaOH	X2	% w/w	0.18	0.68	1.18	1.68	2.18
Methanol	X3	ml/g	2.5	4.5	6.5	9	11.5
Temp.	X4	°C	25	35	45	55	65
Time	X5	h	0.05	0.7	1.35	2	2.65

In all the experiments particle size range of 300-500 μm and stirrer speed needed to keep the particles in suspension (400 rpm) were kept constant. The experimental observations were analyzed by quadratic model equation (3.5).

The complete design matrix of CCD for the variable combinations (with coded variables in parenthesis) and experimental results are listed in Table 4.13 for in-situ methanolysis and Table 4.16 for in-situ ethanolysis, respectively.

4.3.4.1 In-situ methanolysis

Experiments carried out as a function of the un-coded variables (with coded variables in the parenthesis) prompted by central composite design technique along with the observed yields for the in-situ methanolysis are presented in Table 4.13.

Table 4.13: Experimental design matrix by CCD technique for in-situ methanolysis along with experimental and model predicted yields

Run Order	BTMAOH, $X_1(x_1)$	NaOH, $X_2(x_2)$	Methanol, $X_3(x_3)$	Temp, $X_4(x_4)$	Time, $X_5(x_5)$	Exper. yield (%)	Predicted yield (%)
1	1.25(0)	0.18(-2)	6.75(0)	45(0)	1.35(0)	78.3	78.40
2	1.25(0)	1.18(0)	6.75(0)	45(0)	2.65(2)	69.7	68.72
3	1.75(1)	1.68(1)	4.50(-1)	35(-1)	2.00(1)	87.9	88.87
4	1.25(0)	1.18(0)	6.75(0)	45(0)	1.35(0)	88.7	88.42
5	0.25(-2)	1.18(0)	6.75(0)	45(0)	1.35(0)	74.5	77.19
6	0.75(-1)	1.68(1)	9.00(1)	35(-1)	2.00(1)	81.2	81.31
7	0.75(-1)	0.68(-1)	4.50(-1)	35(-1)	2.00(1)	71.1	70.69
8	0.75(-1)	1.68(1)	9.00(1)	55(1)	0.70(-1)	71.3	70.36
9	0.75(-1)	1.68(1)	4.50(-1)	35(-1)	0.70(-1)	66.1	65.23
10	1.25(0)	1.18(0)	6.75(0)	25(-2)	1.35(0)	87.4	86.30
11	1.75(1)	0.68(-1)	9.00(1)	55(1)	0.70(-1)	77.5	77.86
12	0.75(-1)	0.68(-1)	4.50(-1)	55(1)	0.70(-1)	61.4	59.94
13	1.25(0)	1.18(0)	6.75(0)	45(0)	1.35(0)	88.1	88.41
14	2.25(2)	1.18(0)	6.75(0)	45(0)	1.35(0)	86.6	83.94
15	1.75(1)	1.68(1)	9.00(1)	35(-1)	0.70(-1)	68.2	69.15
16	0.75(-1)	0.68(-1)	9.00(1)	35(-1)	0.70(-1)	73.2	72.78
17	1.75(1)	1.68(1)	9.00(1)	55(1)	2.00(1)	79.4	80.29
18	1.75(1)	0.68(-1)	4.50(-1)	55(1)	2.00(1)	74.7	75.08
19	1.75(1)	0.68(-1)	9.00(1)	35(-1)	2.00(1)	76.2	77.61
20	0.75(-1)	1.68(1)	4.50(-1)	55(1)	2.00(1)	81.1	80.18
21	1.75(1)	1.68(1)	4.50(-1)	55(1)	0.70(-1)	68.4	68.32
22	1.25(0)	1.18(0)	6.75(0)	45(0)	1.35(0)	88.9	88.41
23	1.25(0)	1.18(0)	6.75(0)	45(0)	1.35(0)	87.9	88.41
24	1.25(0)	1.18(0)	2.25(-2)	45(0)	1.35(0)	71.1	72.07
25	0.75(-1)	0.68(-1)	9.00(1)	55(1)	2.00(1)	75.7	75.21
26	1.25(0)	1.18(0)	6.75(0)	45(0)	0.05(-2)	47.7	48.70
27	1.25(0)	1.18(0)	6.75(0)	65(2)	1.35(0)	84.2	85.32
28	1.25(0)	1.18(0)	6.75(0)	45(0)	1.35(0)	87.8	88.41
29	1.25(0)	2.18(2)	6.75(0)	45(0)	1.35(0)	85.7	85.64
30	1.25(0)	1.18(0)	6.75(0)	45(0)	1.35(0)	89.1	88.41
31	1.25(0)	1.18(1)	11.25(2)	45(0)	1.35(0)	80.7	79.76
32	1.75(1)	0.68(-1)	4.50(-1)	35(-1)	0.70(-1)	65.1	65.53

FAME yields obtained during in-situ methanolysis at various reaction conditions (Table 4.13) were analyzed by method of variance (ANOVA) to establish the constants of the quadratic equation (3.5). After determining the constants of quadratic equation (3.5) for FAME yield as shown in Table 4.14, statistical model equation (4.1) is established to estimate the yield of FAME. The variables in equation (4.1) were coded according to equation (3.6) of chapter 3.

$$\begin{aligned} Y_{FAME} = {} & 88.41 + 1.69x_1 + 1.81x_2 + 1.92x_3 - 0.25x_4 + 5x_5 - 1.96x_1^2 - 1.6x_2^2 - 3.13x_3^2 \\ & - 0.65x_4^2 - 7.43x_5^2 - 0.49x_1 x_2 - 1.03x_1 x_3 + 0.29x_1 x_4 + 0.12x_1 x_5 - 2.1x_2 x_3 \\ & - 0.43x_2 x_4 + 2.2x_2 x_5 + 0.6x_3 x_4 - 1.97x_3 x_5 - 0.72x_4 x_5 \end{aligned} \quad (4.1)$$

FAME yields predicted by this regression model equation are included in Table 4.13 together with the experimental observations.

The significance of the model terms were evaluated statistically. Table 4.14 shows the relative effect of the linear, quadratic and interaction of variables on FAME yield in terms of p and t values. A smaller p-value (<0.05) or a greater absolute t-value indicated higher significance of the corresponding coefficient in the model. From this it can be concluded that for in-situ methanolysis, the linear terms x_1 (BTMAOH), x_2 (NaOH), x_3(volume of alcohol per weight of seed) and x_5(reaction time) significantly influenced the yields of FAME while the reaction temperature term x_4 has least significance (due to the high p-value and low t-value). All the quadratic coefficients of x_1, x_2, x_3, x_4 and x_5 have a significant effect on the yield of FAME. All the interaction terms have significant influence of the yield of FAME except the interaction terms involving reaction temperature term x_4 which have least significance as presented in Table 4.14.

Table 4.14: T and p values for the regression coefficients in the second order model equation (4.1)

Term	Coeff	SE Coeff.	t-value	p-value
Constant	88.4125	0.6846	129.146	0.000
x_1	1.6875	0.3504	4.817	0.001
x_2	1.8125	0.3504	5.173	0.000
x_3	1.9208	0.3504	5.483	0.000
x_4	-0.2458	0.3504	-0.702	0.497
x_5	5.0042	0.3504	14.283	0.000
x_1x_1	-1.9625	0.3504	-6.193	0.000
x_2x_2	-1.6000	0.3504	-5.049	0.000
x_3x_3	-3.1250	0.3504	-9.861	0.000
x_4x_4	-0.6500	0.3504	-2.051	0.0659
x_5x_5	-7.4250	0.3504	-23.430	0.000
x_1x_2	-0.4937	0.4291	-1.151	0.003
x_1x_3	-1.0313	0.4291	-2.403	0.035
x_1x_4	0.2937	0.4291	0.685	0.508
x_1x_5	0.1188	0.4291	0.277	0.787
x_2x_3	-2.1063	0.4291	-4.909	0.000
x_2x_4	-0.4313	0.4291	-1.005	0.336
x_2x_5	2.1938	0.4291	5.113	0.000
x_3x_4	0.6062	0.4291	1.413	0.185
x_3x_5	-1.9688	0.4291	-4.588	0.001
x_4x_5	-0.7187	0.4291	-1.675	0.122

Table 4.15 presents results of statistical analysis of the regression coefficients in terms of F-test and P-test. Large F-test values and very low probability values ($p \leq 0.05$ [201] confirm the validity of model equation 4.1. The 'lack of fit tests' (compares the residual error to the pure error) from replicated design experimental points indicated a high F –test value of 16.84 and a 0.4% of pure error [202].

Table 4.15: The regression analysis of the least square fit and parameter estimate

Source	Degree of freedom	Sum of squares	Mean squares	F-value	P-value
Regression	20	2947.33	2947.33	50.02	0.000
Linear terms	5	838.19	838.19	56.91	0.000
Square terms	5	1859.50	1859.50	126.24	0.000
Interaction terms	10	249.64	249.64	8.47	0.000
Residual Error	11	32.40	32.40		0.001
Lack of Fit	6	30.88	13.62	16.84	0.001
Pure Error	5	1.53	1.53		0.004

The parity plot also (Figure 4.10) compares the observed experimental FAME yield with the predicted values obtained using quadratic model equation with R^2 value of 0.989.

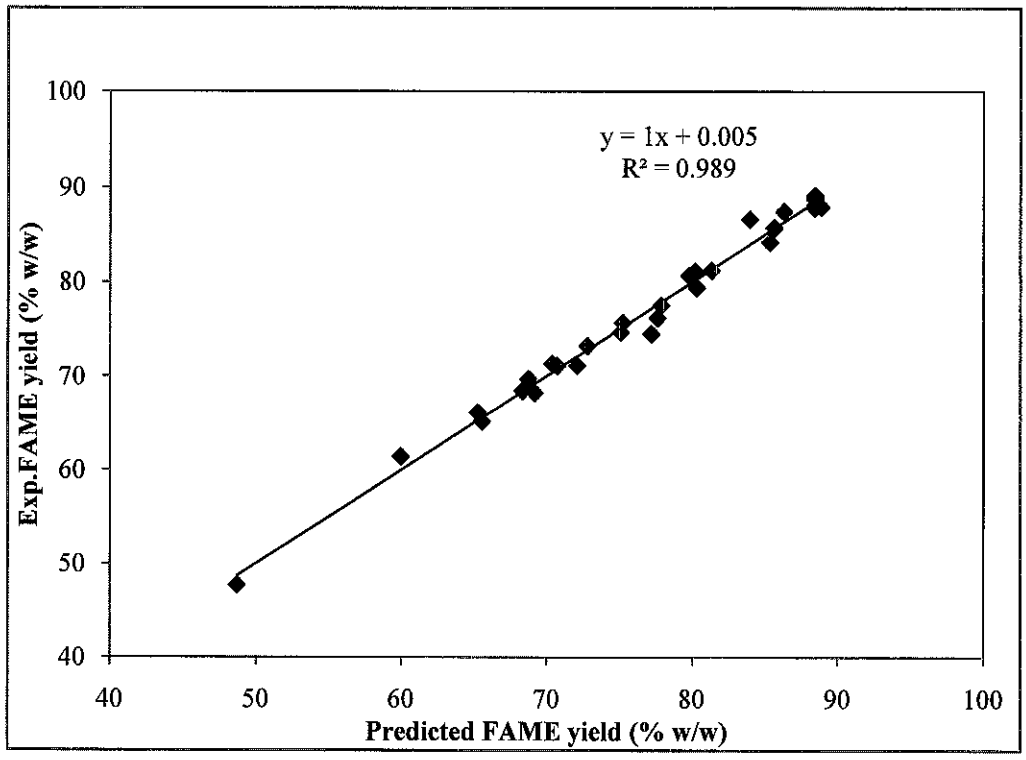


Figure 4.10: The parity plot of experiment FAME yield versus model predicted FAME yield

i) The individual and interaction effect of the reaction variables on FAME yield

The response surface plots for the yield of FAME as a function of two factors at a time while keeping the other three factors at their center point level were plotted in a three dimensional surface with the contour plot at the bottom as shown in Figure 4.11. The elliptical shape of the contour plot indicates a good interaction of the two variables on the response and circular shape indicates less interaction effects between the variables to affect the response [202].

Figure 4.11 (a) presents the yield of FAME as a function of molar ratio of BTMAOH to NaOH and percentage weight ratio of alkaline catalyst NaOH to jatropha curcas seed. Maximum yield was observed with BTMAOH to NaOH molar ratio of to about 1.6 and NaOH to seed ratio of up 1.28% w/w. Increase in concentration of BTMAOH and NaOH helped in promoting the catalytic reaction. However, further overloading of NaOH decreased the yield slightly due to saponification reaction was favored at high concentration of NaOH.

Figure 4.11 (b) presents the effect of volume of methanol to jatropha curcas seed particles on the yield of FAME. Increasing the amount of methanol has a positive effect on the yield of FAME (up to 6.5ml/g of jatropha curcas seeds). However, further increasing of methanol (> 7.5ml/g of jatropha curcas seeds) has a negative effect on the yield. The over loading of methanol would reduce the concentration of the catalyst (decrease catalyst activity) and also dissolve the product biodiesel into the glycerol phase that could affect the biodiesel recovery process that causes the reduction of the yield since some of the biodiesel may be lost with the byproduct glycerin.

Figure 4.11 (c) indicates the interaction between BTMAOH and reaction temperature. As the transesterification reaction between the immiscible phases is controlled by diffusion processes, the effect of temperature is expected to be very slight. An increase in temperature can promote saponification reactions as well; the yield of biodiesel can even decrease with temperature as observed.

Figure 4.11(d) depicts the interaction effect of BTMAOH and reaction time on the yield of FAME. It is observed that yield of FAME increased up to a certain reaction time (nearly 1.7h) beyond which it decreased slightly. The decrease in yield may be due to formation of soap for heating at extended reaction time; the formation of soap was observed during the experiment.

The interaction effects of methanol with reaction temperature on the yields of FAME were exhibited in Figure 4.11(e). The yield of products improved with increasing both the volume of alcohol and reaction time, however further increasing of both the alcohol volume and reaction time slightly reduces the yield due to solubility.

Figure 4.11(f) shows the effects of NaOH and reaction temperature on the yield. NaOH has a positive effect on the yield of FAME up to a certain marginal value (1.48% w/w). Further increase in its concentration or temperature has the negative impact due to saponification.

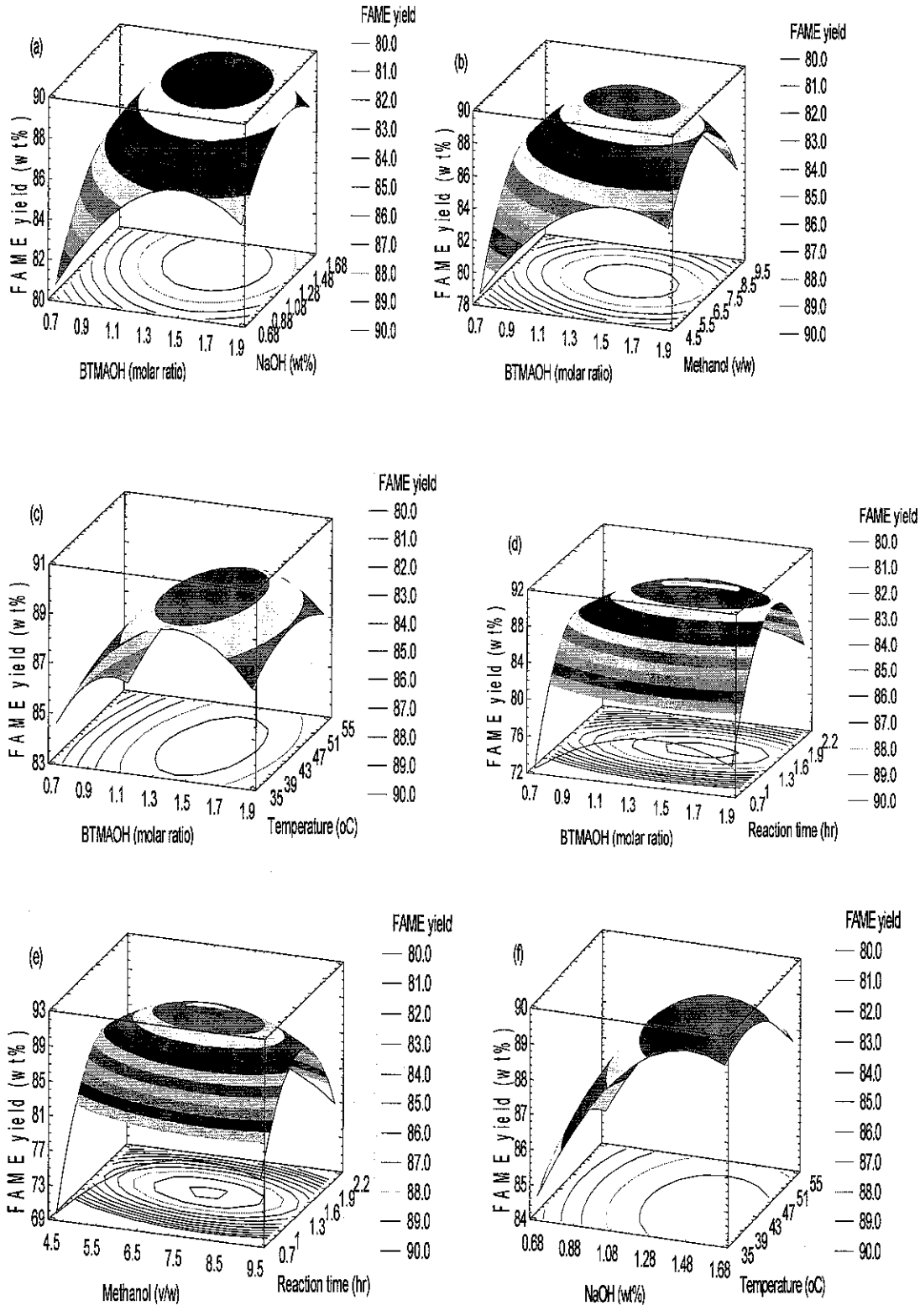


Figure 4.11: Response surface plots of the two combined variables of different combination on FAME yield

4.3.4.2 In-situ ethanolysis

Similar to in-situ methanolysis, experiments on in-situ ethanolysis were carried out as a function of the un-coded variables prompted by central composite design technique (with coded variables in the parenthesis); the experimental plan along with the observed yields are presented in Table 4.16.

Table 4.16: Experimental design matrix by CCD technique for in-situ ethanolysis

Run Order	BTMAOH, X1(x1)	NaOH, X2(x2)	Ethanol, X3(x3)	Temperature, X4(x4)	Time, X5(x5)	Exp.yield (%)	Pred.Yield (%)
1	1.25(0)	0.18(-2)	6.75(0)	45(0)	1.35(0)	90.2	90.38
2	1.75(1)	1.68(1)	9.00(1)	55(1)	2.00(1)	96.2	96.1
3	2.25(2)	1.18(0)	6.75(0)	45(0)	1.35(0)	96.8	98.41
4	1.75(1)	0.68(-1)	4.50(-1)	55(1)	2.00(1)	91.3	91.33
5	1.75(1)	1.68(1)	4.50(-1)	55(1)	0.70(-1)	86.5	85.1
6	1.25(0)	1.18(0)	6.75(0)	45(0)	1.35(0)	99.8	99.17
7	1.25(0)	1.18(0)	6.75(0)	65(2)	1.35(0)	93.3	94.23
8	0.75(-1)	0.68(-1)	4.50(-1)	35(-1)	2.00(1)	89.1	89.66
9	1.25(0)	1.18(0)	6.75(0)	45(0)	1.35(0)	99.4	99.17
10	1.75(1)	0.68(-1)	9.00(1)	35(-1)	2.00(1)	91.7	91.97
11	1.25(0)	1.18(0)	2.25(-2)	45(0)	1.35(0)	84.2	85.23
12	1.75(1)	1.68(1)	4.50(-1)	35(-1)	2.00(1)	95.8	95.65
13	1.25(0)	1.18(0)	6.75(0)	45(0)	0.05(-2)	68.0	71.13
14	0.75(-1)	1.68(1)	4.50(-1)	55(1)	2.00(1)	95.2	95.39
15	0.75(-1)	0.68(-1)	4.50(-1)	55(1)	0.70(-1)	77.9	77.17
16	1.25(0)	1.18(0)	6.75(0)	45(0)	1.35(0)	99.2	99.17
17	0.75(-1)	1.68(1)	4.50(-1)	35(-1)	0.70(-1)	80.3	79.39
18	1.25(0)	1.18(0)	6.75(0)	45(0)	2.65(2)	90.8	89.14
19	0.75(-1)	1.68(1)	9.00(1)	55(1)	0.70(-1)	85.4	84.54
20	0.75(-1)	0.68(-1)	9.00(1)	55(1)	2.00(1)	86.1	86.71
21	1.25(0)	1.18(0)	11.25(2)	45(0)	1.35(0)	90.3	90.74
22	1.25(0)	1.18(0)	6.75(0)	45(0)	1.35(0)	99.7	99.17
23	0.75(-1)	1.68(1)	9.00(1)	35(-1)	2.00(1)	94.7	95.13
24	1.75(1)	0.68(-1)	9.00(1)	55(1)	0.70(-1)	88.8	87.78
25	0.25(-2)	1.18(0)	6.75(0)	45(0)	1.35(0)	93.3	93.16
26	1.25(0)	1.18(0)	6.75(0)	45(0)	1.35(0)	98.7	99.17

27	0.75(-1)	0.68(-1)	9.00(1)	35(-1)	0.70(-1)	87.9	87.41
28	1.75(1)	0.68(-1)	4.50(-1)	35(-1)	0.70(-1)	82.3	81.23
29	1.25(0)	2.18(2)	6.75(0)	45(0)	1.35(0)	95.4	96.69
30	1.25(0)	1.18(0)	6.75(0)	25(-2)	1.35(0)	94.6	95.14
31	1.75(1)	1.68(1)	9.00(1)	35(-1)	0.70(-1)	88.5	87.3
32	1.25(0)	1.18(0)	6.75(0)	45(0)	1.35(0)	99.7	99.17

FAEE yields obtained during in-situ ethanolysis at various reaction conditions (Table 4.16) were analyzed by method of variance (ANOVA) to establish the constants of the quadratic model equation (3.5). The variables in model equation (3.5) are coded according to equation (3.6) from which model equation that predicts the yield of FAEE was established as shown in equation (4.2).

$$Y_{FAEE} = 99.17 + 1.31x_1 + 1.58x_2 + 1.38x_3 - 0.23x_4 + 4.5x_5 - 0.85x_1^2 - 1.41x_2^2 2 - 2.8x_3^2 - 1.12x_4^2 - 4.76x_5^2 - 0.1x_1 x_2 - 0.14x_1x_3 + 0.74x_1x_4 - 0.29x_1x_5 - 0.43x_2x_3 - 0.68x_2x_4 + 1.24x_2x_5 - 0.6x_3x_4 - 1.64x_3x_5 - 0.13x_4x_5 \quad (4.2)$$

FAEE yields predicted by this regression model equation are included in Table 4.16 together with the experimental observations.

The significance of the model terms were evaluated statistically. Table 4.17 shows the relative effect of the linear, quadratic and interaction of variables on FAEE yield in terms of p and t values. A smaller p-value (<0.05) or a greater absolute t-value indicated higher significance of the corresponding coefficient in the model. It can be seen that for in-situ ethanolysis (Table 4.17) the yield of FAEE is significantly influenced by all the linear as well as quadratic terms of x_1 (BTMAOH), x_2 (NaOH), x_3(volume of alcohol per gm of seed) and x_5(reaction time) except the reaction temperature term x_4. The interaction terms involving NaOH with reaction time (x_2x_5) and volume of alcohol per weight of jatropha curcas l seeds with reaction time (x_3x_5) also have high significance influence on the yield of FAEE as compared to the remaining interaction terms.

Table 4.17: t and p values for the regression coefficients in the model equation (4.2)

Term	Coeff.	SE Coeff.	t-value	p-value
Constant	99.1716	0.6538	151.688	0.000
x_1	1.3125	0.3346	3.923	0.002
x_2	1.5792	0.3346	4.720	0.001
x_3	1.3792	0.3346	4.122	0.002
x_4	-0.2292	0.3346	-0.685	0.508
x_5	4.5042	0.3346	13.462	0.000
x_1x_1	-0.8466	0.3026	-2.797	0.017
x_2x_2	-1.4091	0.3026	-4.656	0.001
x_3x_3	-2.7966	0.3026	-9.241	0.000
x_4x_4	-1.1216	0.3026	-3.706	0.003
x_5x_5	-4.7591	0.3026	-15.725	0.000
x_1x_2	-0.1062	0.4098	-0.259	0.800
x_1x_3	-0.1437	0.4098	-0.351	0.732
x_1x_4	0.7437	0.4098	1.815	0.097
x_1x_5	-0.2937	0.4098	-0.717	0.488
x_2x_3	-0.4312	0.4098	-1.052	0.315
x_2x_4	0.6813	0.4098	1.662	0.125
x_2x_5	1.2438	0.4098	3.035	0.011
x_3x_4	-0.6063	0.4098	-1.479	0.167
x_3x_5	-1.6438	0.4098	-4.011	0.002
x_4x_5	-0.1312	0.4098	-0.320	0.755

Table 4.18 presents results of statistical analysis of the regression coefficients in terms of F-test and P-test. Large F-test values (29.65) and very low probability values ($p \leq 0.05$) confirm the validity of model equation (4.2). The 'lack of fit tests' (compares the residual error to the pure error) from replicated design experimental points indicated a high F–test value of 27.53 and a 0.1% of pure error which intern confirms the validity of the model to predict the yield of FAEE [202].

Table 4.18: Regression analysis of the least square fit and parameter estimate

Source	Degree of freedom	Sum of squares	Mean squares	F-value	P-value
Regression	20	1592.99	1592.990	29.65	0.000
Linear	5	635.01	635.005	47.27	0.000
Square	5	862.70	862.704	64.22	0.000
Interaction	10	95.28	95.281	3.55	0.0025
Residual Error	11	29.55	29.554		
Lack of Fit	6	28.69	28.686	27.53	0.001
Pure Error	5	0.87	0.868		

The parity plot (Figure 4.12) compares the observed experimental FAEE yield with the predicted values obtained using quadratic model equation with R^2 value of 0.981. The parity plot signifies 98.1% of the variability in the data is accounted to the quadratic model equation demonstrating the empirical model is adequate enough to represent and explain most of the variability.

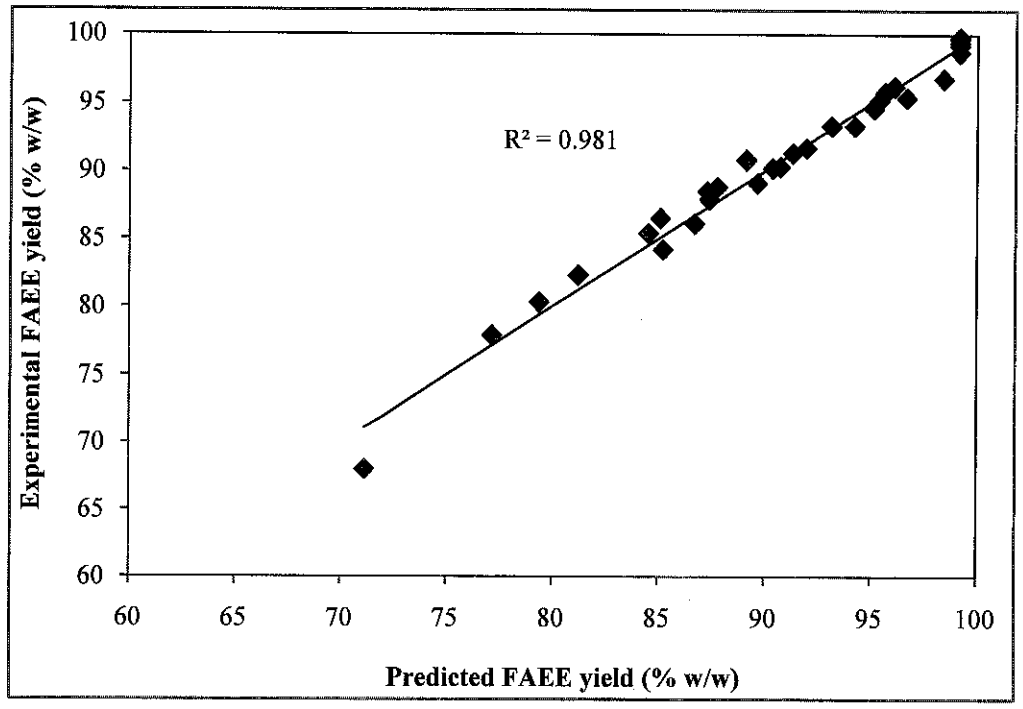


Figure 4.12: parity plot of experiment FAEE yield versus model predicted FAEE yield.

i) Individual and interaction effects of the reaction variables on FAEE yield

The response surface plots for the yield of FAEE as a function of two variables at a time while keeping the other three variables at their center point level were plotted in a three dimensional surface with the contour plot at the bottom as shown in Figure 4.13.

Figure 4.13 (a) to (f) illustrate a parametric interaction effects of the two variables on the yield of FAEE. Trends for the yield of FAEE are similar to the trends for the yield of FAME as shown in Figure 4.11. However, higher yields are obtained by the in-situ ethanolysis as compared to yields obtained by in-situ methanolysis due to better miscibility of ethanol in oil as compared to methanol.

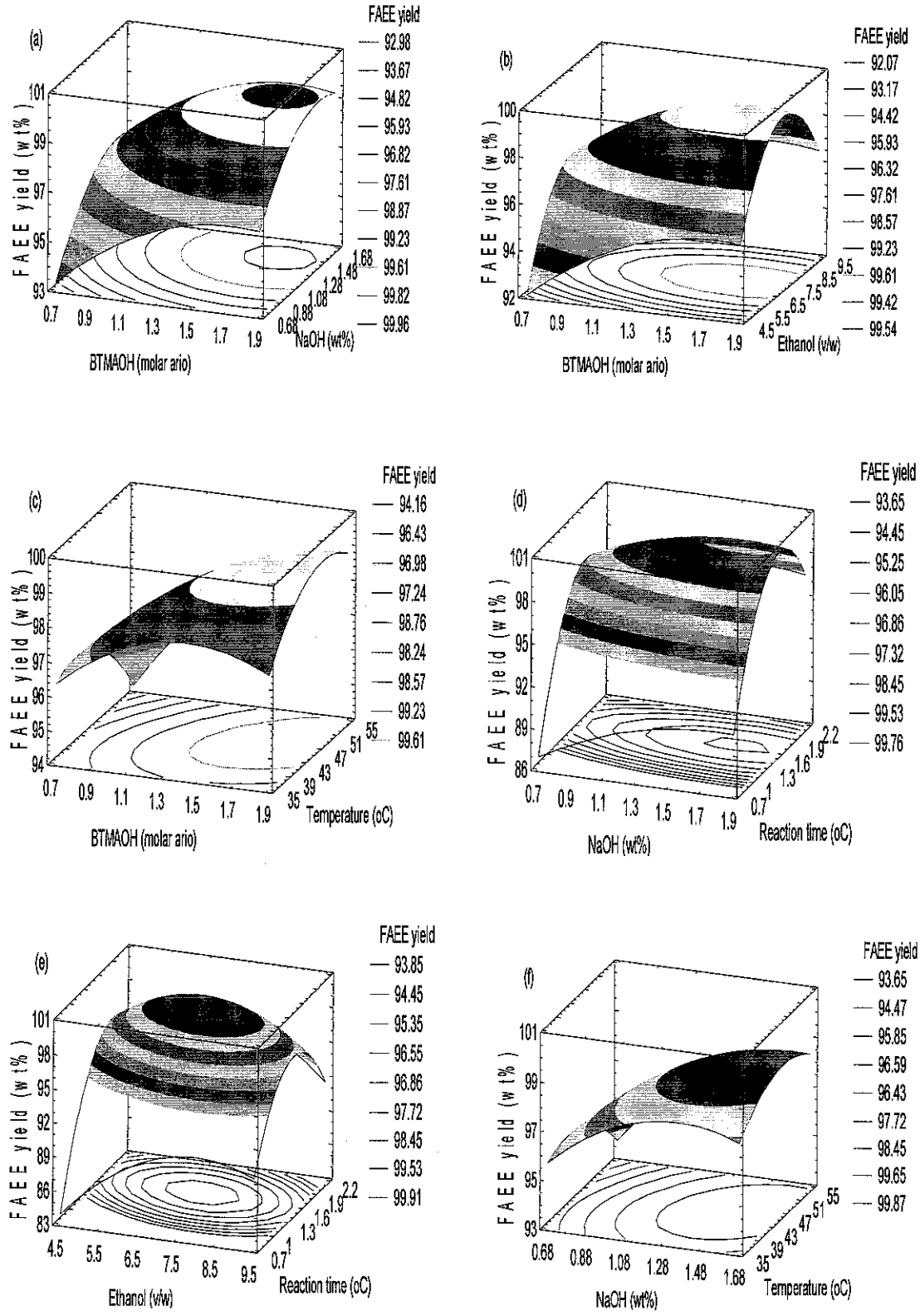


Figure 4.13: Response surface plots of the combined variables of different combination on FAEE yield.

4.3.4.3 Optimum reaction conditions of in-situ transesterification reaction

Optimum reaction variables of in-situ methanolysis and in-situ ethanolysis and the corresponding expected maximum yields of FAME and FAEE was established using response surface analysis response optimizer as presented in Table 4.19, respectively.

Experiments were conducted in duplicate at the optimal condition to test the significance of the model predictions. Experimentally observed yield of FAME (89.8±0.7% w/w) was in close agreement with the expected maximum yield suggested (91.75% w/w) by the model equation (4.1). Similarly, the experimentally observed yield of FAEE (99.4± 0.4% w/w) was in close agreement with the expected maximum yield suggested (99.74% w/w) by the model equation (4.2). Table 4.19 depicts the optimum process variables for both in-situ ethanolysis and methanolysis along with the maximum predicted yields using the model equations and the maximum yields experimentally observed at the optimum condition.

Table 4.19: Optimum operating conditions for maximum FAME and FAEE yield for in-situ transesterification reaction

Factor	Unit	Optimum value for FAME yield	Optimum value for FAEE yield
Ratio of BTMAOH to NaOH	mol/mol	1.42	1.62
Ratio of NaOH to Jatropha seeds	% w/w	1.52	1.38
Ratio of ethanol to Jatropha seeds	ml/g	5.92	6.5
Reaction temperature	^{o}C	38	35
Reaction time	min	103	95
Predicted optimum FAME yield	% w/w	91.75	-
Exp. FAME yield	% w/w	89.8± 1.37	-
Predicted optimum FAEE yield	% w/w	-	99.74
Exp. optimum FAEE yield	% w/w	-	99.4±0.4

4.4 Microwave irradiation pretreatment of jatropha curcas prior to in-situ transesterification reaction

Microwave energy is more recently used to increase the reaction rate of conventional transesterification reaction though microwave heating of oil-alcohol reaction mixture can cause risk of handing high volatile alcohol under microwave irradiation particularly at commercial scale of biodiesel processing. However, microwave heat pretreatment of seed particles prior to in-situ transesterification reaction can make oil molecules more reactive. In this study, the effect of microwave pretreatment of jatropha curcas seed particles was investigated. In-situ transesterification experiments were conducted at different reaction condition with microwave pretreated jatropha curcas seed particles. Section 4.4.1 discusses the effect of microwave pretreatment of jatropha curcas seed particles during in-situ methanolysis and in-situ ethanolysis in the presence of NaOH as alkaline catalyst. Section 4.4.2 describes the combined effect of microwave heat pretreatment of jatropha curcas seed particles and use of BTMAOH as a PTC on alkaline in-situ methanolysis/ethanolysis reaction. Section 4.4.3 presents the individual and interaction effects of process variables and optimum operating conditions investigated using response surface methodology. The detailed experimental results and observations are presented and discussed in subsequent sections below.

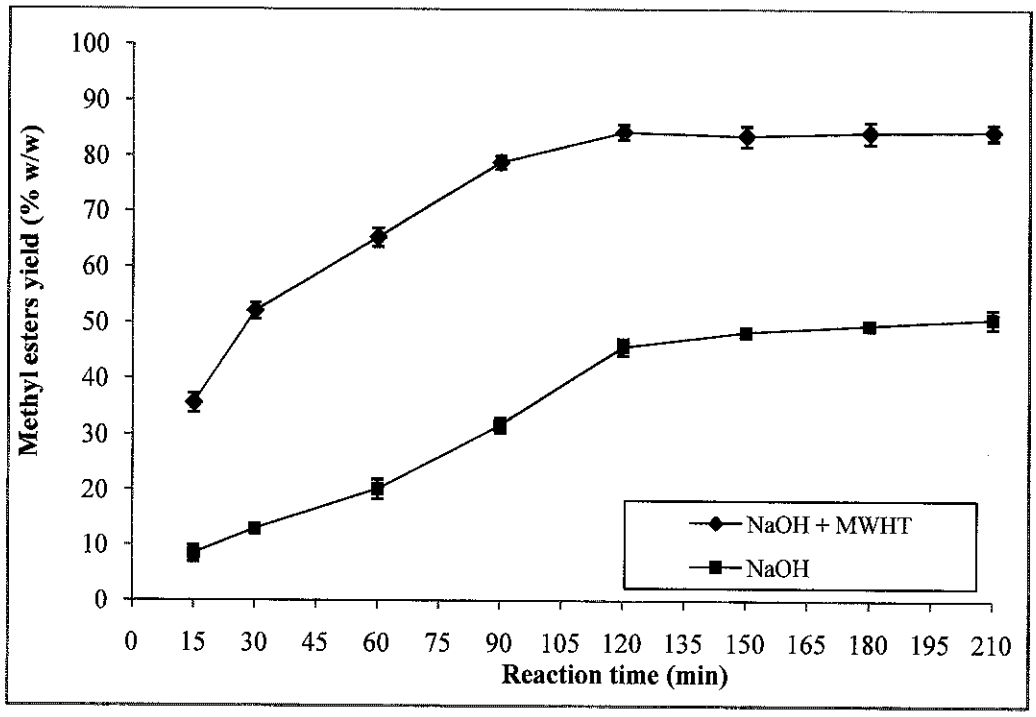
4.4.1 Alkaline in-situ methanolysis and ethanolysis using microwave pretreated jatropha curcas seed particles

In-situ transesterification of microwave radiation pretreated jatropha curcas seed particles with methanol and ethanol in the presence of NaOH as alkaline catalyst was investigated. The reaction conditions were summarized in Table 4.20. For comparison, experiments were also conducted with seed particles not treated by microwave radiation.

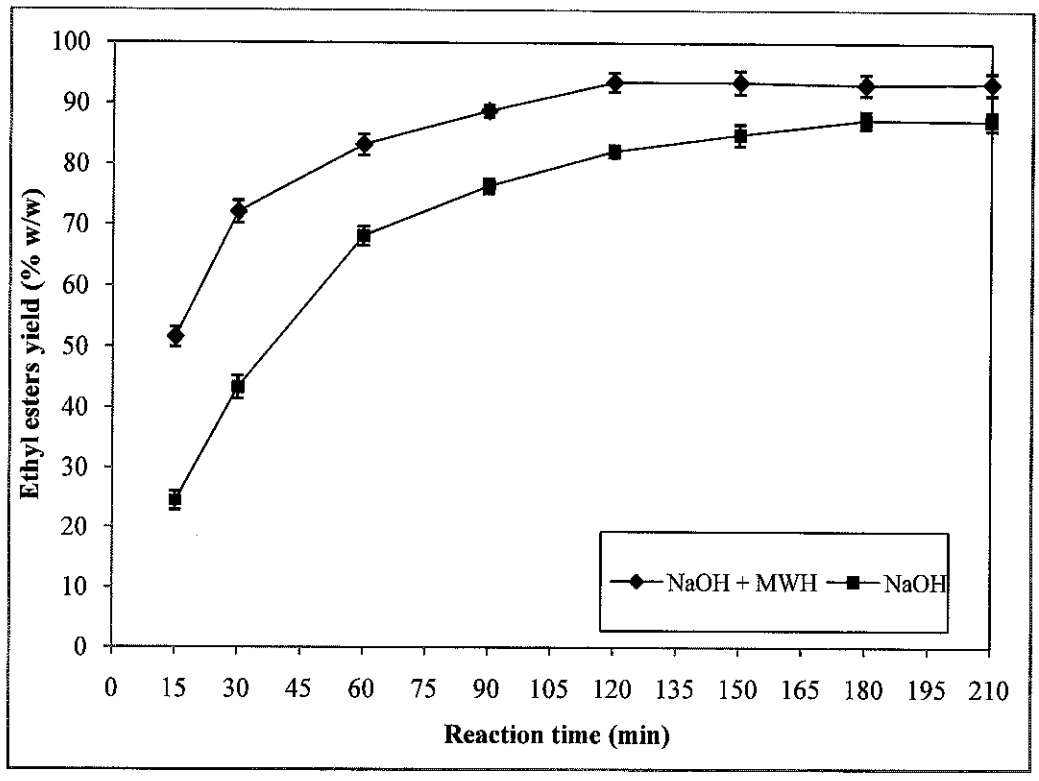
Table 4.20: Reaction condition of alkaline in-situ methanolysis and ethanolysis of microwave treated jatropha curcas seed particles

Test Variables	**Unit**	**Quantity**
MWHP	watt	70
MWHT	min	4.5
NaOH/Jatropha Seed	% w/w	1.013
Methanol(Ethanol)/Jatropha seed	ml/g	7.5
Reaction temperature	°C	30
Mixing speed	rpm	400
Reaction. time	min	15, 30, 60, 90, 120. 150, 180, 210

The yield of FAME and FAEE produced using both microwave irradiation pretreated and untreated seed particles were plotted as a function of reaction time as shown in Figure 4.14 (a) and in Figure 4.14 (b), respectively. For in-situ methanolysis reaction catalyzed by only NaOH as alkaline catalyst, pretreatment of jatropha curcas seed particles with microwave irradiation has increased FAME yield from 49.7% w/w to 84.3% w/w while reducing the reaction time from 240 minutes to 120 minutes as compared to microwave untreated jatropha curcas seed particles in-situ methanolysis reaction. Similarly, for in-situ ethanolysis reaction catalyzed by only NaOH as alkaline catalyst, pretreatment of jatropha curcas seed particles with microwave irradiation has increased FAEE yield from 87.4% w/w to 93.6% w/w while reducing the reaction time from 180 minutes to 120 minutes as compared to microwave untreated jatropha curcas seed particles in-situ ethanolysis reaction. Thus, further investigation of the effect of microwave pretreatment of jatropha curcas seed particles on the in-situ methanolysis and in-situ ethanolysis reaction rates and yields of FAME and FAEE while using BTMAOH as a PTC together with NaOH as alkaline catalyst were conducted in the following section 4.4.2.



a) In-situ methanolysis



b) In-situ ethanolysis

Figure 4.14: Effect of microwave irradiation pretreatment of jatropha curcas particles on alkaline in-situ methanolysis and in-situ ethanolysis

4.4.2 Alkaline in-situ methanolysis and ethanolysis reaction using microwave treated jatropha curcas seed particles assisted by BTMAOH as a PTC

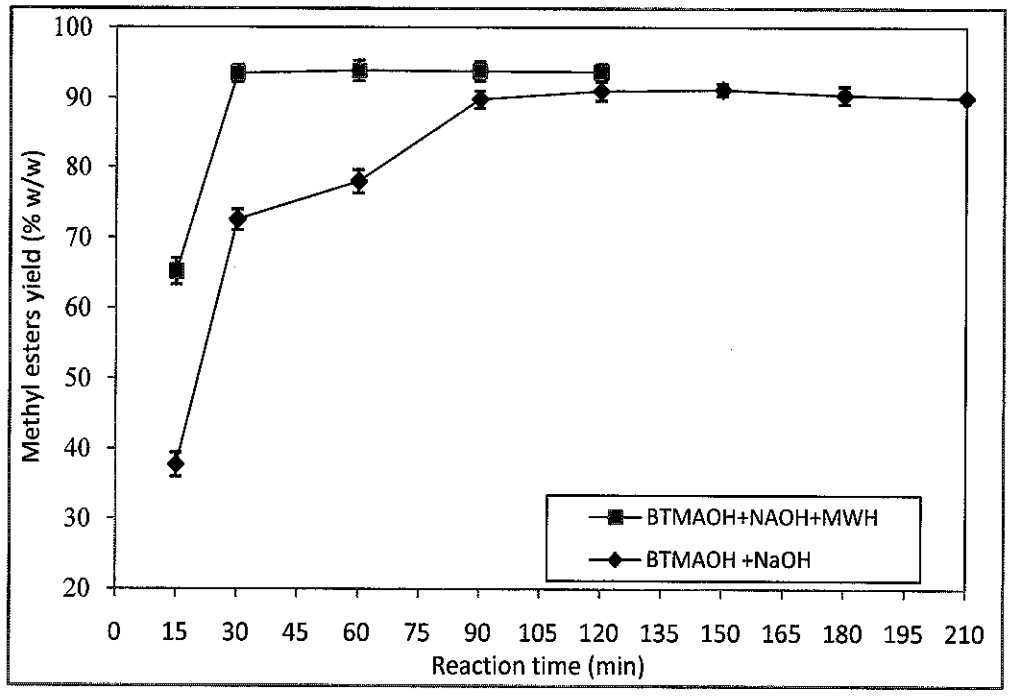
Observing the positive effect of microwave pretreatment of jatropha curcas seed particles, microwave pretreated jatropha curcas seed particles in-situ transesterification experiment was conducted using BTMAOH as a PTC together with NaOH as alkaline catalyst. The reaction variables were kept constant as presented in Table 4.21 while measuring the yield of FAME and FAEE with time. For comparison, the reaction was repeated with jatropha curcas seed particle not treated by microwave radiation under the same reaction conditions.

Table 4.21: Reaction conditions of alkaline in-situ methanolysis and ethanolysis of microwave pretreated jatropha curcas particles using BTMAOH as PTC.

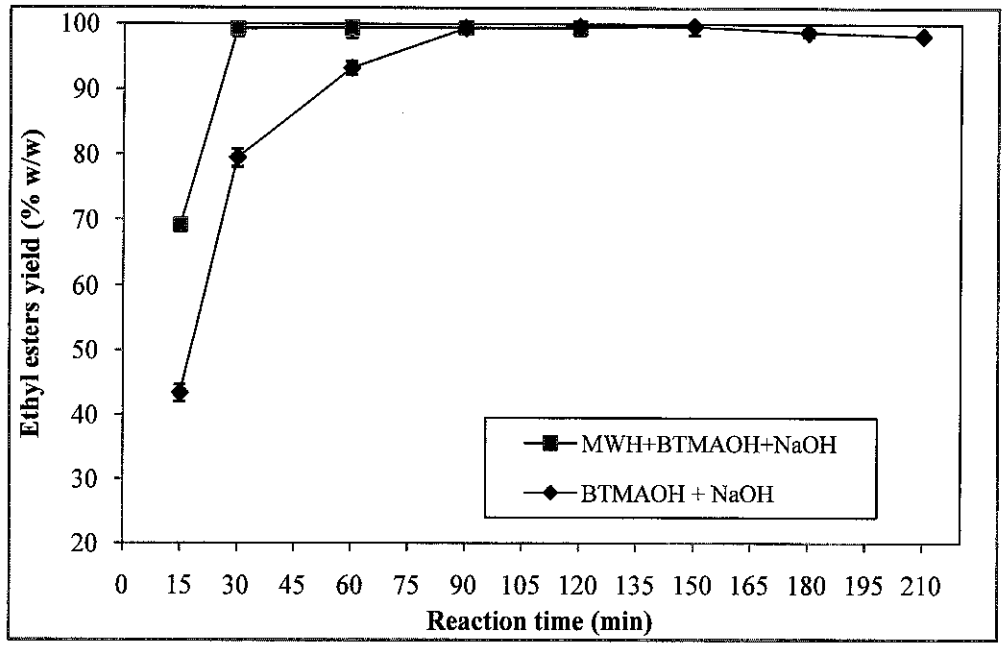
Reaction Variables	**Unit**	**Quantity**
MWHP	watt	70
MWHT	min	4.5
PTC/NaOH	mol/mol	1
NaOH/Jatropha Seed	% w/w	1.013
Alcohol/Jatropha seed	ml/g	7.5
Reaction temperature	^{o}C	30
Mixing speed	rpm	400
Reaction time	min	15, 30, 60, 90, 120. 150, 180, 210

Figure 4.15 (a) and Figure 4.15 (b) exhibited the yield of FAME and FAEE increased drastically when in-situ transesterification reactions were conducted with microwave pretreated seed particles as compared to microwave untreated seeds. During in-situ methanolysis (Figure 4.15 (a)), 93.5% w/w maximum FAME yield was achieved in 30 minutes as compared to 89.8% FAME yield observed in 90 minutes for microwave untreated seeds of the same reaction condition. Similarly, during in-situ ethanolysis (Figure 4.15 (b)) 99.5% w/w maximum FAEE yield was produced in 30 minutes of reaction time as compared to 99.4% w/w of FAEE yield produced in 90 minutes while using microwave untreated seed particles of the same reaction condition. From both in-situ methanolysis and in-situ ethanolysis experiment, it can

be observed that microwave treatment of seed particles has significant effect to increase the rate of reaction and reduce the reaction time from 90 minutes to about 30 minutes; however, no significant increase was observed in the yield of FAME and FAEE.



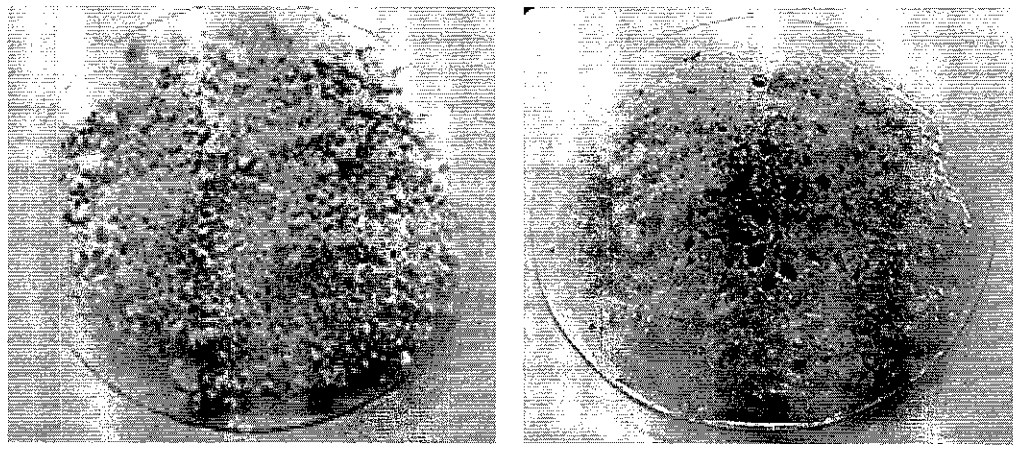
a) In-situ methanolysis



b) In-situ ethanolysis

Figure 4.15: Effect of microwave pretreatment of jatropha curcas on alkaline in-situ methanolysis and in-situ ethanolysis assisted by BTMAOH as a PTC

On application of microwave radiation, the oil molecules oscillate rapidly resulting in molecular collisions and intense local frictional heat; this excitation can improve reactivity as well as loosen and rupture the cellular structure of the seeds. After heating of jatropha curcas seed particles with microwave heat, the seed particles changed its color from faded white to brown with rapture and loosen spongy cellular structure with jatropha oils exposed on the surface of the seeds as shown in Figure 4.16. Thus, microwave preheating of jatropha curcas seed particles, in addition to exiting the reacting molecules, increases the extraction of oils from the seeds through the swallow, rapture and loosens cellular structure of the seeds due to microwave irradiation heating. This interesting result needs to be investigated in greater detail to obtain optimal reaction conditions.



a) Before treatment b) After treatment

Figure 4.16: Physical observations of jatropha curcas seed particles before and after microwave irradiation heat pre treatment

4.4.3 Parametric study and optimization of microwave heat pretreated jatropha curcas seeds in-situ transesterification in the presence of alkaline BTMAOH.

Optimum operating conditions for in-situ transesterification of microwave pretreated jatropha curcas seeds can be determined using response surface methodology (RSM) of central composite design (CCD). Yield of biodiesel produced by in-situ transesterification, Y, depends mainly on the five independent variables: - microwave heating power, MWHP (X_1), microwave heating time, MWHT (X_2), BTMAOH

concentration (X_3), volume of alcohol per weight of oil seed (X_4) and reaction time(X_5). According to RSM experimental design technique, it was considered that each variable can take five different levels from low (-2), (-1), (0), (1) and to high (2). For the 5 independent variables at 5 levels using CCD method requires 32 (= 2^5) experiments. Out of these, 6 experiments were replicated at center points to evaluate the error. Based on a set of preliminary experiments range of the variables, step size and the central value were chosen as shown in Table 4.22.

Table 4.22: Experimental range and level of the independent variables

Variable	**Coded Symb.**	**Unit**	**Range and levels**				
			-2	**-1**	**0**	**1**	**2**
MWHP	X_1	watt	25	50	75	100	125
MWHT	X_2	min.	0.5	2	3.5	5	6
BTMAOH	X_3	mol/mol	0.25	0.75	1.25	1.75	2.25
Ethanol	X_4	ml/g	4.5	6.0	7.5	9.0	10.5
R. time	X_5	min.	15	30	45	60	75

In all the experiments particle size, reaction temperature and stirrer speed needed to keep the particles in suspension were kept constant. The individual and interaction effect of process variables and the optimal conditions needed to achieve maximum yield were investigated using CCD technique of RSM for in-situ methanolysis and in-situ ethanolysis reaction assisted by BTMAOH as a PTC and NaOH as alkaline catalyst. The observations were analyzed by second order model equation (3.5).

The complete design matrix of CCD for the variable combinations (with coded variables in parenthesis) and experimental results are listed in Table 4.23 for in-situ methanolysis and Table 4.26 for in-situ ethanolysis, respectively.

4.4.3.1 In-situ methanolysis of microwave heat pretreated jatropha curcas

Experiments carried out as a function of the un-coded variables (with coded variables in the parenthesis) prompted by central composite design technique along with the observed yields for the in-situ methanolysis are presented in Table 4.23.

FAME yields obtained during in-situ methanolysis at various reaction conditions were analyzed by method of variance (ANOVA) to establish the constants of the quadratic model equation (3.5). Thus, the model equation that predicts the yield of FAME at different variable combination of Table 4.23 was established as shown in equation (4.3). The variables in equation (4.3) were coded according to equation (3.6) of chapter 3.

$$\begin{aligned} Y_{FAME} = 93.69 \; & +1.39x_1+1.24x_2+0.85x_3+0.90x_4+2.03x_5-2.76x_1^2-0.11x_2^2 \\ & -2.39x_3^2-1.32x_4^2-2.31x_5^2-1.36x_1x_2-0.044x_1x_3-0.41x_1x_4-0.72x_1x_5 \\ & +1.84x_2x_3-0.12x_2x_4-1.34x_2x_5-0.32x_3x_4-0.36x_3x_5-1.54x_4x_5 \end{aligned} \quad (4.3)$$

FAME yields predicted by this regression model equation are included in Table 4.23 together with the experimental observations.

Table 4.23: Experimental design matrix by CCD technique for in-situ methanolysis

Run Order	MWHP, X_1 (watt)	MWHT, X_2 (min)	BTMAOH, X_3 (mol/mol)	Methanol, X_4 (ml/g seed)	R. time, X_5 (min)	Exp. yield (% w/w)	Pre. yield (% w/w)
1	75(0)	3.5(0)	1.25(0)	7.5(0)	45(0)	94.2	93.69
2	100(1)	5(1)	0.75(-1)	6.0(-1)	60(1)	88.2	88.28
3	50(-1)	5(1)	1.75(1)	6.0 (-1)	60(1)	87.8	86.79
4	50(-1)	5(1)	1.75(1)	9.0(1)	30(-1)	87.3	86.44
5	75(0)	3.5(0)	1.25(0)	10.5(2)	45(0)	90.5	90.21
6	75(0)	3.5(0)	1.25(0)	7.5 (0)	45(0)	93.8	93.69
7	75(0)	3.5(0)	1.25(0)	4.5(-2)	45(0)	85.3	86.63
8	50(-1)	5(1)	0.75(-1)	9.0(1)	60(1)	89.1	88.69
9	100(0)	2(-1)	1.75(1)	6.0 (-1)	60(1)	92.4	92.54
10	50(-1)	2(-1)	1.75(1)	6.0 (-1)	30(-1)	78.2	77.20
11	100(1)	5(1)	1.75(1)	6.0 (-1)	30(-1)	84.2	83.83
12	75(0)	3.5(0)	1.25(0)	7.5 (0)	45(0)	93.8	93.69
13	75(0)	3.5(0)	0.25(-2)	7.5 (0)	45(0)	82.3	82.41
14	50(-1)	2(-1)	1.75(1)	9.0(1)	60(1)	87.2	86.85
15	100(1)	5(1)	1.75(1)	9.0(1)	60(1)	82.9	83.18
16	100(1)	2(-1)	1.75(1)	9.0(1)	30(-1)	88.2	88.49
17	50(-1)	2(-1)	0.75(-1)	9.0(1)	30(-1)	77.3	76.91
18	75(0)	0.5(-2)	1.25(0)	7.5 (0)	45(0)	90.8	90.79
19	75(0)	3.5(0)	1.25(0)	7.5 (0)	15(-2)	79.4	80.41
20	100(1)	2(-1)	0.75(-1)	6.0 (-1)	30(-1)	78.1	78.19
21	100(1)	2(-1)	0.75(-1)	9.0(1)	60(1)	85.3	86.04
22	75(0)	3.5(0)	1.25(0)	7.5 (0)	45(0)	93.7	93.69
23	75(0)	6.5(2)	1.25(0)	7.5 (0)	45(0)	94.7	95.74
24	100(1)	5(1)	0.75(-1)	9.0(1)	30(-1)	88.8	89.04
25	75(0)	3.5(0)	1.25(0)	7.5 (0)	45(0)	92.3	93.69
26	125(2)	3.5(0)	1.25(0)	7.5 (0)	45(0)	86.7	85.44
27	50(-1)	2(-1)	0.75(-1)	6.0 (-1)	60(1)	82.9	82.35
28	50(-1)	5(1)	0.75(-1)	6.0 (-1)	30(-1)	83.2	82.14
29	75(0)	3.5(0)	1.25(0)	7.5 (0)	45(0)	95.4	93.69
30	25(-2)	3.5(0)	1.25(0)	7.5 (0)	45(0)	77.6	79.89
31	75(0)	3.5(0)	1.25(0)	7.5 (0)	75(2)	88.5	88.53
32	75(0)	3.5(0)	2.25(2)	7.5 (0)	45(0)	84.9	85.83

The significance of the model terms were evaluated statistically. Table 4.24 shows the relative effect of the linear, quadratic and interaction variables in terms of p and t values. A smaller p-value (<0.05) or a greater absolute t-value indicated higher significance of the corresponding coefficient in the model. All the linear terms were significant to influence the yields of FAME. All the squared terms except the squared term of x_2 (MWHT) were also significantly influence the yield of FAME. The interaction terms involving x_1*x_2 (MWHP and MWHT), x_2*x_3 (MWHT and BTMAOH), x_2*x_5 (MWHT and reaction time), and x_4x_5 (volume of alcohol per weight of seeds and reaction time) were found to be significant to affect reaction rate and FAME yield while the remaining interaction terms were least significant.

Table 4.24: t and p values for the regression coefficients

Term	**Coef**	**SE Coef**	**T**	**P**
Constant	93.6943	0.5684	164.8380	0.0000
X_1	1.3875	0.2909	4.7700	0.0010
X_2	1.2375	0.2909	4.2540	0.0010
X_3	0.8542	0.2909	2.9360	0.0140
X_4	0.8958	0.2909	3.0800	0.0100
X_5	2.0292	0.2909	6.9760	0.0000
X_1 X_1	-2.7568	0.2631	-10.4770	0.0000
X_2 X_2	-0.1068	0.2631	-0.4060	0.6930
X_3 X_3	-2.3943	0.2631	-9.1000	0.0000
X_4 X_4	-1.3193	0.2631	-5.0140	0.0000
X_5 X_5	-2.3068	0.2631	-8.7670	0.0000
X_1 X_2	-1.3562	0.3563	-3.8070	0.0030
X_1 X_3	-0.0437	0.3563	-0.1230	0.9040
X_1 X_4	-0.4062	0.3563	-1.1400	0.2780
X_1 X_5	-0.7187	0.3563	-2.0170	0.0690
X_2 X_3	-1.8438	0.3563	-5.1750	0.0000
X_2 X_4	-0.1062	0.3563	-0.2980	0.7710
X_2 X_5	-1.3438	0.3563	-3.7720	0.0030
X_3 X_4	-0.3187	0.3563	-0.8950	0.3900
X_3 X_5	-0.3563	0.3563	-1.0000	0.3390
X_4 X_5	-1.5438	0.3563	-4.3330	0.0010

Table 4.25 presents results of statistical analysis of the regression coefficients in terms of F-test and P-test. Large F-test values (21.65) and very low probability values ($p \leq 0.05$) confirm the validity of model equation (4.3). The 'lack of fit tests' (compares the residual error to the pure error) from replicated design experimental points indicated a high F –test value of 2.92 and a 13% of pure error [202].

Thus, the empirical model is adequate to represent and explain most of the variability.

Table 4.25: The regression analysis of the least square fit and parameter estimate

Source	**DF**	**Sum of squares**	**Adj Sum of Square**	**Adj Mean Square**	**F-value**	**P-value**
Regression	20	879.310	879.310	43.9655	21.65	0.000
Linear	5	218.549	218.549	43.7098	21.52	0.000
Square	5	495.145	495.145	99.0290	48.76	0.000
Interaction	10	165.616	165.616	16.5616	8.16	0.001
Residual Error	11	22.339	22.339	2.0308		
Lack-of-Fit	6	17.385	17.385	2.8976	2.92	0.130
Pure Error	5	4.953	4.953	0.9907		

The parity plot as shown in Figure 4.17 also compares the observed experimental FAME yield with the model predicted values of FAME. The parity plot signifies 97.52% of the variability in the data is accounted to the quadratic model equation. Thus, the empirical model is adequate enough to represent and explain most of the variability.

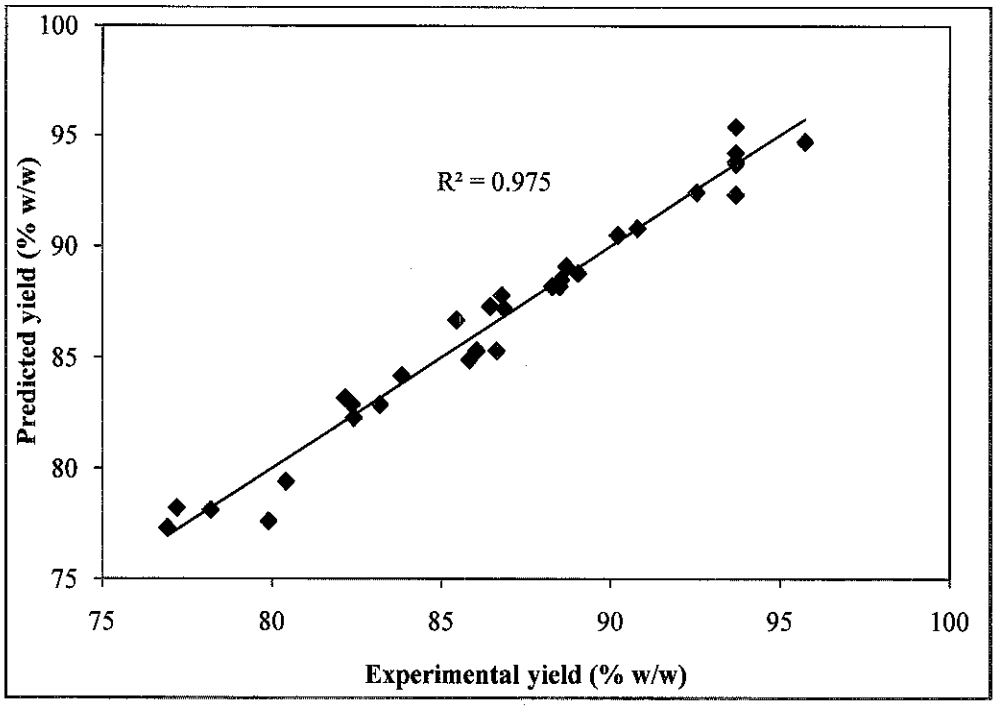


Figure 4.17: The parity plot of experimentally observed yield versus model equation predicted yield

i) The individual and interaction effect of the reaction variables on FAME yield

Understanding the individual and cross effect of process variables is a key to optimize the reaction conditions to achieve the desired product qualitatively and quantitatively. Thus, the empirical model is plotted on a three dimensional surfaces with the contour plot at the bottom representing the response (FAME yield) as a function of two reaction variables within the investigated experimental range while keeping the other variables constant at their center points as shown in the Figure 4.18.

Figure 4.18 (a) illustrates the interaction effect of MWHP and MWHT on the yield of FAME. High yield of FAME was attained with MWHP in the range of 85w to 100w and MWHT of about 4.5minutes. Further increasing both variables have a negative effect on the yield of FAME. At higher MWHP and longer heating time the seeds were burned forming ashes and while conducting in-situ transesterification reaction, the yield of FAME was reduced slightly. On the other hand at lower MWHP and MWHT, the microwave energy (electromagnetic irradiation) may not be enough

to rapture the seeds, initiate collision and friction between molecules of oil to give intense localized heating and increase reactive extractability.

The elliptical nature of the contour plot at the bottom of response surface plot of the yield of FAME as a function of MWHP and BTMAOH indicated the interaction effect of MWHP and BTMAOH concentration is significant to affect the yield of FAME as presented in Figure 4.18 (b). The yield of FAME was lower at lower BTMAOH concentration and MWHP. The yield increased with increasing both the MWHP and BTMAOH concentration. However, increasing MWHP beyond 100watt and the concentration of BTMAOH greater than 1.25 mole BTMAOH/mole of NaOH did not have significant impact. At lower BTMAOH, there may not be sufficient BTMAOH to promote better catalytic performance of PTC. A similar trend was observed on the interaction effects of MWHP and the ratio of the volume of methanol to mass of seeds as presented in Figure 4.18(c). Increasing the ratio of volume of alcohol to weight of seeds to about 7.5ml/g increased the yield of FAME. However, further increasing of the alcohol volume has slightly a negative effect due to solubility of FAME at much excess alcohol volume.

Figure 4.18 (d) presents the response surface plots of the interaction effects of MWHP and reaction time on the yield of FAME. It can be observed that maximum yield of FAME was achieved at about 85 to 100watt and about 35 to 40 minutes of reaction time. Further increasing the reaction time has negative effect on the yield of FAME.

Figures 4.18(e) and 4.23(f) illustrate the interaction effect of MWHT with the concentration of BTMAOH and volume of methanol on FAME yield, respectively. In both cases, the yield of FAME increased with increasing the MWHT and the maximum yield can be obtained in the range 4.5 to 5 minutes of MWHT of jatropha curcas seed particles; however, the concentration of BTMAOH should be kept to about 1.25mol/mol of NaOH and the volume of methanol to seed ratio of up to 7.5ml/g. It was also observed that the cross effects of MWHT with BTMAOH and volume of alcohol was less significant as compared to their individual effects.

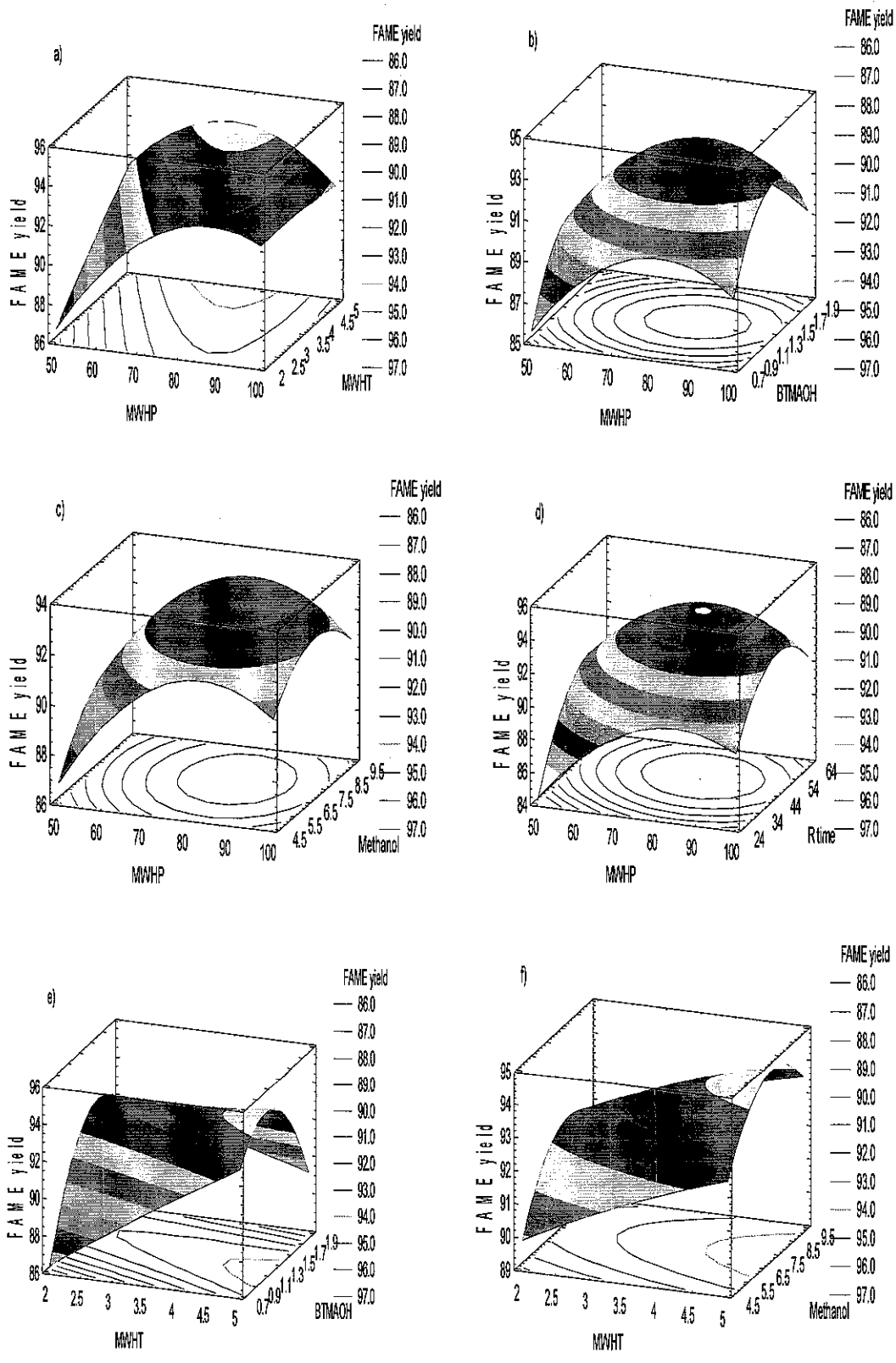


Figure 4.18: Response surface plots of the combined variables of different combination on FAME yield

4.4.3.2 In-situ ethanolysis of microwave heat pretreated jatropha curcas

Similarly, for in-situ ethanolysis of microwave heat pretreated jatropha curcas seed particles in-situ ethanolysis experiments were designed using RSM for parametric interaction study and establishment optimum reaction condition. The designed experiments were carried out as a function of the un-coded variables (with coded variables in the parenthesis) prompted by CCD technique along with the observed yields as presented in Table 4.26.

The statistical method of variance (ANOVA) was used to establish the constants of quadratic model equation (3.5) using the yields of FAEE obtained during in-situ ethanolysis at various reaction conditions of Table 4.26. Thus, the model equation that predicts the yield of FAEE at different coded variable combination of Table 4.26 is established as shown in equation (4.4).

$$\begin{aligned} Y_{FAEE} = {} & 96.92 + 0.53x_1 + 0.52x_2 + 1.44x_3 + 0.62x_4 + 1.43x_5 + 0.42x_1^2 + 0.11x_2^2 \\ & - 0.85x_3^2 - 1.1x_4^2 - 0.31x_5^2 - 0.66x_1x_2 + 0.95x_1x_3 + 0.54x_1x_4 - 0.0875x_1x_5 \\ & + 0.13x_2x_3 - 0.61x_2x_4 - 0.44x_2x_5 - 0.4x_3x_4 + 0.58x_3x_5 - 0.04x_4x_5 \end{aligned} \quad (4.4)$$

FAME yields predicted by this regression model equation are included in Table 4.26 together with the experimental observations.

The significance of the model terms were tested using statistical methods. Table 4.27 shows the relative effect of the linear, quadratic and interaction variables in terms of p and t values. A smaller p-value (<0.05) or a greater absolute t-value indicated higher significance of the corresponding coefficient in the model. Like in-situ methanolysis, during in-situ ethanolysis all linear terms have significant effect on the yield of FAEE. The squared terms of x_1 (MWHP), x_3 (BTMAOH) and x_4 (volume of alcohol per weight of seeds) have shown significant interaction effects while the remaining squared terms have least significant comparatively. The cross terms of the process variables combination of x_1*x_2, x_1*x_3, x_2*x_4 and x_3*x_5 have also significant effect to influence the yield of FAEE while the interaction effect of the remaining cross terms were less significant to affect the yield of FAEE.

Table 4.26: Experimental design matrix by CCD technique for in-situ ethanolysis

Run Order	MWHP (watt)	MWHT (min)	BTMAOH (mol/mol of NaOH)	Ethanol (ml/g seed)	R. time (min)	Exp. yield (% w/w)	Pred. yield (% w/w)
1	100(1)	2(-1)	0.75(-1)	6.0(-1)	30(-1)	91.1	90.28
2	50(-1)	2(-1)	0.75(-1)	9.0(1)	30 (-1)	93.2	92.96
3	100(1)	5(1)	0.75(-1)	6.0 (-1)	60(1)	92.9	92.39
4	75(0)	3.5(0)	1.25(0)	7.5 (0)	75(2)	98.6	98.37
5	75(0)	6.5(2)	1.25(0)	7.5 (0)	45(0)	97.7	98.37
6	25(-2)	3.5(0)	1.25(0)	7.5 (0)	45(0)	97.2	97.54
7	50(-1)	2(-1)	0.75(-1)	6.0 (-1)	60(1)	93.7	93.36
8	100(1)	5(1)	0.75(-1)	9.0(1)	30 (-1)	94.2	93.79
9	50(-1)	5(1)	1.75(1)	6.0 (-1)	60(1)	99.2	99.00
10	125(2)	3.5(0)	1.25(0)	7.5 (0)	45(0)	98.9	99.64
11	100(1)	2(-1)	0.75(-1)	9.0(1)	60(1)	96.8	96.84
12	50(-1)	2(-1)	1.75(1)	6.0 (-1)	30 (-1)	91.6	91.08
13	75(0)	3.5(0)	2.25(2)	7.5 (0)	45(0)	96.3	96.42
14	75(0)	3.5(0)	1.25(0)	7.5 (0)	45(0)	97.7	96.92
15	100(1)	2(-1)	1.75(1)	9.0(1)	30 (-1)	97.4	97.27
16	100(1)	5(1)	1.75(1)	6.0 (-1)	30 (-1)	97.2	96.52
17	75(0)	3.5(0)	1.25(0)	7.5 (0)	45(0)	96.3	96.92
18	75(0)	3.5(0)	1.25(0)	10.5(2)	45(0)	94.2	93.77
19	75(0)	3.5(0)	1.25(0)	7.5 (0)	45(0)	96.7	96.92
20	75(0)	0.5(-2)	1.25(0)	7.5 (0)	45(0)	95.9	96.31
21	75(0)	3.5(0)	1.25(0)	7.5 (0)	45(0)	97.6	96.92
22	50(-1)	5(1)	1.75(1)	9.0(1)	30 (-1)	94.1	94.00
23	50(-1)	2(-1)	1.75(1)	9.0(1)	60(1)	96.2	96.55
24	75(0)	3.5(0)	1.25(0)	4.5(-2)	45(0)	89.8	91.31
25	75(0)	3.5(0)	1.25(0)	7.5 (0)	45(0)	96.5	96.92
26	75(0)	3.5(0)	1.25(0)	7.5 (0)	45(0)	97.8	96.92
27	50(-1)	5(1)	0.75(-1)	9.0(1)	60(1)	95.4	95.48
28	75(0)	3.5(0)	1.25(0)	7.5 (0)	15(-2)	91.7	93.01
29	75(0)	3.5(0)	0.25(-2)	7.5(0)	45(0)	89.7	90.66
30	100(1)	2(-1)	1.75(1)	6.0 (-1)	60(1)	99.3	99.07
31	100(1)	5(1)	1.75(1)	9.0(1)	60(1)	99.4	99.58
32	50(-1)	5(1)	0.75(-1)	6.0 (-1)	30 (-1)	95.7	94.91

Table 4.27: t and p values for the regression coefficients in the second order model equation (4.4)

Term	Coef	SE Coef	T	P
constant	96.9205	0.4127	234.849	0.000
x_1	0.5250	0.2112	2.486	0.030
x_2	0.5167	0.2112	2.446	0.032
x_3	1.4417	0.2112	6.826	0.000
x_4	0.6167	0.2112	2.920	0.014
x_5	1.3417	0.2112	6.353	0.000
$x_1 * x_1$	0.4170	0.1910	2.183	0.050
$x_2 * x_2$	0.1045	0.1910	0.547	0.595
$x_3 * x_3$	-0.8455	0.1910	-4.426	0.001
$x_4 * x_4$	-1.0955	0.1910	-5.734	0.000
$x_5 * x_5$	-0.3080	0.1910	-1.612	0.135
$x_1 * x_2$	-0.6625	0.2587	-2.561	0.026
$x_1 * x_3$	0.9500	0.2587	3.673	0.004
$x_1 * x_4$	0.5375	0.2587	2.078	0.062
$x_1 * x_5$	-0.0875	0.2587	-0.338	0.742
$x_2 * x_3$	0.1250	0.2587	0.483	0.638
$x_2 * x_4$	-0.6125	0.2587	-2.368	0.037
$x_2 * x_5$	-0.4375	0.2587	-1.691	0.119
$x_3 * x_4$	-0.4000	0.2587	-1.546	0.150
$x_3 * x_5$	0.5750	0.2587	2.223	0.048
$x_4 * x_5$	-0.0375	0.2587	-0.145	0.887

The significant of the model equation (4.4) used to estimate the yield of FAEE was also justified using the least square fit and parameter estimate. The regression analysis result of the least square fit and parameter estimate as shown in Table 4.34 indicate the significance of the quadratic model equation which is justified by its large Fisher F-test values of 10.41 and very low probability values ($p \leq 0.05$). It was also noted that the 'lack of fit tests' which compared the residual error to the 'pure error' from replicated design points indicated a 'lack of fit F-value' of 3.51, which significantly imply that there are only a 9.5% chance that a 'lack of fit F-value' could occur (Table 4.28).

Table 4.28: Regression analysis of the least square fit and parameter estimate

Source	DF	Sum of squares	Adj Sum of Square	Adj Mean Square	F-value	P-value
Regression	20	222.884	222.884	11.1442	10.41	0.000
Linear	5	115.232	115.232	23.0463	21.53	0.000
Square	5	64.257	64.257	12.8515	12.00	0.000
Interaction	10	43.395	43.395	4.3395	4.05	0.015
Residual Error	11	11.776	11.776	1.0706		
Lack-of-Fit	6	9.516	9.516	1.5860	3.51	0.095
Pure Error	5	2.260	2.260	0.4520		

The parity plot as shown in Figure 4.19 also compares the observed experimental FAEE yield with the model predicted values of FAEE. The parity plot signifies 94.96 % of the variability in the data is accounted to the quadratic model equation. Thus, the empirical model is adequate enough to represent and explain most of the variability.

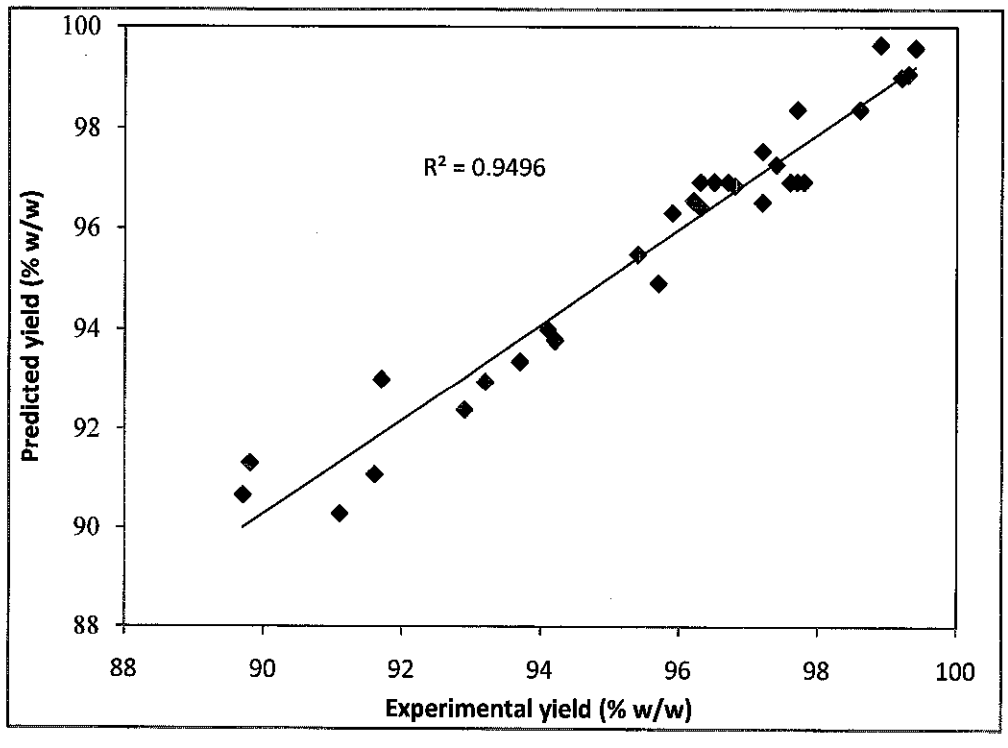
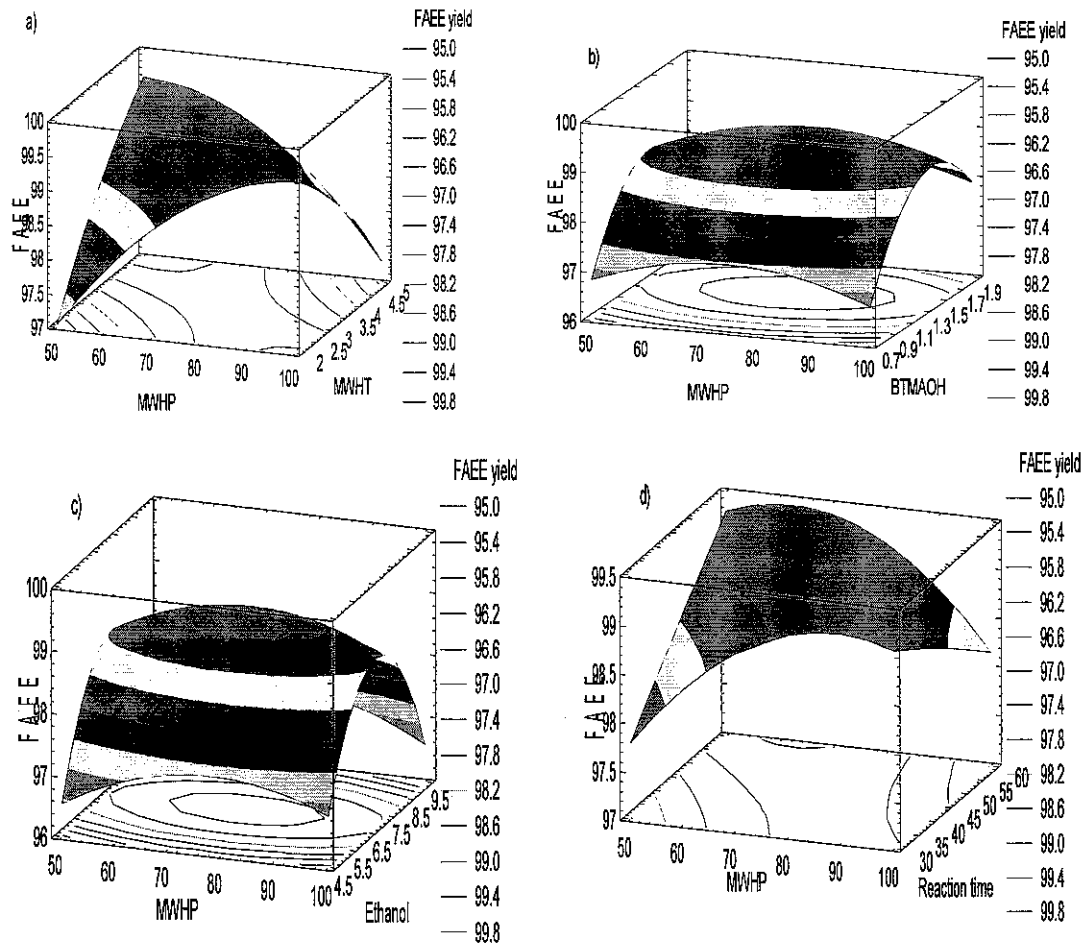


Figure 4.19: The parity plot of experimentally observed yield versus model equation predicted yield

i) The individual and interaction effect of the reaction variables on FAEE yield

The investigation of the effect of the individual variables and their interaction effect on FAEE yield were conducted by plotting the response surface for the yield of FAEE with the contour plot at the bottom as a function of two reaction variables within the investigated experimental range while keeping the other variables at their center points as shown in the Figure 4.20 (a) to (f).

The effect of the variables on the yield of FAEE demonstrated similar trends with the parametric effect on the yield of FAME as shown in Figure 2.18 (a) to (f) except that higher yields are obtained during in-situ ethanolysis as compared to the yields obtained during in-situ methanolysis due to better solubility of ethanol with oils.



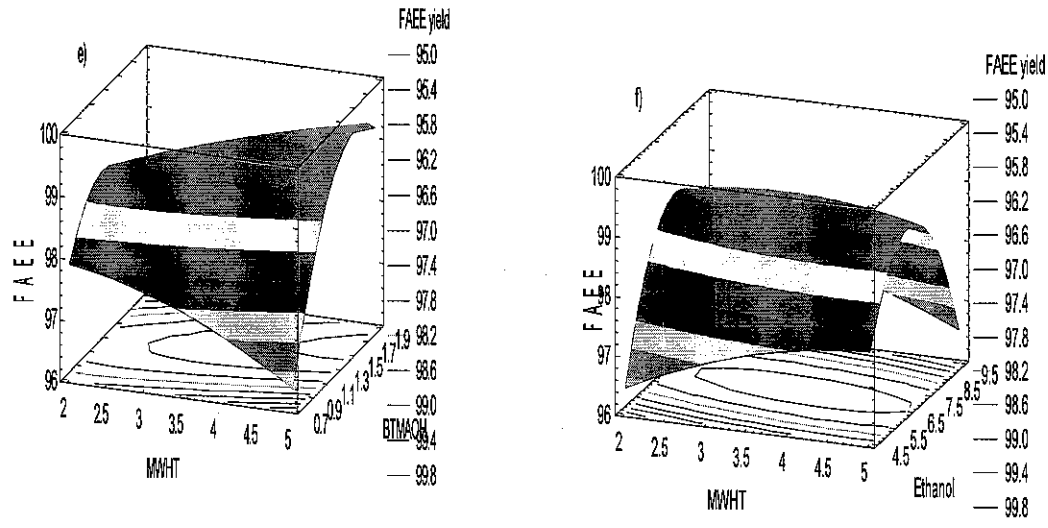


Figure 4.20: Response surface plots of two combined variables of different combination on FAEE yield

4.4.3.3 Optimum reaction conditions

Statistical tools of response surface central composite design technique response surface analysis response optimizer was used to determine the optimum reaction variables of in-situ methanolysis and in-situ ethanolysis reactions of microwave irradiation heat treated jatropha curcas seed particles. The optimum value of reaction variables predicted by response surface optimizer and the corresponding expected maximum yields of FAME and FAEE are presented in Table 4.29, respectively.

To test and validate the significance of the model predictions, experiments were conducted in duplicate at the optimal condition. The experimental result demonstrated that for in-situ methanolysis reaction, experimentally observed yield of FAME (93.7±1.53% w/w) is in close agreement with the expected maximum yield suggested (96.75% w/w) by the model equation (4.3). Similarly, for in-situ ethanolysis reaction, the experimentally observed yield of FAEE (99.5 ± 0.12% w/w) is in close agreement with the expected maximum yield suggested (99.61% w/w) by the model equation (4.4). The maximum yields of both FAME and FAEE is in close agreement with the experimental results indicating the model equation reasonability predicts the yield of FAME and FAEE at the different variables combination obtained using CCD of RSM.

Table 4.29: Optimum operating conditions of FAME and FAEE production by in-situ transesterification method

Factor	Unit	Optimum value for FAME yield	Optimum value for FAEE yield
Microwave heating power, MWHP	watt	85	85
Microwave heating tine, MWHT	min	4.5	4.5
BTMAOH concentration	mol/mol	1.25	1.25
volume of methanol to weight of seeds	ml/g	7.5	7.5
Reaction time	min	37	30
Predicted optimum FAME yield	% w/w	96.75	-
Experimental optimum FAME yield	% w/w	93.7±1.53	-
Predicted optimum FAEE yield	% w/w	-	99.61
Experimental optimum FAEE yield	% w/w	-	99.5±0.12

4.5 Quality of FAME and FAEE produced at optimal operating conditions

For a biodiesel to be used as a diesel fuel, the fuel need to satisfy the quality assurance parameters set by the ASTM D 6751-07 and EN-14. These standards specify the minimum requirement of biodiesel to be used as a fuel. The physical and chemical properties of fatty acid methyl esters (FAME) and fatty acids ethyl esters (FAEE) produced as a biodiesel at optimal condition using phase transfer catalysis and microwave irradiation pretreated jatropha curcas seed particles of the present work were analyzed if the fuels fulfill the requirements of ASTM D 6751-07 and EN-14. The results of the analysis are presented in Table 4.30 along with the requirements set by the ASTM D 6751-07 and EN-14 standards. It can be seen that the properties of both FAME and FAEE produced at optimal condition are within the requirements of international standards of biodiesel as a fuel.

Table 4.30: Properties of fatty acid methyl esters and fatty acid ethyl esters as compared to international standards

Parameters	Unit	FAME	FAEE	ASTM D 6751	EN-14
Kin. Viscosity, 40°C	mm2/s	4.9	4.8	1.9-6	
Sp. gravity	-	865	867	-	860-900
Acid number	mgKOH/g	0.03	0.03	0.5max	
Free glycerin	%mass	0.014	0.012	0.02max	
monoglycerides	%mass	0.028	0.031	-	<0.8
diglycerides	%mass	0.06	0.08	-	<0.2
triglycerides	%mass	0.08	0.06	-	<0.2
Total glycerides	%mass	0.2	0.18	0.24	-
Iodine value		101	101	-	120
Cloud point	°C	6	7	-	-
Pour point	°C	8	8	-	-
Water content	% v/v	0.001	0.001	0.05max	-
Flash point	°C	168	170	130min	-
Heating value	Cal/mol	9833	9896	-	-

4.6 Summary

Graded particles of Jatropha curcas seed [300-500 μm in size range with moisture content of (1.3 ±0.17)% w/w, oil content of (52.8±0.16% w/w), free fatty acid percentage of (0.67%), saponification value of (201.82±0.23mgof KOH/g), Iodine value of (101±1.2mgI_2/g of oil)] were used for investigating in-situ transesterification with alkaline methanol/ethanol. Alkaline catalysts such as sodium hydroxide can catalyze the transesterification reactions due to the low FFA content.

Maximum yield obtained and the reaction time required for in-situ transesterification of jatropha curcas seed particles with alkaline methanol and ethanol were given in the following table:

Table 4.31: Maximum FAME and FAEE yield and reaction time

In-situ transesterification with Alkaline NaOH catalys	**Reaction time**	**Yield**
FAME	240 min	49.7±2.47%w/w
FAEE	210 min	89.2±1.56% w/w

The reaction rates between the sparingly soluble oil and alcohol phases can be enhanced by phase transfer catalysis. Three compounds - Cethyltrimethylammonium bromide (CTMAB), benzyltrimethylammonium hydroxide (BTMAOH) and crown ether (CE) – were tested for their phase transfer catalytic effect on in-situ transesterification. It was observed that reaction rates were greatly improved with BTMAOH as a phase transfer catalyst. Response surface methodology was adopted to investigate for optimum operating conditions to enhance reaction rates and yield of biodiesel using BTMAOH for in-situ transesterification with alkaline methanol/ethanol. Optimum reaction time and yield obtained for FAME and FAEE were given in the following table:

Table 4.32: Optimum reaction time for BTMAOH as PTC catalyzed transesterification and maximum yield of FAME and FAEE

In-situ transesterification	**With only NaOH alkaline catalyst**		**With NaOH as alkaline catalyst + BTMAOH as PTC**	
	Reaction Time	**Yield**	**Reaction Time**	**Yield**
FAME	240 min	49.7±2.47%w/w	103 min	89.8±0.7% w/w
FAEE	210 min	89.2±1.56 % w/w	95 min	99.4±0.4% w/w

It can be seen that yield in presence of BTMAOH as PTC was higher in shorter reaction time compared with simple alkali catalyzed in-situ transesterification reaction.

Effect of pretreatment of jatropha seed particles with microwave radiation prior to in-situ transesterification of jatropha curcas seed particles with alkali in presence of BTMAOH as PTC was investigated and the optimum results are summarized in the following table:

Table 4.33: Optimum reaction time for microwave pretreated jatropha particles transesterification and maximum yield of FAME and FAEE

In-situ transesterification	**With NaOH + BTMAOH as PTC**		**With NaOH + BTMAOH as PTC and 85 W MWH pretreatment of seeds for 4.5 min**	
	R. Time	**Yield**	**R. Time**	**Yield**
FAME	103 min	89.8±0.7% w/w	37min	93.7±1.53% w/w
FAEE	95 min	99.4±0.4% w/w	30min	99.5± 0.12% w/w

It can be seen that pretreatment of seed particles with microwave radiation reduced reaction time drastically while achieving higher yield. The physical and chemical prosperities of FAME and FAEE produced at optimal conditions compare well with ASTM and EN-14 international biodiesel standards.

CHAPTER 5

MECHANISM AND MODELING OF REACTION KINETICS

5.1 Introduction

This chapter presents reaction kinetics of in-situ transesterification of jatropha curcas seed particles assisted by phase transfer catalysis, reaction mechanism of phase transfer catalysis during in-situ transesterification and mathematical modeling of reaction mechanism based kinetics. Section 5.2 demonstrates the reaction kinetics of in-situ transesterification of jatropha curcas seed particles assisted by benzyltrimethylammonium hydroxide (BTMAOH) as a phase transfer catalyst (PTC) while section 5.3 presents the reaction kinetics of in-situ transesterification of microwave irradiation pretreated jatropha curcas seed particles with alkaline methanol and ethanol in the presence of BTMAOH. Phase transfer catalytic reaction mechanism of PTC and mechanism based mathematical modeling of the kinetics are discussed in section 5.4. Section 5.5 summarizes the result and discussion of chapter five.

5.2 In-situ transesterification of jatropha curcas seeds in the presence of alkaline BTMAOH as a PTC.

5.2.1 Empirical reaction kinetics

Jatropha oil is mainly a mixture of triglycerides of C_{16} to C_{18} fatty acids with an average molecular weight of 878 g/mol as presented in chapter 4 Table 4.2. Fatty acid triglycerides can be further transesterified with lighter alcohols in presence of a catalyst (alkaline/acidic/enzymatic materials) to produce biodiesel and glycerol. The reaction can be slow as the alcohols and oils are not very soluble. Soap may also be

formed by the undesirable fatty oils reaction with alkalis. In spite of the heterogeneity due to limited solubility among the different phases, estimation of an effective empirical rate constant assuming the system to be a pseudo homogeneous phase can provide useful information for the reactor design calculations. The expected overall reactions are as shown in equation (5.1).

$$\text{Triglycerides} + 3\ \text{Alcohol} \xleftrightarrow{\text{NaOH, BTMAOH}} 3\ \text{Biodiesel} + \text{Glycerol}$$

$$\text{Triglycerides} + \text{NaOH} \longrightarrow \text{Soap} + \text{Glycerol} \qquad (5.1)$$

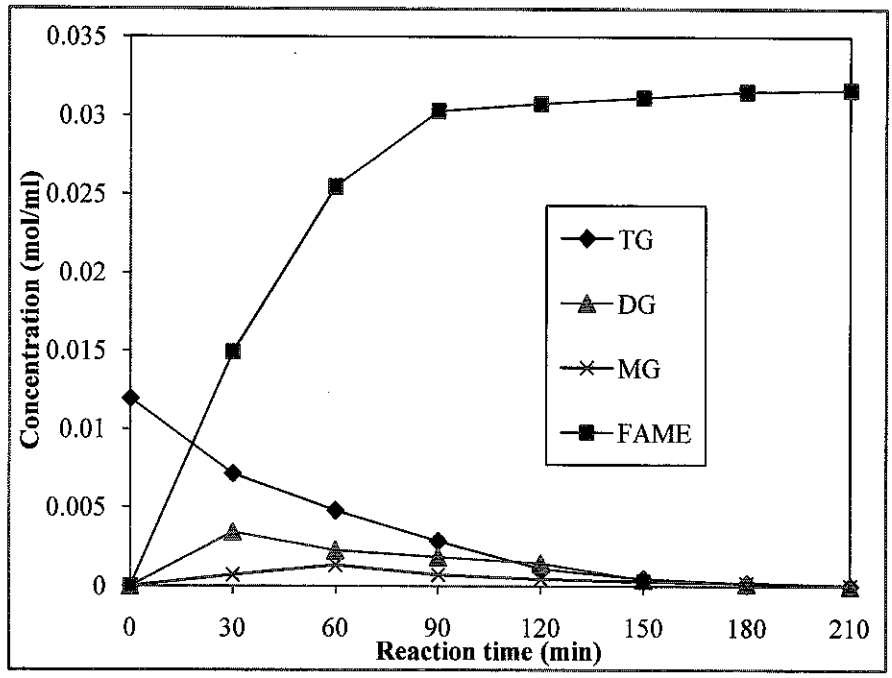
One mol of triglycerides requires three moles of alcohol to produce 3 moles of biodiesel and one mol of glycerol. The undesirable saponification reaction which can produce soap needs to be suppressed to improve the economics. The alkaline transesterification reaction is mildly exothermic and reversible in nature though the reverse reaction is very slow [71]. Use of excess alcohol can drive the reaction to completion. Dependence of the reaction kinetics on concentration of reactants and temperature through activation energy needs to be experimentally measured and correlated by empirical of the reaction rate equation (5.2).

$$-\frac{d[TG]}{dt} = \bar{k}\,[TG]^n \qquad (5.2)$$

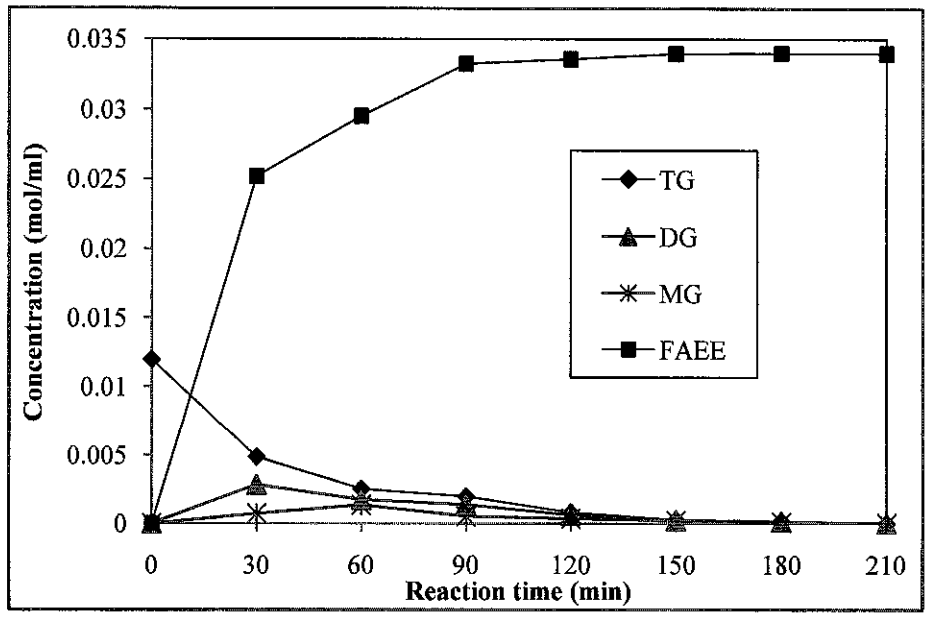
The apparent rate constant $\bar{k}$ can depend on concentration of catalyst, ratio of alcohol to oil, temperature and level of mixing.

In-situ transesterification reaction with alkaline methanol and ethanol using BTMAOH as a PTC was investigated at optimal conditions (chapter 4 section 4.3.4.3) in a batch reactor (at temperatures of 30, 40, 50, and 60°C). The reaction was terminated at the end of specific reaction time (30, 60, 90, 120, 150, 180 and 210 minutes) and the product oil layer was recovered by washing with water. The product oil layer was analyzed using gas chromatography (GC) technique as per ASTM D 65 84-00 testing procedure [196]. Typical chromatograms are included in APPENDIX-B. Molar concentration of triglycerides, diglycerides, monoglycerides and FAME/FAEE

estimated from the chromatograms using the internal reference standards with reaction time are shown in Figure 5.1 (a) and (b).



a) In-situ methanolysis



b) In-situ methanolysis

Figure 5.1 Reaction profiles of TG, DG, MG and FAME and FAEE for in-situ methanolysis and ethanolysis as a function of reaction time

It can be seen that diglycerides and monoglycerides are intermediates which are formed and get converted to biodiesel simultaneously. The overall reaction rate of

triglycerides conversion was estimated by differential analysis [203] to obtain order of reaction and rate constant as per equation(5.2) for triglycerides conversion during in-situ methanolysis as well as in-situ ethanolysis at various temperatures and the corresponding reaction rate equations are shown in Table 5.1.

Table 5.1: The reaction rate equation for triglycerides conversion during in-situ methanolysis and ethanolysis at different reaction temperature

Temp, °K	In-situ methanolysis	In-situ ethanolysis
	Rate equation, $-r_{[TG]}$, (mol/ml.min)	Rate equation, $-r_{[TG]}$ (mol/ml.min)
303	$-r_{TG} = 0.0139[TG]^{0.8587}$	$-r_{TG} = 0.03164[TG]^{1.053}$
313	$-r_{TG} = 0.0193[TG]^{0.9704}$	$-r_{TG} = 0.04235[TG]^{1.211}$
323	$-r_{TG} = 0.0277[TG]^{1.1768}$	$-r_{TG} = 0.05168[TG]^{1.211}$
333	$-r_{TG} = 0.0334[TG]^{1.264}$	$-r_{TG} = 0.07125[TG]^{1.253}$

The result shows that the order of the reaction is nearly one for both methanolysis as well as ethanolysis for the range of operating conditions investigated. Assuming the order of reaction to be one, rate constant were re-evaluated at each temperature for further kinetics analysis and presented in table 5.2.

Table 5.2: Reaction rate constants of in-situ methanolysis and ethanolysis reaction at different reaction temperature

Temp. (°K)	1/T	In-situ methanolysis		In-situ ethanolysis	
		Reaction order, n	Rate constant, k	Reaction order, n	Rate cons., k
303	0.0033	1	0.01637	1	0.030133
313	0.0032	1	0.01832	1	0.041097
323	0.0031	1	0.02853	1	0.050132
333	0.0030	1	0.03343	1	0.055363

Reaction rate constant is a temperature dependent term and can be represented by Arrhenius' law as presented in equation (5.3);

$$k = k_A e^{\frac{-Ea}{RT}} \tag{5.3}$$

Where: E_a is activation energy of the reaction, k_A is frequency factor and R is universal gas constant.

Arrhenius plots of both in-situ methanolysis and ethanolysis reactions are shown in Figure 5.2. The activation energy of the reaction was found to be 21,641J/mol for in-situ methanolysis and 17,078J/mol for in-situ ethanolysis. A similar investigation reported by Marjanovic´ et al. [204] showed that the activation energy of base-catalyzed sunflower oil transesterification reaction was in the range of 8,300 to 35,100J/mole. However, Doell et al. [205] reported in their work the activation energies of trans-methylation of soybean oil as 63,000J/mol. Present values are relatively less and this could be due to diffusion effects inherent in in-situ transesterification reactions.

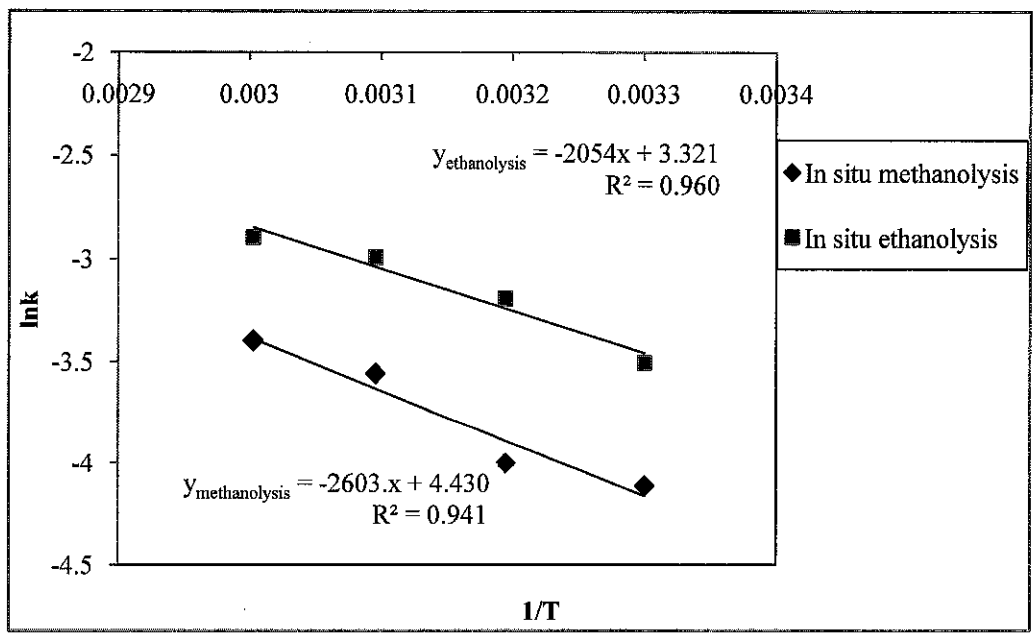


Figure 5.2: Arrhenius' plots of lnk versus 1/T

The empirical rate equation obtained using experimental results can be rewritten in terms of reaction temperature and conversion as a function of reaction time as;

For in-situ methanolysis reaction equation (5.4),

$$-r_{TG} = 84\,[TG]_o\, e^{\left(-\frac{21641}{8.314T}\right)}(1-X_{TG}) \tag{5.4}$$

Similarly for in-situ ethanolysis reaction equation (5.5);

$$-r_{TG} = 28\,[TG]_o\, e^{\left(-\frac{17078}{8.314T}\right)}(1-X_{TG}) \tag{5.5}$$

5.2.2 Validation of the rate equations

The reactor used in present work is a batch reactor; the performance report for a batch reaction can be evaluated based on resident time of the reaction using equation (5.6).

$$t = TG_0 \int_0^{X_{TG}} \frac{dX_{TG}}{-r_{TG}} \tag{5.6}$$

For a first order equation

$$X_{TG} = 1 - e^{-kt} \tag{5.7}$$

For in-situ methanolysis reaction, the rate constant, k is

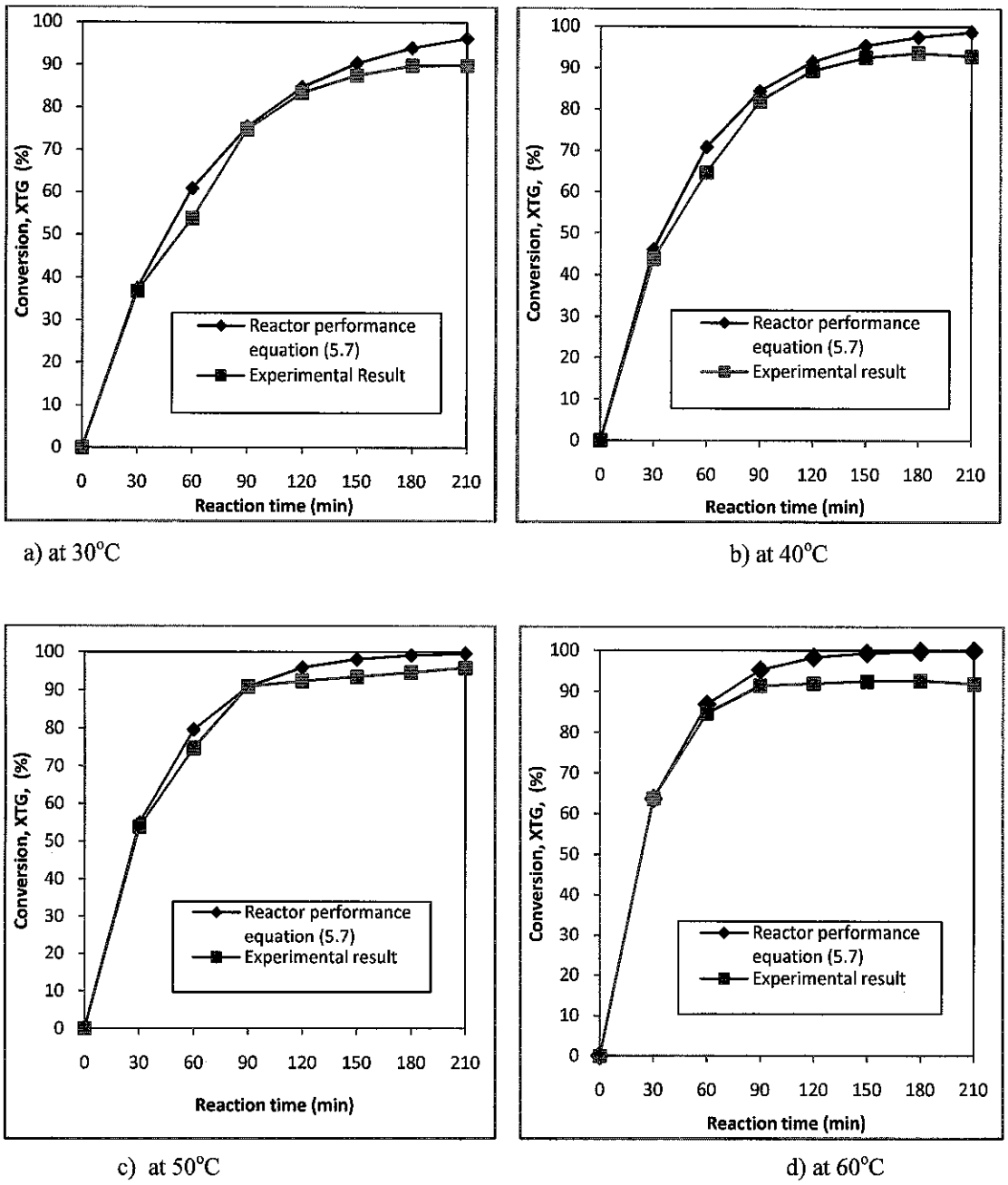
$$k = 84\, e^{\left(-\frac{21641}{8.314T}\right)} \tag{5.8}$$

Similarly for in-situ ethanolysis reaction, the rate constant is

$$k = 28\, e^{\left(-\frac{17078}{8.314T}\right)} \tag{5.9}$$

Where, k = reaction rate constant (min^{-1}) and T = reaction temperature (^oK).

The results of triglycerides conversion, X_{TG} obtained using equation (5.7) and substituting the values of reaction rate constant k of equation (5.8) for in-situ methanolysis and equation (5.9) for in-situ ethanolysis as a function of reaction time, t at different reaction temperatures compare well with experimental observations as a shown in Figure 5.3 and 5.4, respectively.



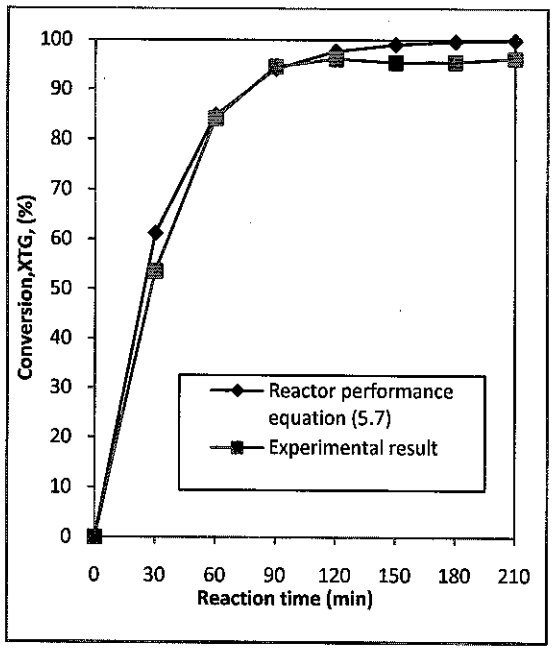
a) at 30°C

b) at 40°C

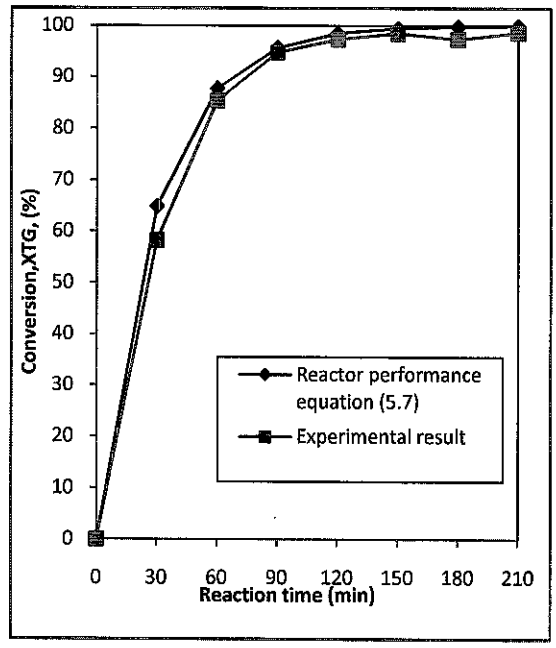
c) at 50°C

d) at 60°C

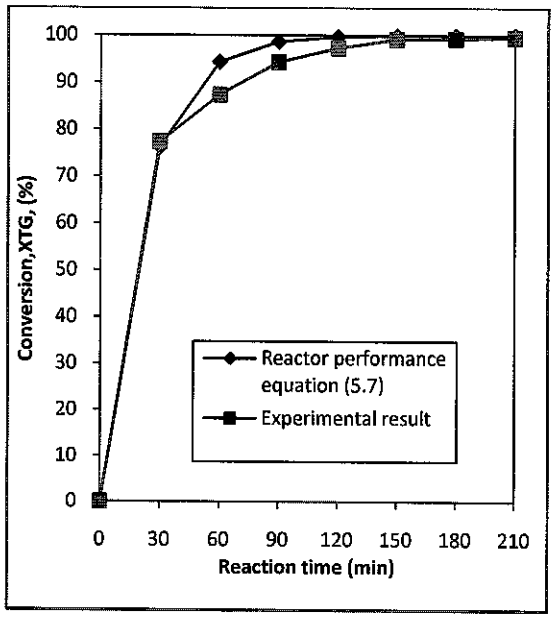
Figure 5.3: Comparisons of experimentally achieved conversion of triglycerides during PTC assisted in-situ methanolysis with the batch reactor performance equation (5.7) at different reaction temperature



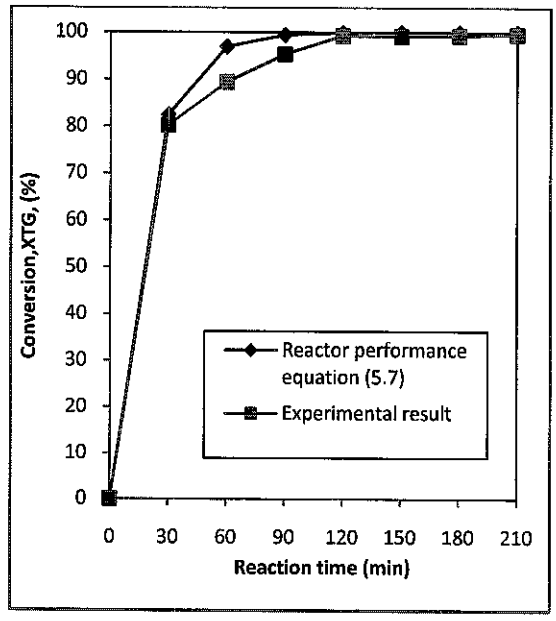
a) at 30°C



b) at 40°C



c) at 50°C



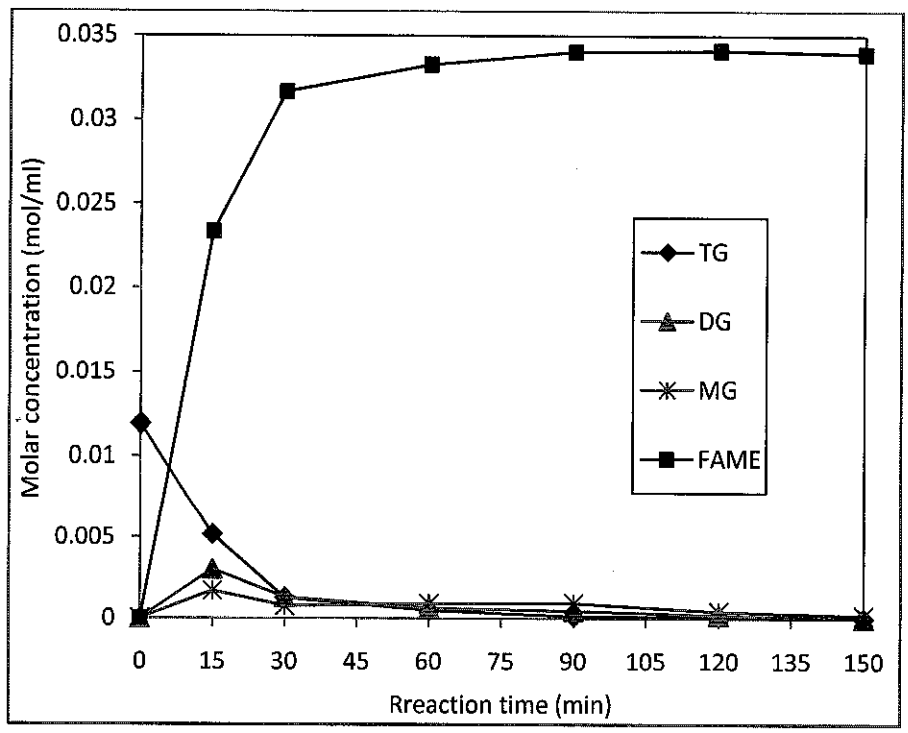
d) at 60°C

Figure 5.4: Comparisons of experimentally achieved conversion of triglycerides during PTC assisted in-situ ethanolysis with the batch reactor performance equation (5.7) at different reaction temperature.

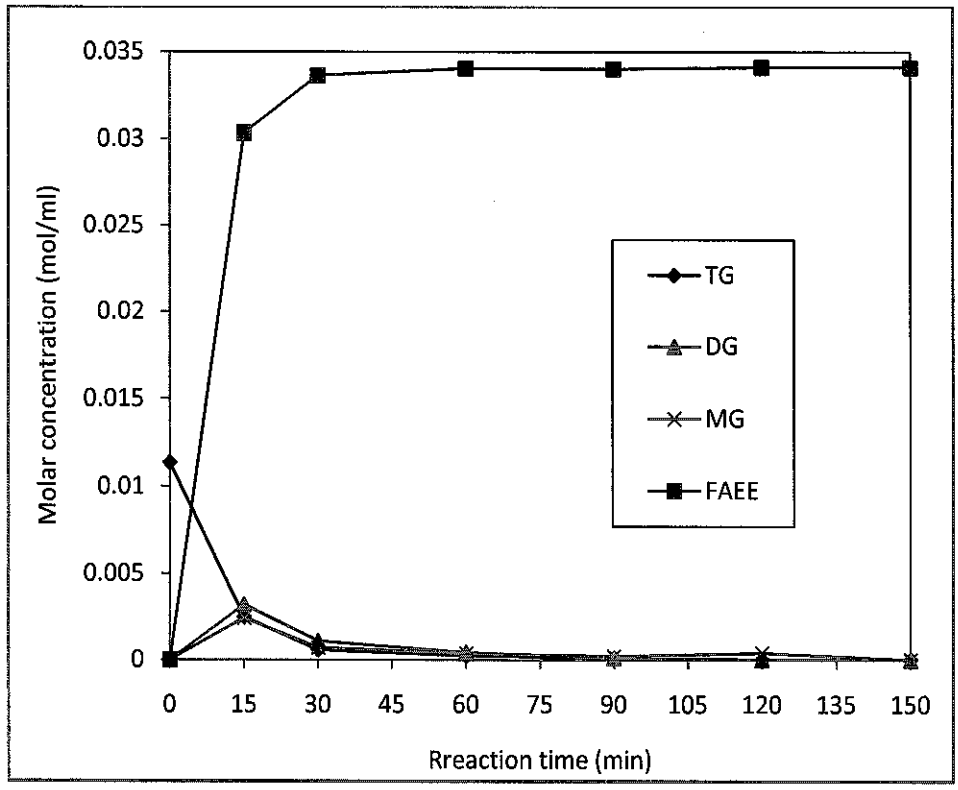
5.3 Reaction kinetics study of microwave heat treated jatropha curcas particles in-situ transesterification

5.3.1 Empirical equations

In-situ transesterification experiments were conducted using microwave pre-treated jatropha seed particles with alkaline methanol and ethanol in the presence of BTMAOH at optimal condition found in chapter 4 section 4.4.3.3 in a batch reactor at specified temperatures of 30, 40, 50, and 60°C. Similar to section 5.2.1, the reaction was terminated at the end of specific time (30, 60, 90, 120 and 150 minutes) and analyzed with GC for its triglycerides, diglycerides, monoglycerides and FAME/FAEE concentration. Figure 5.5 (a) and (b) presents molar concentration of triglycerides, diglycerides, monoglycerides and FAME/FAEE estimated from the chromatogram.



a) In-situ methanolysis



b) In-situ ethanolysis

Figure 5.5: The plot of the concentration of TG, DG, MG and FAEE at a reaction temperature of (a) 30°C, (b) 40°C, (c) 50°C and (d) 60°C as a function of reaction time.

The overall reaction rate of triglycerides conversion was estimated by differential analysis to obtain order of reaction and rate constant as per equation (5.2) for methyl as well as ethyl esters produced using microwave irradiation pre-treated jatropha curcas seed particles at various temperatures and the corresponding reaction rate equations are shown in Table 5.3.

Table 5.3: The reaction rate equation for triglycerides conversion for microwave pretreated jatropha particles in-situ methanolysis and ethanolysis

R. temp, °K	In-situ methanolysis	In-situ ethanolysis
	Rate equation, $-r_{TG}$, (mol/ml.min)	Rate equation, $-r_{TG}$ (mol/ml.min)
303	$-r_{TG} = 0.04917[TG]^{1.148}$	$-r_{TG} = 0.05689[TG]^{1.139}$
313	$-r_{TG} = 0.05167[TG]^{1.155}$	$-r_{TG} = 0.06699[TG]^{1.194}$
323	$-r_{TG} = 0.05712[TG]^{1.169}$	$-r_{TG} = 0.06855[TG]^{1.198}$
333	$-r_{TG} = 0.05859[TG]^{1.172}$	$-r_{TG} = 0.074175[TG]^{1.208}$

Similar to in-situ methanolysis and ethanolysis transesterification with microwave untreated jatropha seed particles, the result shows that the order of the reaction is nearly one for both methanolysis as well as ethanolysis for the range of operating conditions investigated. However, the reaction rate constant is increased significantly for both in-situ methanolysis and in-situ ethanolysis as compared to microwave untreated seed particles. Thus, assuming the order of reaction to be one, rate constant are reevaluated at each temperature for further kinetics analysis and presented in table 5.4.

Table 5.4: Reaction rate constants of microwave pretreated jatropha particles in-situ methanolysis and ethanolysis reaction

Temp. (°K)	1/T	In-situ methanolysis		In-situ ethanolysis	
		Reaction order, n	Rate constant, k	Reaction order, n	Rate cons., k
303	0.0033	1	0.04328	1	0.05497
313	0.0032	1	0.04856	1	0.06562
323	0.0031	1	0.05498	1	0.06824
333	0.0030	1	0.06479	1	0.07241

Arrhenius' plots of both in-situ methanolysis and ethanolysis reactions are shown in Figure 5.6 for investigating the rate dependence on reaction temperature using activation energy of the reaction. Thus, the activation energy of the reaction was

found to be 11,224J/mol for in-situ methanolysis and 7320J/mol for in-situ ethanolysis, respectively.

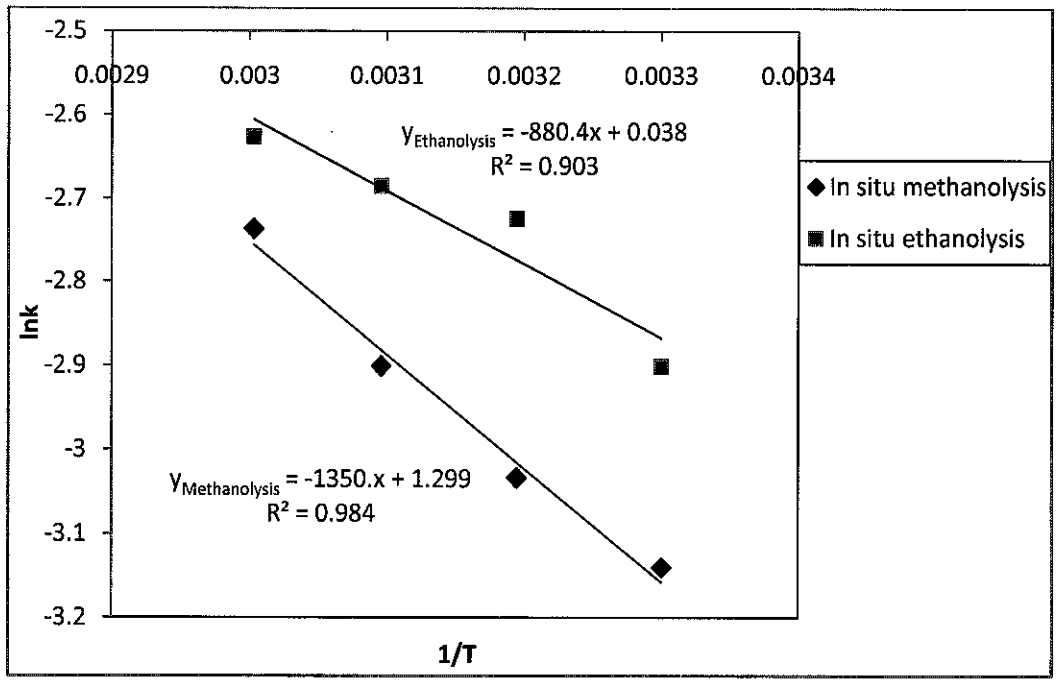


Figure 5.6: Arrhenius plots of lnk vs 1/T

The empirical rate equation obtained using experimental results can be rewritten in terms of reaction temperature and conversion as a function of reaction time as;

For in-situ methanolysis reaction,

$$-r_{TG} = 4[TG]_o e^{\left(-\frac{11224}{8.314T}\right)}(1-X_{TG}) \tag{5.10}$$

Similarly for in-situ ethanolysis reaction;

$$-r_{TG} = 2[TG]_o e^{\left(-\frac{7320}{8.314T}\right)}(1-X_{TG}) \tag{5.11}$$

5.3.2 Validation of the rate equations

The reactor used in the present work is a batch reactor, the performance report for a batch reactor can be evaluated based on resident time of the reaction shown in equation (5.6) [206].

For in-situ methanolysis and in-situ ethanolysis reaction, substituting the values of $-r_{TG}$ from equation (5.10) and (5.11) to equation (5.6) gives equation (5.12), a reactor performance evaluation equation;

$$X_{TG} = 1 - e^{-kt} \tag{5.12}$$

For in-situ methanolysis

$$k = 4e^{\left(-\frac{11224}{8.314\,T}\right)} \tag{5.13}$$

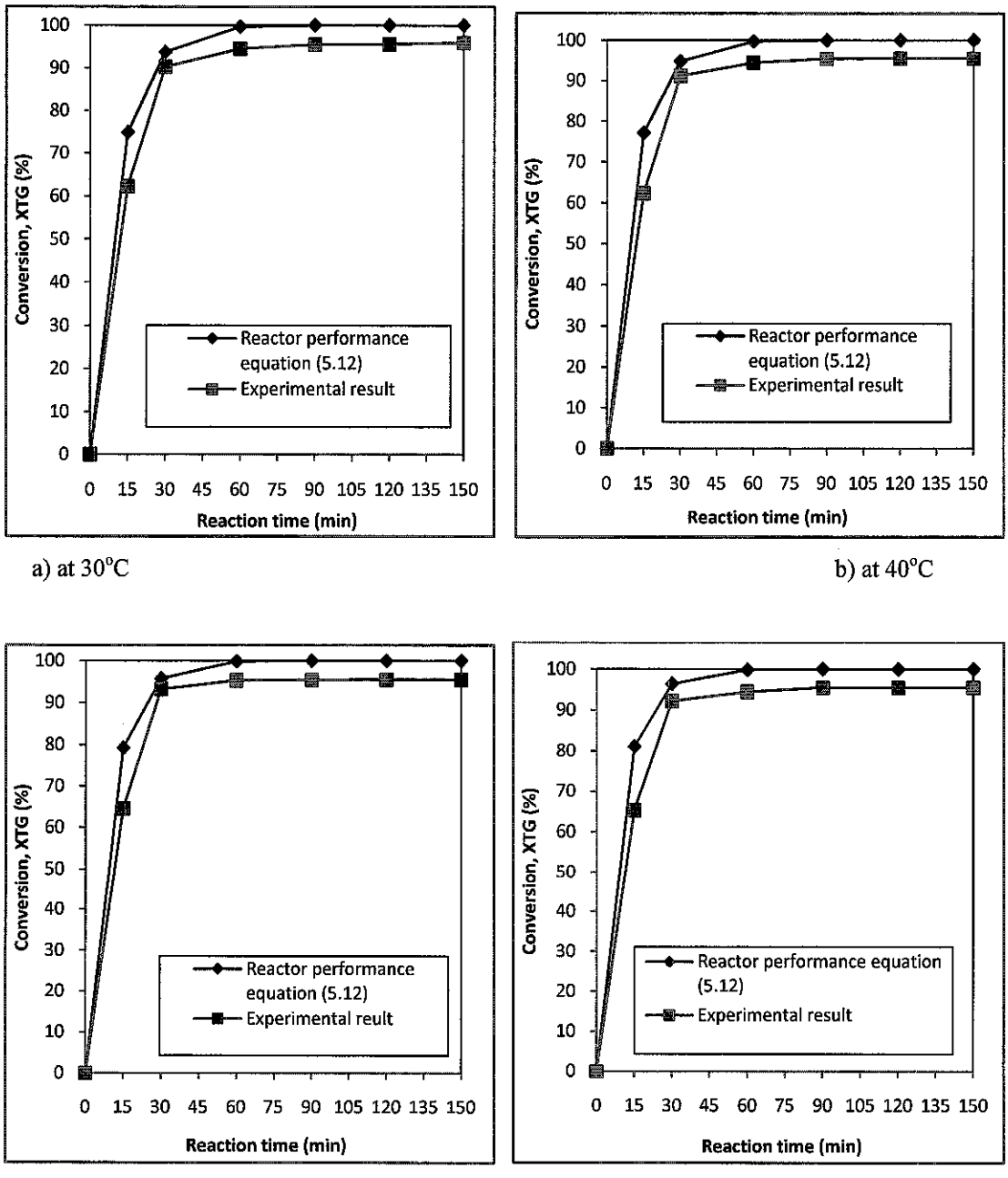
For in-situ ethanolysis

$$k = 3e^{\left(-\frac{1749}{8.314\,T}\right)} \tag{5.14}$$

The results of triglycerides conversion, X_{TG} obtained using equation (5.12) after substitution of the value of k of equation (5.13) for in-situ methanolysis and equation (5.14) for in-situ ethanolysis as a function of reaction time, t at different reaction temperatures compare well with experimental observations as a shown in Figure 5.7 and 5.8, respectively.

Comparison of the reaction rate constants of in-situ methanolysis and in-situ ethanolysis reaction for microwave irradiation treated jatropha curcas seeds prior to transesterification reaction and untreated seeds particles, it was observed that microwave irradiation pre-treatment of jatropha curcas seed has increased the rate of reaction drastically. For a typical reaction rate investigated at 30°C, microwave pretreatment of jatropha curcas seed particles enhanced the reaction rate constant of triglycerides conversion from 0.01637 to 0.04328min^{-1} for in-situ methanolysis and

from 0.03013 to 0.05497min^{-1} for in-situ ethanolysis as compared to microwave heat untreated jatropha curcas seed particles. Hence, use of microwave irradiation pre-treatment of jatropha curcas seed particles and phase transfer catalysis technique for in-situ transesterification reaction is promising.



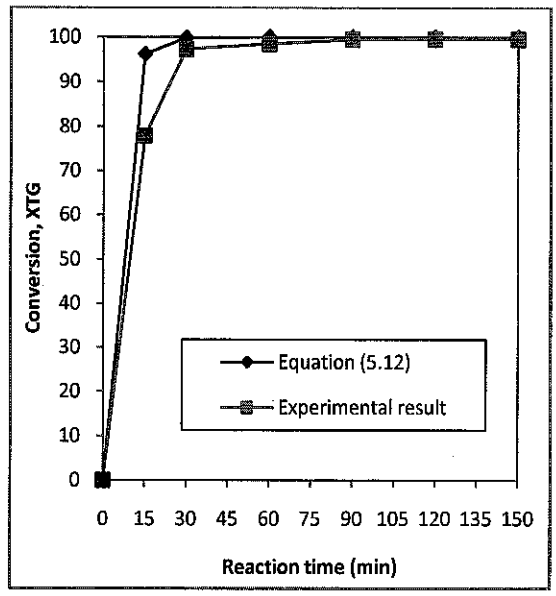
a) at 30°C

b) at 40°C

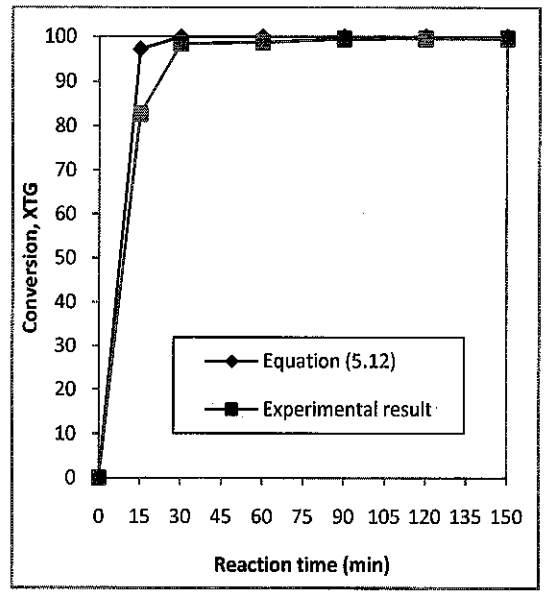
c) at 50°C

d) at 60°C

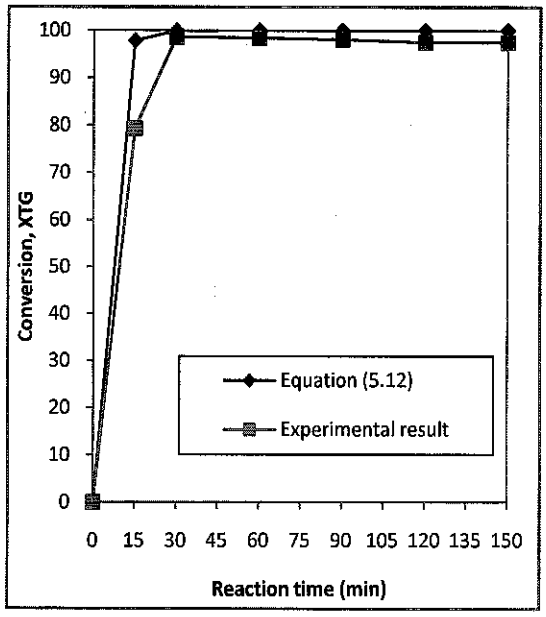
Figure 5.7: Comparisons of experimentally achieved conversion of triglycerides during in-situ methanolysis of microwave irradiation pre-treated jatropha curcas oil with the batch reactor performance equation (5.12) at different reaction temperature.



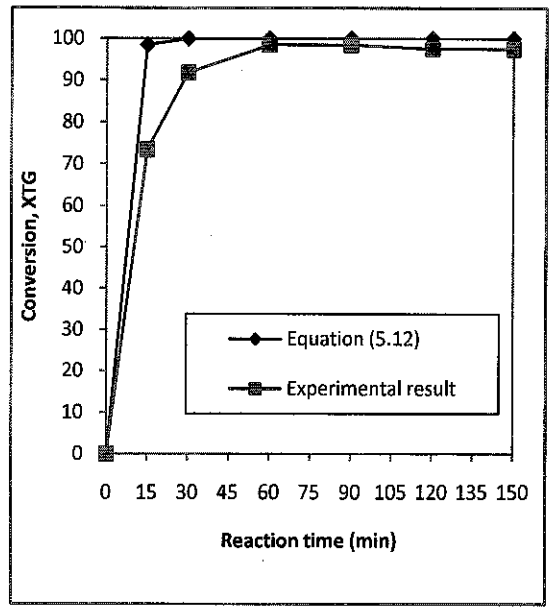
a) at 30°C



b) at 40°C



c) at 50°C



d) at 60°C

Figure 5.8: Comparisons of experimentally achieved conversion of triglycerides during in-situ ethanolysis of microwave irradiation pre-treated jatropha curcas oil with the batch reactor performance equation (5.12) at different reaction temperature.

5.4 PTC catalyzed transesterification reaction mechanism and kinetics Modeling

Lighter alcohols and vegetable oils are sparingly soluble and hence the transesterification reactions are very slow. Presence of alkaline catalysts was observed to enhance the transesterification reactions. Also, phase transfer catalysis can accelerate reactions between reactants located in different immiscible phases by forming soluble complexes with the reactants which can migrate between the phases. Addition of basic catalysts along with PTC helps in the deprotonation of the alcohol phase and helps formation of alkaline alcohol-oxide which can easily complexes with the cations of PTC. Experiments in the present work indicated alkaline in-situ transesterification reactions are better enhanced with the use of phase transfer catalysis as compared to using alkaline catalysis alone. Understanding the mechanism of PTC and corresponding kinetics can be useful for scale up and design. The reaction mechanism of PTC assisted alkaline in-situ transesterification using ethanol is proposed in section 5.4.1 while section 5.4.2 presents the mathematical modeling of the reaction kinetics of PTC during in-situ transesterification. The model validation with the experimental result is discussed in section 5.4.3.

5.4.1 Reaction Mechanism

Based on the principles of Starks' extraction mechanism [159], in-situ transesterification of jatropha curcas oil seed assisted by phase transfer catalysis alone as well as phase transfer catalysis together with alkaline catalyst reaction mechanisms were developed as shown in Figure 5.9 and Figure 5.10, respectively. While developing the reaction mechanism due to excess amount of alcohol used in the reaction mixture and small in size of jatropha curcas seeds which are also rapture and loose, diffusion mass transfer resistance within the seed particles is assumed to be negligible. Accordingly, the reaction mechanisms were developed by taking in to consideration the reactions in the alcohol phase (deprotonation of hydrogen from the reactant alcohol and rate of complex formation) and oil phase (biodiesel and diglycerides complex formation), mass transfer of the complexes between the oil phase and the alcohol phases, partition of the complexes between the two phases.

5.4.1.1 Reaction mechanism of in-situ transesterification assisted by PTC alone

The reactor contains alcohol phase and oil phase. The alcohol phase contains alcohol (ROH) and phase transfer catalysts (PTC, abbreviated as QX) where as the oil phase contains triglycerides (TG). PTC (QX) reacts with alcohol (ROH) to form reactive PTC alcohol-oxide complex (Q^+OR^-) by deprotinating H^+ from the reagent alcohol while liberating H^+X^- into the alcohol phase. The complex (Q^+RO^-) disperses and dissolve into oil phase and reacts with triglycerides (TG) to produce one mole of biodiesel and a second active catalyst-reactant ion pairs of PTC diglycerides complex (Q^+DG^-). Then, Q^+DG^- moves back to the alcohol phase to react with ROH to form DG and release Q^+RO^- which can traverse back to oil phase. DG in the alcohol phase reacts with with alcohol to produce monoglycerides and biodiesel; monoglycerides further react with alcohol to produce glycerin and biodiesel (Figure 5.9). Thus, the complex pairs (Q^+RO^-) and (Q^+DG^-) facilitate phase transfer of the reactants to enhance the reaction rates.

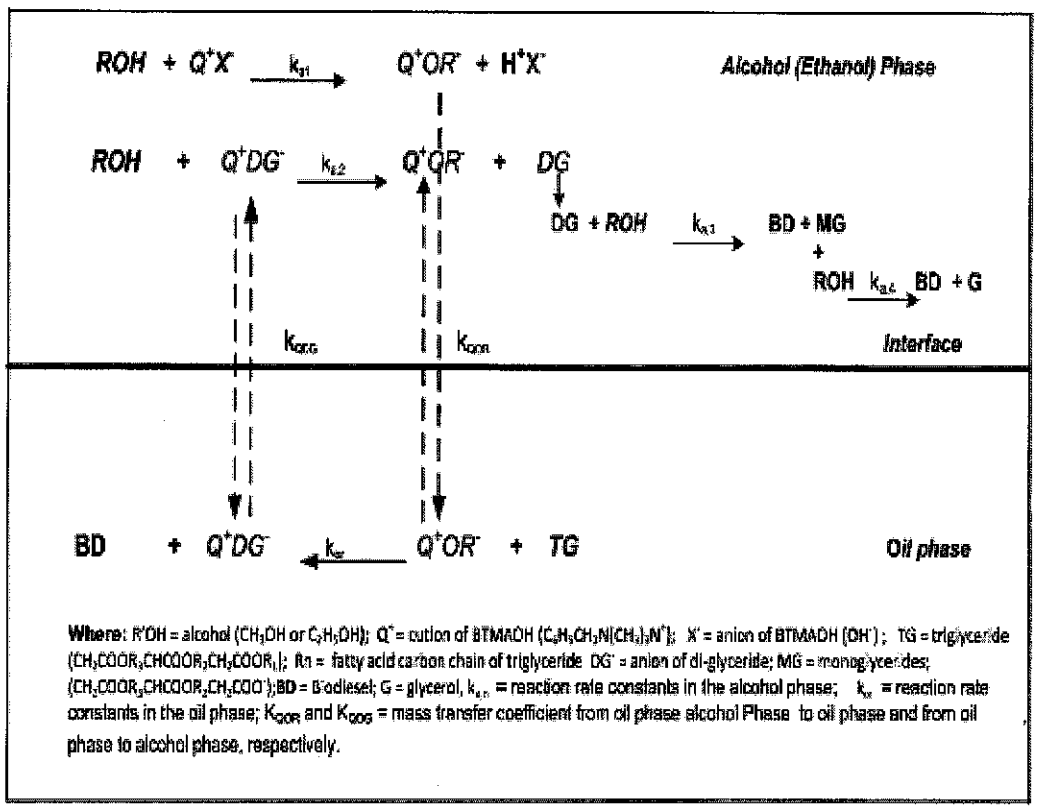


Figure 5.9: Schematic representation of the mechanism of PTC alone assisted transesterification reaction

5.4.1.2 Reaction mechanism of in-situ transesterification assisted by PTC together with NaOH

The reactor contains alcohol phase and oil phase. The alcohol phase contains alcohol (ROH), sodium hydroxide (NaOH) and phase transfer catalysts (PTC, abbreviated as QX) where as the oil phase contains triglycerides (TG). Sodium hydroxide (NaOH) reacts with alcohol (ROH) to form a mole of H_2O and reactive sodium alco-oxide (Na^+OR^-) by deprotinating H^+ from the reagent alcohol. Na^+OR^- complexes with the cation in the PTC (Q^+X^-) to form the first active catalyst-reactant complex ions pairs (Q^+RO^-) while liberating Na^+X^- into the alcohol phase. The complex (Q^+RO^-) disperses and dissolve into oil phase and reacts with triglycerides (TG) to produce one mole of biodiesel and a second active catalyst-reactant ion pairs of PTC diglycerides complex (Q^+DG^-). Then, Q^+DG^- moves back to the alcohol phase to react with Na^+RO^- to form Na^+DG^- and release Q^+RO^- which can traverse back to oil phase. Na^+DG^- in the alcohol phase reacts with H_2O produced during alco-oxide formation to release diglycerides DG and NaOH; Diglycerides react with alcohol to produce monoglycerides and biodiesel; monoglycerides further react with alcohol to produce glycerin and biodiesel (Figure 5.10). Thus, the complex pairs (Q^+RO^-) and (Q^+DG^-) facilitate phase transfer of the reactants to enhance the reaction rates.

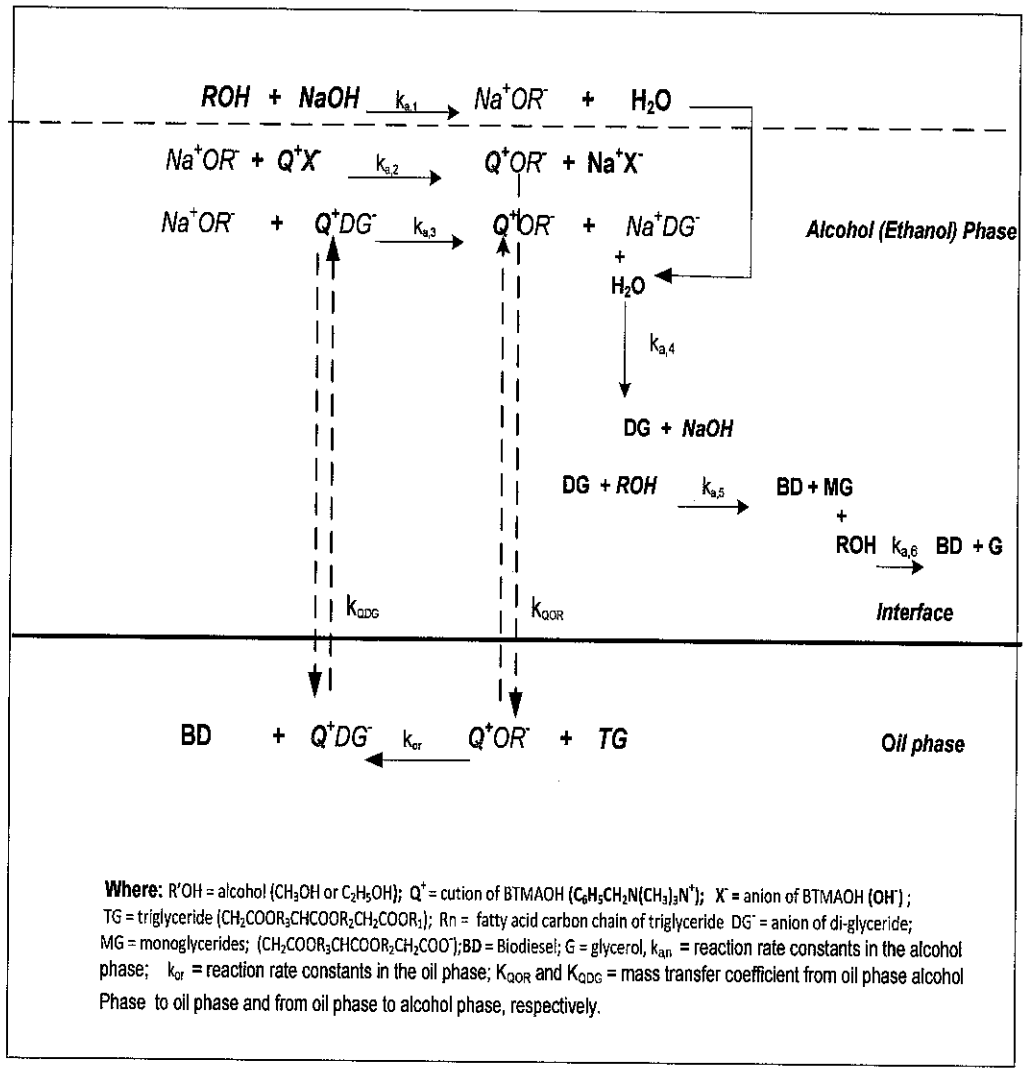


Figure 5.10: Schematic representation of the mechanism of PTC together with NaOH assisted transesterification reaction

5.4.2 Modeling of Reaction Kinetics

The use of PTC together with alkaline catalyst is relatively faster than the use of PTC alone. Thus, the PTC reaction kinetics model is developed for the reaction catalyzed by PTC together with alkaline catalyst based on the mechanism presented in Figure 5.10. The model equations were developed by taking in to account the reactions in the alcohol phase and oil phase, mass transfer of the complexes between the two phases, the distribution (partitioning) of the complexes between the two phases as presented in the following section:

Formation of the first active catalyst-reactant complex in the alcohol phase:

The catalysts NaOH react with alcohol to form complexes NaOR which in turn reacts with QX to form the PTC alcohol complex QOR as shown in equations (5.15) and (5.16)

$$ROH + NaOH \xrightarrow{k_{a,1}} NaOR + H_2O \quad (5.15)$$

$$NaOR + QX \xrightarrow{k_{a,2}} QOR + NaX \quad (5.16)$$

The complexes QOR and NaOR can get dissolved in oil phase by mass transfer. The complex QOR is more soluble in oil phase and easily dissolved into the oil phase compared to NaOR.

Formation of the second active catalyst reactant complex in the oil phase:

QOR reacts with TG to form biodiesel (BD) and another catalyst reactant complex of catalyst-diglycerides complex (QDG) which is more soluble in alcohol phase as presented in equation (5.17).

$$QOR + TG \xrightarrow{k_{or}} QDG + BD \quad (5.17)$$

The complex QDG easily moves to alcohol phase and reacts with NaOR to form sodium diglycerides (NaDG) while releasing the complex QOR which can transfer back to oil phase to facilitate further reaction as shown in equation (5.18).

$$QDG + NaOR \xrightarrow{k_{a,3}} QOR + NaDG \quad (5.18)$$

NaDG reacts with H_2O produced during alcohol-oxide (RO^-) formation to form diglycerides DG while releasing the catalyst NaOH. Diglycerides react with alcohol to produce monoglycerides and biodiesel; monoglycerides further react with alcohol to produce glycerin and biodiesel.

Concentration of the complexes in each phase are related through partition coefficients as can be seen in equation (5.19 and (5.20)

$$M_{QOR} = \frac{[QOR]_o}{[QOR]_a} \tag{5.19}$$

$$M_{QDG} = \frac{[QDG]_o}{[QDG]_a} \tag{5.20}$$

The net overall in-situ transesterification reaction depends on the rate of transfer of the complexes between the two phases.

The rate of consumption of triglycerides, TG and production of biodiesel is given by equation (5.21);

$$\frac{-d[TG]_o}{dt} = k_{or}[TG]_o[QOR]_o \tag{5.21}$$

The overall mass balance of the active catalyst complexes, QOR and QDG in oil phase and alcohol phase;

i) Mass balance on QOR in the oil phase and alcohol phase;

Concentration of PTC-alcohol complex in oil phase $[QOR]_o$ is dictated by

- mass transfer of the complex from alcohol phase at concentration $[QOR]_a$ to oil phase $[QOR]_o$ and
- Consumption by reaction in the oil phase as shown in equation (5.22).

$$\frac{dV_o[QOR]_o}{dt} = k_{QOR}A\left([QOR]_a - \frac{[QOR]_o}{M_{QOR}}\right) - k_{or}V_o[TG]_o[QOR]_o \tag{5.22}$$

Concentration of PTC-alcohol complex in alcohol phase $[QOR]_a$ is determined by

- its formation by reaction of PTC and the complex $[QDG]_a$ with $[NaOR]_a$ as well as by

- mass transfer of the complex from oil phase at concentration $[QOR]_o$ to alcohol phase at concentration $[QOR]_a$ as shown in equation (5.23).

$$\frac{dV_a[QOR]_a}{dt} = k_{a,2}V_a[QX]_a[NaOR]_a + k_{a,3}V_a[QDG]_a[NaOR]_a - k_{QOR}A\left([QOR]_a - \frac{[QOR]_o}{M_{QOR}}\right) \quad (5.23)$$

ii) Mass balance on QDG in the oil phase and alcohol phase:

Concentration of PTC-diglycerides complex in oil phase $[QDG]_o$ is dictated by

- its formation by the reaction between triglycerides and PTC-alcohol complex in oil phase $[QOR]_o$ and
- mass transfer of the complex from oil phase at concentration $[QDG]_o$ to alcohol phase at $[QDG]_a$ as presented in equation (5.24)

$$\frac{dV_o[QDG]_o}{dt} = k_{or}V_o[TG]_0[QOR]_o - k_{QDG}A\left([QDG]_o - M_{QDG}[QDG]_a\right) \quad (5.24)$$

Concentration of PTC-alcohol complex in alcohol phase $[QDG]_a$ is determined by

- mass transfer of the complex from oil phase at concentration $[QDG]_o$ to alcohol phase at concentration $[QDG]_a$ and
- its consumption by reaction with $[NaOR]_a$ as shown in equation (5.25)

$$\frac{dV_a[QDG]_a}{dt} = k_{QDG}A\left([QDG]_o - M_{QDG}[QDG]_a\right) - k_{a,3}V_a[NaOR]_a[QDG]_a \quad (5.25)$$

In equations (22) to (25): k_{QOR} and k_{QDG} are overall mass transfer coefficients and M_{QOR} and M_{QDG} are partition (distribution) coefficients of the complexes, respectively.

The initial amount of PTC, Q_0 which is commonly denoted by QX added into the system is given by equation (5.26);

$$Q_o = QX = V_o\left([QOR]_o + [QDG]_o\right) + V_a\left([QOR]_a + [QDG]_a\right) \tag{5.26}$$

The initial conditions of the species are given by equation (5.27);

$at \quad t = 0$

$$\begin{aligned} [TG]_o &= [TG]_{o,0} \\ [QX]_a &= [QX]_{a,0} \\ [NaOH]_a &= [NaOH]_{a,0} \\ [QOR]_{o,0} &= [QDG]_{o,0} = 0 \\ [QOR]_{a,0} &= [QDG]_{a,0} = 0 \end{aligned} \tag{5.27}$$

At large excess amount of alcohol, the catalyst reactant complexes is traversing steadily between the phases. With steady state approximation;

$$\frac{d[QOR]_o}{dt} = \frac{d[QOR]_a}{dt} = \frac{d[QDG]_o}{dt} = \frac{d[QDG]_a}{dt} = 0 \tag{5.28}$$

Then the above equations (5. 22) to (5.25) are reduced to;

$$k_{QOR}A\left([QOR]_a - \frac{[QOR]_o}{M_{QOR}}\right) - k_{or}V_o[TG]_o[QOR]_o = 0 \tag{5.29}$$

$$k_{a,2}V_a[QX]_a[NaOR]_a + k_{a,3}V_a[NaOR]_a[QDG]_a - k_{QOR}A\left([QOR]_a - \frac{[QOR]_o}{M_{QOR}}\right) = 0 \tag{5.30}$$

$$k_{or}V_o[TG]_0[QOR]_o - k_{QDG}A\left([QDG]_O - M_{QDG}[QDG]_a\right) = 0 \quad (5.31)$$

$$k_{QDG}A\left([QDG]_O - M_{QDG}[QDG]_a\right) - k_{a,3}V_a[NaOR]_a[QDG]_a = 0 \quad (5.32)$$

From equation (5.29) rearranging;

$$[QOR]_a = \left(\frac{1}{M_{QOR}} + \frac{k_{or}V_o[TG]_o}{k_{QOR} * A}\right) * [QOR]_o \quad (5.33)$$

From equations (5.29) and (5.30) rearranging and substituting;

$$[QDG]_a = \left(\frac{k_{or}V_o}{k_{a,3}V_a}\frac{[TG]_o}{[NaOR]_a}\right) * [QOR]_o + \frac{k_{a,2}}{k_{a,3}}[QX]_a \quad (5.34)$$

From equation (31) and (32) rearranging and substituting

$$[QDG]_o = \left(M_{QDG} * \frac{k_{or}V_o}{k_{a,3}V_a}\frac{[TG]_o}{[NaOR]_a} + \frac{k_{or}V_o}{k_{QDG} * A}[TG]_o\right) * [QOR]_o \quad (5.35)$$

Combining equation (5.26) and equations (33) to (35) and rearranging, the concentration of QOR in the oil phase is given by equation (36)

$$\frac{Q_o}{V_o[QOR]_o} = 1 + \frac{V_a}{V_o}\left[\frac{1}{M_{QOR}} + \frac{k_{or}V_o[TG]_o}{k_{QOR}A} + \frac{k_{or}V_o[TG]_o}{k_{a,3}V_a[NaOR]_a}\right] + \frac{k_{or}V_o[TG]_o}{k_{QDG}A} + \frac{k_{or}V_o[TG]_o}{k_{a,3}V_a[NaOR]_a}\{M_{QOR}\} + \frac{k_{a,2}}{k_{a,3}}[QX]_a \quad (5.36)$$

Apparent Rate Constant, k_{app}:

From equation (5.21) the rate of consuming TG is given by;

$$\frac{-d[TG]_o}{dt} = k_{or}[TG]_o[QOR]_o \tag{5.37}$$

where

$$k_{app} = k_{or}[QOR]_o \tag{5.38}$$

$$\frac{-d[TG]_o}{dt} = k_{app}[TG]_o \tag{5.39}$$

$$at \quad t = 0, \quad [TG]_o = [TG]_{o,0} \tag{5.40}$$

Defining the conversion of TG as X_{TG};

$$X_{TG} = 1 - \frac{[TG]_o}{[TG]_{o,0}} \tag{5.41}$$

Using the reaction rate equation (4.39), the conversion of triglycerides, X_{TG} in equation (41) can be expressed as;

$$-\ln(1 - X_{TG}) = k_{app}\, t \tag{5.42}$$

The value of k_{app} can be obtained from the experimental data from the slope of the straight line by plotting $-\ln(1-X_{TG})$ versus time at various experimental conditions.

Together, the equation may be summarized as

$$\frac{k_{or}Q_o}{V_o\, k_{app}} = \left(\frac{V_a}{V_o M_{QOR}} + \frac{k_{or}[TG]_o V_o}{A}\left\{\frac{V_a}{V_o k_{QOR}} + \frac{1}{k_{QDG}}\right\} + \frac{V_o M_{QOR}}{V_a}\frac{k_{or}[TG]_o}{k_{a,3}[NaOR]_a} + +1 + \frac{k_{a,2}}{k_{a,3}}[QX]_a \right) \tag{5.43}$$

Where:

$$k_{app} = k_{or}\,[QOR\,]_o$$

5.4.3 Result and discussions

Experimental investigation is the only way to evaluate PTC to choose the best one. In this work, three PTCs - cetyltrimethylammonium bromide (CTMAB), benzyltrimethylammonium hydroxide (BTMAOH) and crown ether (CE) - were selected as possible phase transfer catalysts for in-situ transesterification of jatropha curcas seed particles. Experimental observations indicated that BTMAOH offered better phase transfer catalytic effect and was used for the detailed investigations. Effect of each variable on the conversion of triglycerides to biodiesel with time was investigated while the other variables (such as agitation speed, reaction temperature, alcohol to oil seed ratio, concentration of PTC and the concentration of NaOH) were kept constant at the optimal values obtained using Response Surface Methodology. The experimental observations are analyzed by the first order kinetics suggested by the reaction mechanism to estimate the apparent rate constant, k_{app}.

5.4.3.1 Choosing the effective PTC

In this work, three PTCs - cetyltrimethylammonium bromide (CTMAB), benzyltrimethylammonium hydroxide (BTMAOH) and crown ether (CE) - were selected as possible phase transfer catalysts for in-situ transesterification of jatropha curcas seed particles. Based on conversions of triglycerides as a function of reaction time at 400 rpm agitation speed and 30°C reaction temperature, the reaction rate constant k_{app} for each PTC, was evaluated by first order kinetics using equation (5.42) as shown in Figure 5.11 and presented in Table 5.5.

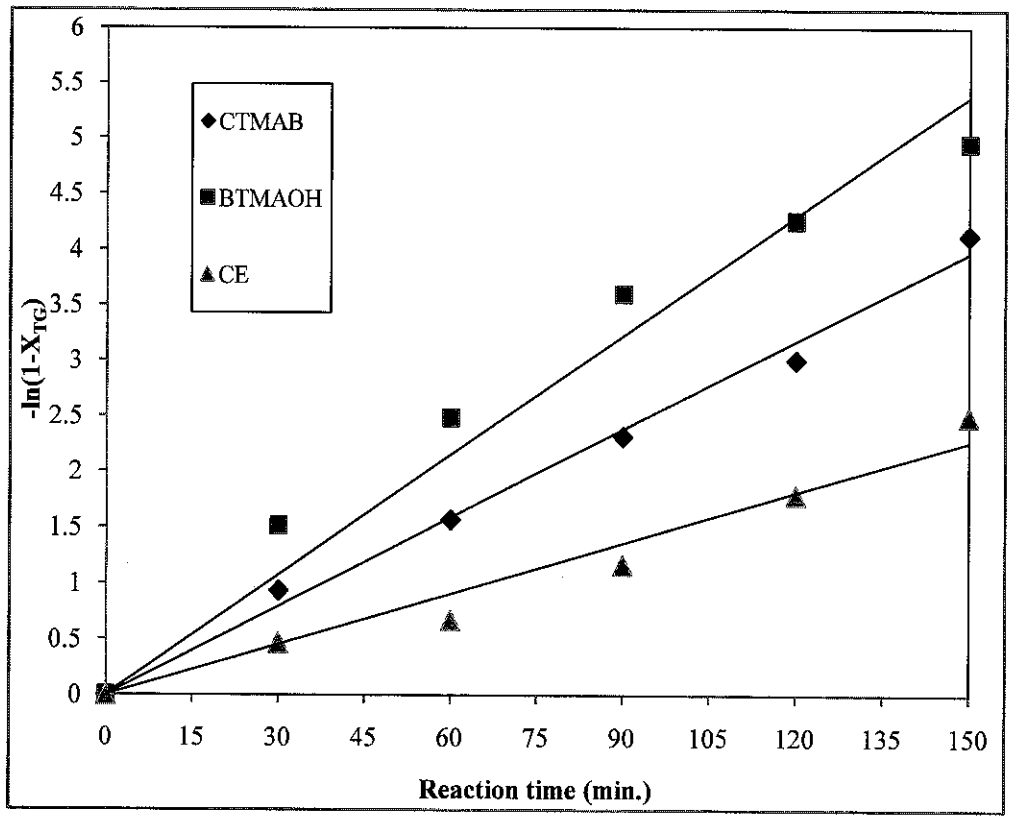


Figure 5.11: Kinetic plots for the catalytic effects of different PTC on the conversion of triglycerides

Table 5.5: Effects of different phase transfer catalysts on the apparent rate constant, $k_{app.}$

PTC Catalyst	k_{app}, min^{-1}
BTMAOH	0.031
CTMAB	0.025
CE	0.016

It can be seen that the apparent rate constant is higher for BTMAOH compared to CTMAB and CE. Thus, BTMAOH was used for the detailed study of the effect of various parameter and results are presented in the following sections.

5.4.3.2 Effect of agitation speed

Suspending the jatropha oil seed particles in alcohol phase using a stirrer is necessary to improve mass transfer rate to facilitate reaction. Effect of the stirrer agitation speed on conversion of triglycerides by in-situ transesterification of jatropha seed particles to biodiesel was investigated at various agitation speeds of 200, 300, 400, 500 and 600rpm. Using equation (5.42) the graph of $-\ln(1-X_{TG})$ was plotted as a function of reaction time as shown in Figure 5.12. Apparent rate constant of the reaction at each agitation speed was obtained from the slope of the graph. Thus, k_{app} was plotted as a function of agitation speed in Figure 5.13. It can be seen that k_{app} increased to a limiting value for stirrer speeds greater than 400 rpm. Thus, conversion of triglycerides can be reaction rate controlled for agitation speed greater than 400rpm.

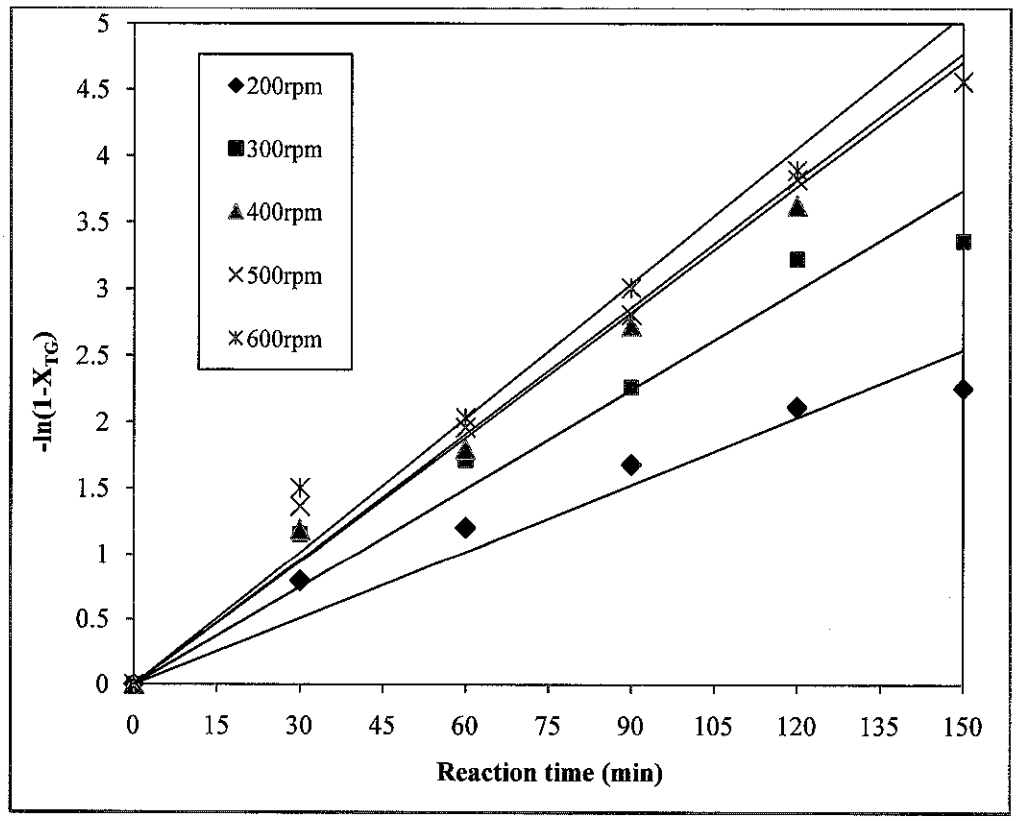


Figure 5.12: kinetic plots for the effect of agitation speeds on the conversion of triglycerides

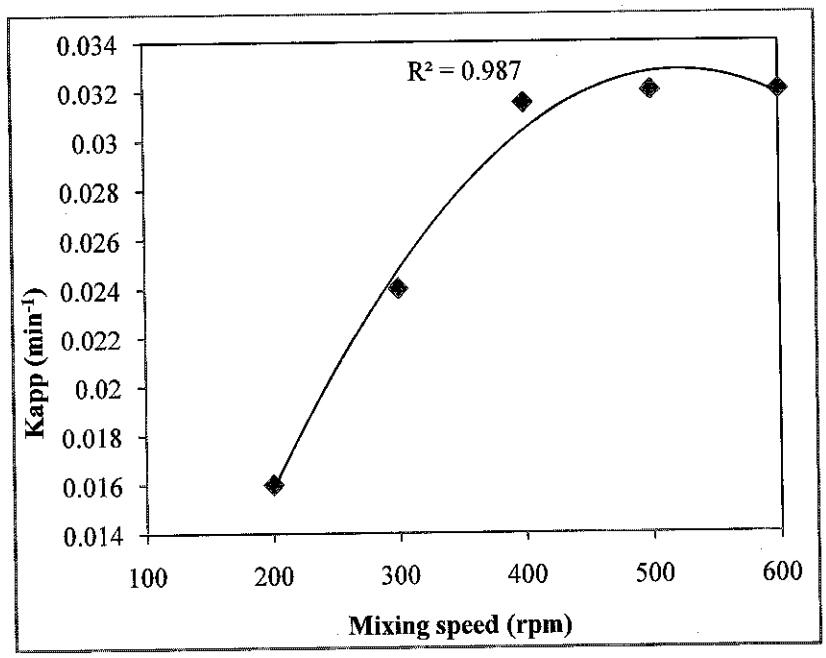


Figure 5.13: effect of agitation speeds on the apparent rate constant, k_{app}.

5.4.3.3 Reaction temperature

Conversion of triglycerides (TG) was investigated at temperatures of 30, 40, 50 and 60°C keeping the stirrer speed at 400 rpm. The results are presented in Figure 5.14 as $-\ln(1-X_{TG})$ versus time and the apparent rate constant (k_{app}) was found for different reaction temperatures. It can be seen that the apparent rate constant (k_{app}) increased with temperature. Using the Arrhenius plot the apparent activation energy was calculated and found to be 17.16kJ/mol (≈17.078kJ/mol obtained as per the empirical model) as shown in Figure 5.15.

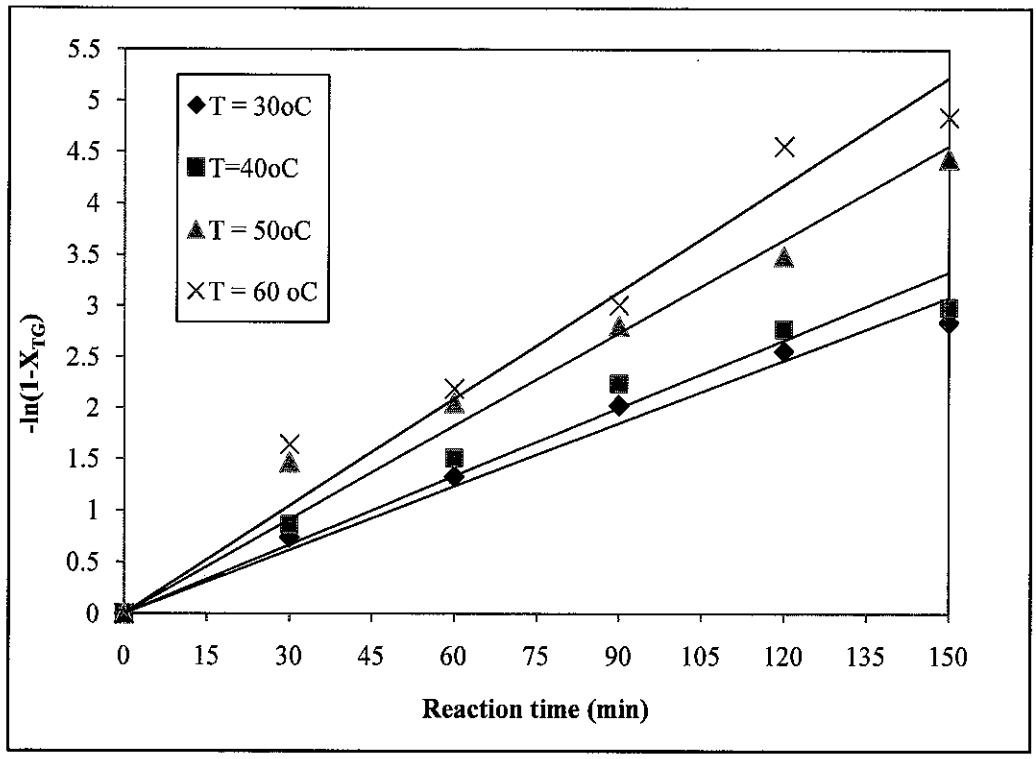


Figure 5.14: kinetic plots for the effect of reaction temperatures on the conversion of triglycerides

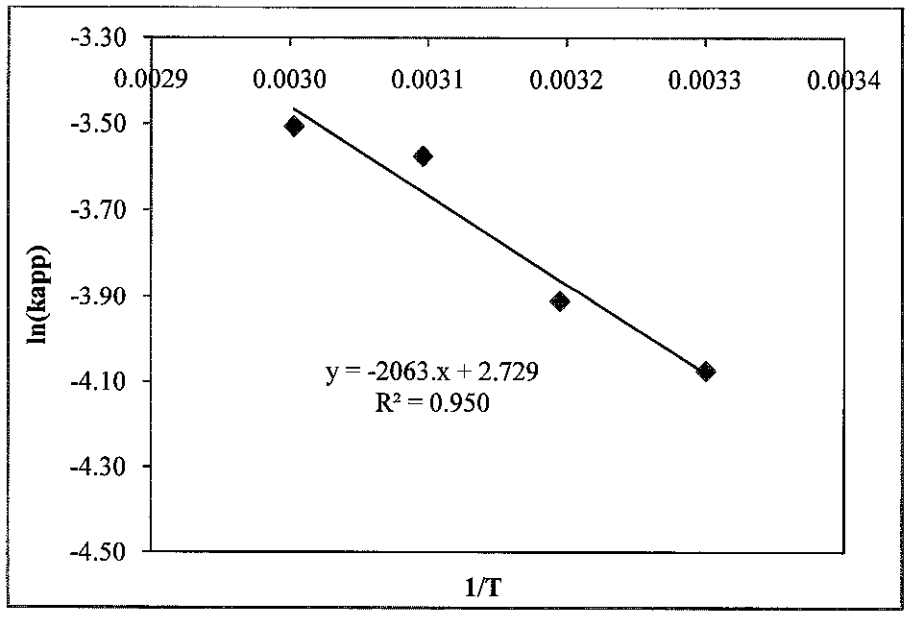


Figure 5.15: Arrhenius plot of the apparent rate constant, k_{app}.

It may be noted that temperature can promote saponification reaction with alkaline transesterification resulting in the undesirable side product (soap) and reduce the yield

of the biodiesel. Maximum biodiesel yield was obtained at reaction temperature of about 30°C as discussed in Chapter 4 section 4.3.2.

5.4.3.4 Effect of ratio of alcohol to oil seed particles

In-situ transesterification reaction was investigated at alcohol to oil seed particles ratios of 4.5, 6, 7.5, 9 and 10.5 ml/g by measuring conversion of triglycerides, X_{TG}, as a function of reaction time to investigate the effect of alcohol to oil seed ratio. A plot of $-\ln(1-X_{TG})$ versus reaction time is presented in Figure 5.16 for a reactions conducted at different ratio of alcohol to oil seeds. The value of k_{app} was determined from the slope of the plot of $-\ln(1-X_{TG})$ versus time for different ratio of alcohol to oil seeds. Table 5.6 presents the value of k_{app} as a function of ratios of alcohol to oil seeds. It can be seen that the apparent rate constant is increased with increasing the ratio of alcohol to oil seeds as expected.

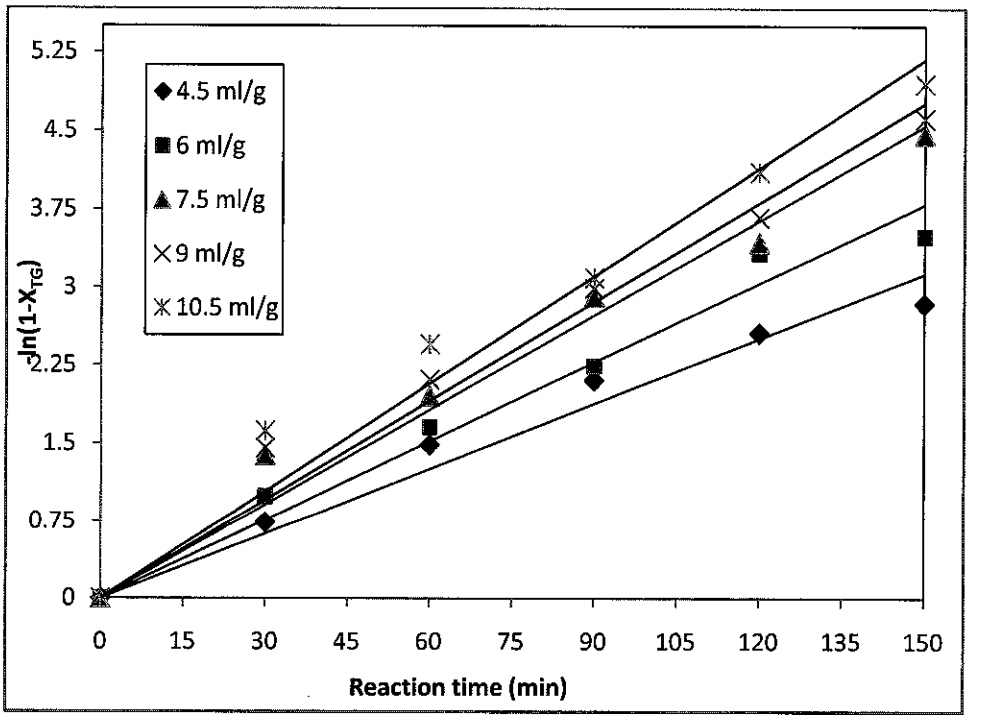


Figure 5.16: kinetic plots for the effect of ratio of ethanol on the conversion of triglycerides

Estimated apparent rate constant as a function of ratio of alcohol to oil seeds are shown in Table. 5.6.

Table 5.6: effects of ratio of alcohol to oil seeds on the apparent rate constant, k_{app}

Ratio of alcohol to oil seeds (ml/g)	k_{app} (min^{-1})
4.5	0.020
6	0.025
7.5	0.030
9	0.031
10.5	0.034

For comparison of the model equation with the experimental observation, equation (5.43) is rearranged as;

$$\frac{Q_o}{V_o k_{app}} = \left(\frac{1}{k_{or}M_{QOR}} + \frac{V_o[TG]_o}{Ak_{QOR}}\right)\left(\frac{V_a}{V_o}\right) + \frac{[TG]_o M_{QOR}}{k_{a,3}[NaOR]_a}\left(\frac{V_o}{V_a}\right) + \frac{V_o[TG]_o}{Ak_{QDG}} + \\ + \frac{1}{k_{or}} + \frac{1}{k_{or}}\frac{k_{a,2}}{k_{a,3}}[QX]_a$$

Let;

$$\psi = \frac{V_a}{V_o}; \quad a = \frac{1}{k_{or}M_{QOR}} + \frac{V_o[TG]_o}{Ak_{QOR}}; \quad b = \frac{[TG]_o M_{QOR}}{k_{a,3}[NaOR]_a};$$

$$c = \left\{\frac{1}{k_{or}} + \frac{V_o[TG]_o}{k_{QDG}A} + \frac{[TG]_o}{k_{a.3}[NaOR]_a} + \frac{k_{a.2}}{k_{or}k_{a.3}}[QX]_a\right\}$$

Then;

$$\frac{1}{k_{app}} = \left(\frac{V_o a}{Q_o}\right)\psi + \left(\frac{V_o b}{Q_o}\right)\frac{1}{\psi} + \left(\frac{V_o c}{Q_o}\right) \qquad (5.44)$$

Data in Table 5.6 is presented in Figure 5.17 as ($1/k_{app}$) as a function of ($1/\psi$). In the range of experimental investigation (ψ<10.5, i.e., $1/\psi$>0.1), the data does not reflect the contribution of the first term and the result may be summarized as

$$\frac{1}{k_{app}} = \left(\frac{V_o b}{Q_o}\right)\frac{1}{\psi} + \left(\frac{V_o}{Q_o}c\right) \tag{5.45}$$

From Figure 5.17 and the slope and intercept of equation (5.45) are determined by linear regression and found to be 141.5 and 15.83. With these values equation (5.45) can be rewritten as;

$$\frac{1}{k_{app}} = \frac{141.5}{\psi} + 15.83 \tag{5.46}$$

The constants are

$$\left(\frac{M_{QOR}}{k_{a.3}}\right)\left\{\frac{V_o}{Q_o}\frac{[TG]_o}{[NaOR]_a}\right\}\Bigg|_{Op.con.} = 141.5;$$

$$\left(\frac{1}{k_{or}} + \frac{V_o[TG]_o}{Ak_{QDG}} + \frac{[TG]_o}{k_{a.3}[NaOR]_a} + \frac{k_{a.2}}{k_{or}k_{a.3}}[QX]_a\right)\frac{V_o}{Q_o}\Bigg|_{Op.con} = 15.83$$

Using the values of the experimental parameters, the unknown model parameters can be obtained as

$$\frac{M_{QOR}}{k_{a,3}} = 1.085;$$

$$\left(\frac{1}{k_{or}} + \frac{111}{Ak_{QDG}} + \frac{130.45}{k_{a.3}} + \frac{1.25}{k_{or}}\frac{k_{a.2}}{k_{a.3}}\right) = 1.885$$

Then the equation may be expressed in a generalized format as

$$\frac{1}{k_{app}} = 1.085\frac{V_o}{Q_o}\frac{[TG]_o}{[NaOR]_a}\frac{V_o}{V_a} + \left(\frac{1}{k_{or}} + \frac{V_o[TG]_o}{Ak_{QDG}} + \frac{[TG]_o}{k_{a.3}[NaOR]_a} + \frac{k_{a.2}}{k_{or}k_{a.3}}[QX]_a\right)\frac{V_o}{Q_o} \quad (5.47)$$

With

$$\left(\frac{1}{k_{or}} + \frac{111}{Ak_{QDG}} + \frac{130.45}{k_{a.3}} + \frac{1.25}{k_{or}}\frac{k_{a.2}}{k_{a.3}}\right) = 1.885$$

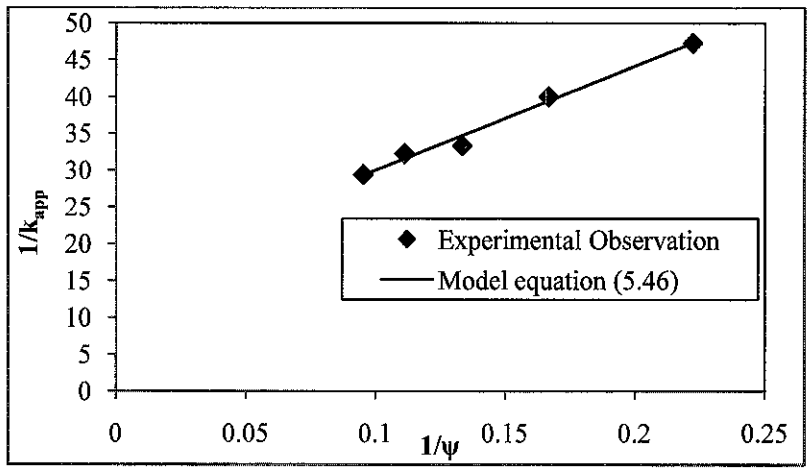


Figure 5.17: Dependence of apparent rate constant k_{app} on alcohol to oil ratio ψ

5.4.3.5 Effect of concentration of PTC

In order to investigate the effect of PTC loading on the conversion of triglycerides, the reaction was studied at five different BTMAOH as PTC concentrations of 0.25, 0.75, 1.25, 1.75 and 2.25 mol/mol of alkaline catalyst. The reaction was also conducted without BTMAOH in the presence of only alkaline catalyst. The plots of $-\ln(1-X_{TG})$ versus reaction time are presented in Figure 5.18. The reaction apparent rate constant (k_{app}) was estimated from the slope of the graph at different BTMAOH loading and presented in Table 5.7.

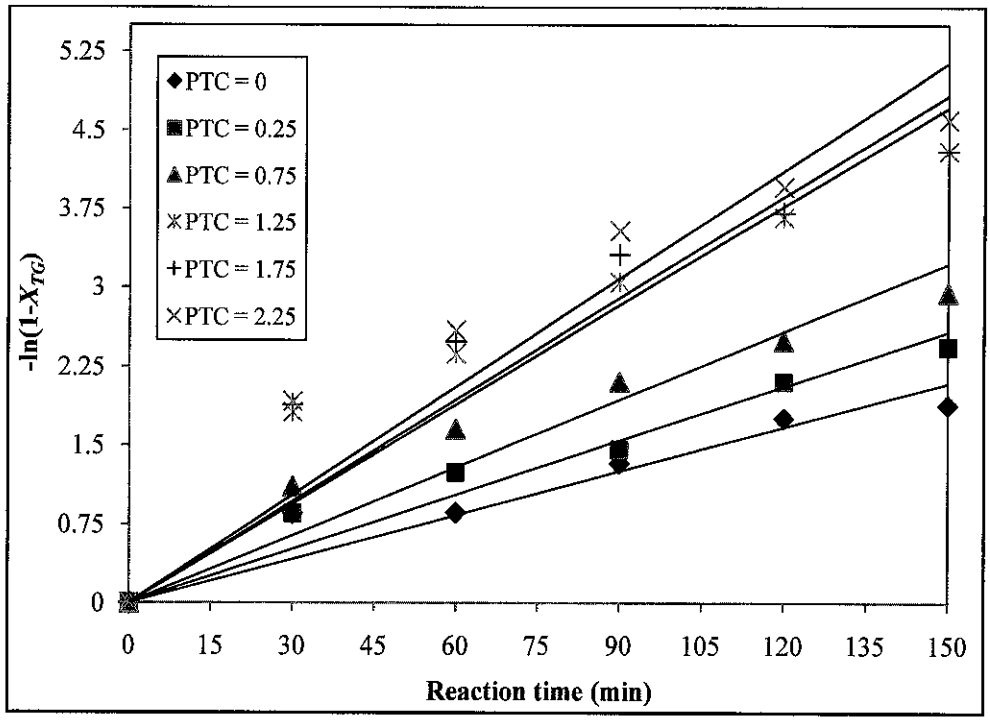


Figure 5.18: kinetic plots for the effect of the concentration of BTMAOH as a PTC on the conversion of triglycerides

Table 5.7: Effects of concentration of BTMAOH as a PTC on the apparent rate constant, k_{app}

BTMAOH concen., Q_0 (mol/mol)	$k_{app.}$ (min^{-1})
0.00	0.0140
0.25	0.0170
0.75	0.0210
1.25	0.0310
1.75	0.0320
2.25	0.0340

To compare the model equation with the experimental observations on the effect of PTC loading, equation (5.47)

$$\frac{1}{k_{app}} = \left[\left(1.085\frac{[TG]_o}{[NaOR]_a}\frac{V_o}{V_a}\right)+\left(\frac{1}{k_{or}}+\frac{V_o[TG]_o}{Ak_{QDG}}+\frac{[TG]_o}{[NaOR]_a}\frac{1}{k_{a.3}}\right)V_o\right]\frac{1}{Q_o}+\frac{V_o}{k_{or}}\frac{k_{a.2}}{k_{a.3}}$$

May be rearranged as;

$$\frac{1}{k_{app}} = \phi \frac{1}{Q_o} + \varsigma \tag{5.48}$$

With

$$\phi = \left[\left(1.085 \frac{[TG]_o}{[NaOR]_a} \frac{V_o}{V_a} \right) + \left(\frac{1}{k_{or}} + \frac{V_o [TG]_o}{A k_{QDG}} + \frac{[TG]_o}{[NaOR]_a} \frac{1}{k_{a.3}} \right) V_o \right]_o$$

$$\varsigma = \frac{V_o}{k_{or}} \frac{k_{a.2}}{k_{a.3}}{}_o$$

Data in the Table 5.7 on ($1/k_{app}$) as a function of ($1/Q_o$) are presented in Figure 5.19 and based on linear regression the results are best correlated as

$$\frac{1}{k_{app}} = 20.69 \frac{1}{Q_o} + 18.79 \tag{5.49}$$

$$\phi = 21.23 + 10.5 \left(\frac{1}{k_{or}} + \frac{111}{A k_{QDG}} + \frac{130.45}{k_{a.3}} \right) = 20.69$$

$$\varsigma = \frac{10.5}{k_{or}} \frac{k_{a,2}}{k_{a,3}} = 18.79$$

However, the parameter

$$\frac{1}{k_{or}} + \frac{111}{A k_{QDG}} + \frac{130.45}{k_{a.3}}$$

is not expected to be negative. As effect of stirrer speed was eliminated for the kinetic experiments and excess alcohol was used, thus, mass transfer parameter A^*k_{QDG} may be expected to be large; the reaction between triglycerides and active complexes in each phase can be fast, the value of k_{or} can also be high. Hence this parameter may be expected to be zero. Together, equation (5.48) can be summarized as:

$$\frac{1}{k_{app}} = \left(1.085V_o \frac{[TG]_o}{[NaOR]_a}\frac{V_o}{V_a}\right)\frac{1}{Q_o} + 1.78V_{oo} \qquad (5.50)$$

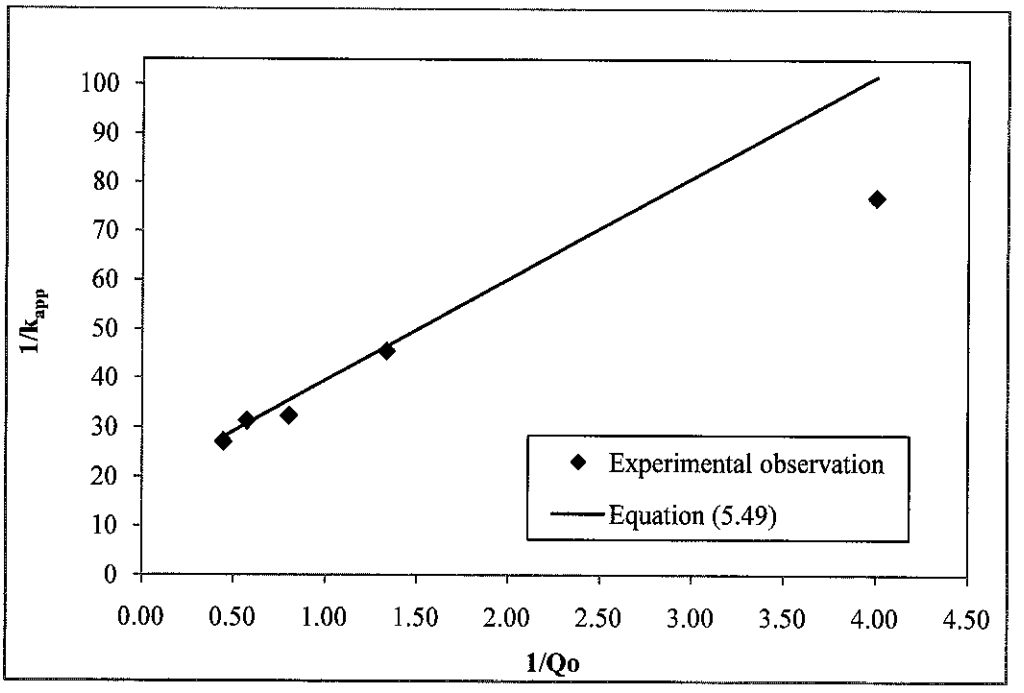


Figure 5.19: plots of $1/k_{app}$ versus 1/Qo for comparison of k_{app} experimentally observed with equation (4.49) at different PTC concentration

5.4.3.6 Effect of sodium hydroxide concentration

Addition of NaOH helped to deprotonate H^+ from the alcohol and forms active anion of Na^+OR^- that can easily complexes with cation of PTC to form PTC-reactant complex (QOR); a complex that can easily dissolve into oil phase. Experiments were conducted at different concentrations of NaOH (0.18, 0.43, 0.68, 0.93 and 1.18 % w/w of jatropha curcas seeds) to investigate the effect of NaOH loading on the apparent reaction rate constant, k_{app}. From the slope of the graph of $-\ln(1-X_{TG})$ versus reaction time as shown in Figure 5.20, the value of k_{app} was determined for investigating the effect of NaOH concentration on the reaction apparent rate constant, k_{app}.

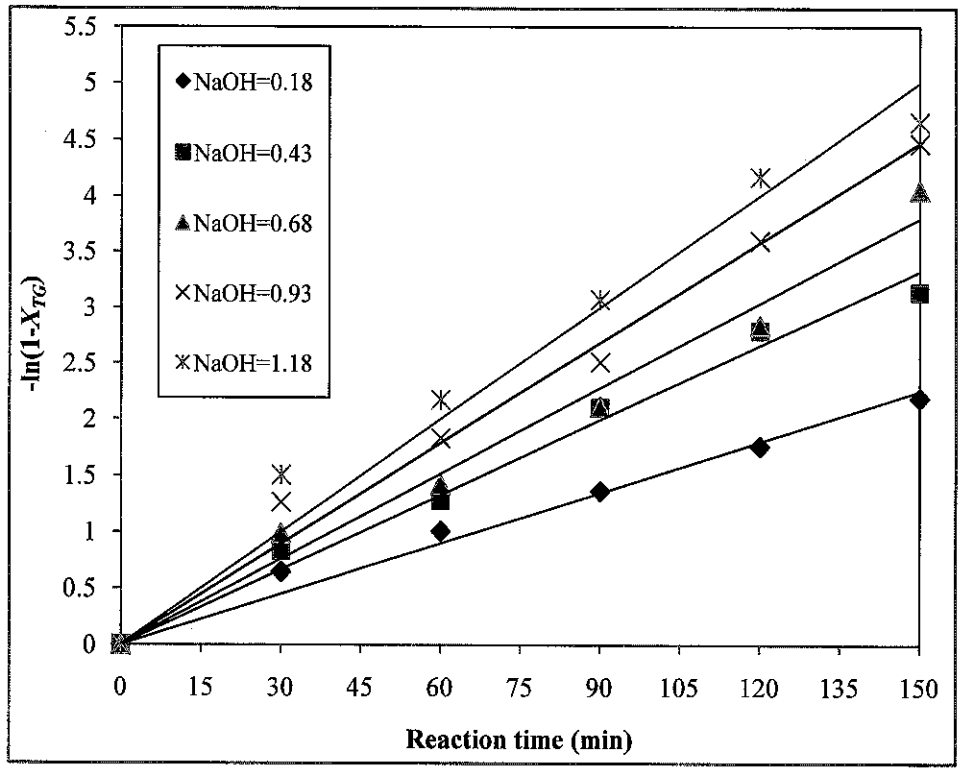


Figure 5.20: kinetic plot for the effect of the concentration of NaOH on the conversion of triglycerides

Estimated apparent rate constants as a function of the concentration of NaOH are shown in Table 5.8.

Table 5.8: Effects of concentration of NaOH on the apparent rate constant, k_{app}

NaOH conc. (% w/w)	k_{app} (min^{-1})
0.18	0.015
0.43	0.018
0.68	0.030
0.93	0.031
1.18	0.033

The apparent rate constant, k_{app} increased with increasing the amount of NaOH loading. Even though increasing the concentration of NaOH increases apparent rate

constant and triglycerides conversion, it was noted that increasing the concentration of NaOH beyond the maximum conversion of triglycerides to biodiesel has negative effect on the yield of biodiesel since saponification reaction is favored at high concentration of alkaline catalyst such as NaOH.

To compare the model equation with the experimental observations on the effect of NaOH loading, equation (5.50) may be rearranged as;

$$\frac{1}{k_{app}} = \left(1.085 \frac{V_o[TG]}{Q_o} \frac{V_o}{V_a}\right) \frac{1}{[NaOH]} + 1.78 V_o \tag{5.51}$$

At excess alcohol volume, the concentration of alkaline catalyst anion reactant complex concentration, Na^+OR^- is approximated by the concentration of NaOH. Data in the Table 5.8 on ($1/k_{app}$) as a function of (1/NaOH) are presented in Figure 5.21 and based on linear regression the results are best correlated as

$$\frac{1}{k_{app}} = 15.96 \frac{1}{[NaOH]} + 15.79 \tag{5.52}$$

This modifies the constants in the equation 5.51as

$$\frac{1}{k_{app}} = \left(1.35[TG] \frac{V_o}{Q_o} \frac{V_o}{V_a}\right) \frac{1}{[NaOH]} + (1.49 V_o) \tag{5.53}$$

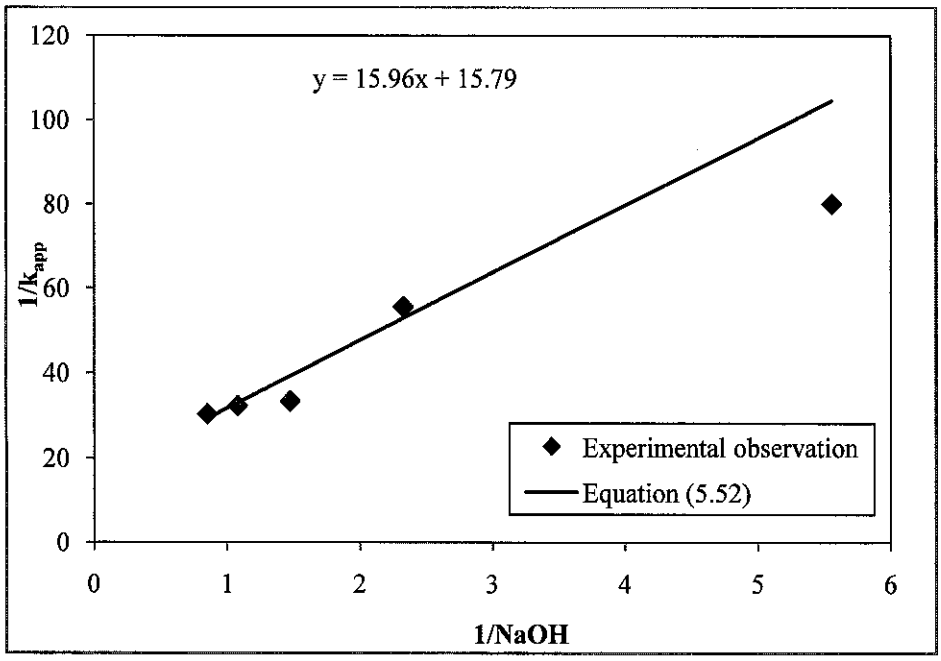


Figure 5.21: plots of $1/k_{app}$ versus 1/NaOH for comparison of k_{app} experimentally observed with equation (4.52) at different NaOH concentration

Thus, the range of values of the model parameters appear to be

$$\left(\frac{111}{Ak_{QDG}}+\frac{1}{k_{or}}+\frac{130.45}{k_{a.3}}\right)\approx 0,\quad \frac{M_{QOR}}{k_{a.3}}\approx 1.085\,to\,1.35,\quad \frac{1}{k_{or}}\frac{k_{a,2}}{k_{a,3}}\approx 1.78\,to\,1.49$$

Assigning values for these parameters as

$$\left(\frac{111}{Ak_{QDG}}+\frac{1}{k_{or}}+\frac{130.45}{k_{a.3}}\right)=0,\quad \frac{M_{QOR}}{k_{a.3}}=1,\quad \frac{1}{k_{or}}\frac{k_{a,2}}{k_{a,3}}=1.8$$

The model equation

$$\frac{1}{k_{app}} = \frac{V_o}{Q_o}\frac{V_o}{V_a}\frac{[TG]_o}{[NaOH]}+1.8V_o \qquad (5.54)$$

is compared with all the experimental data (parity plot) as presented in Figure 5.22.

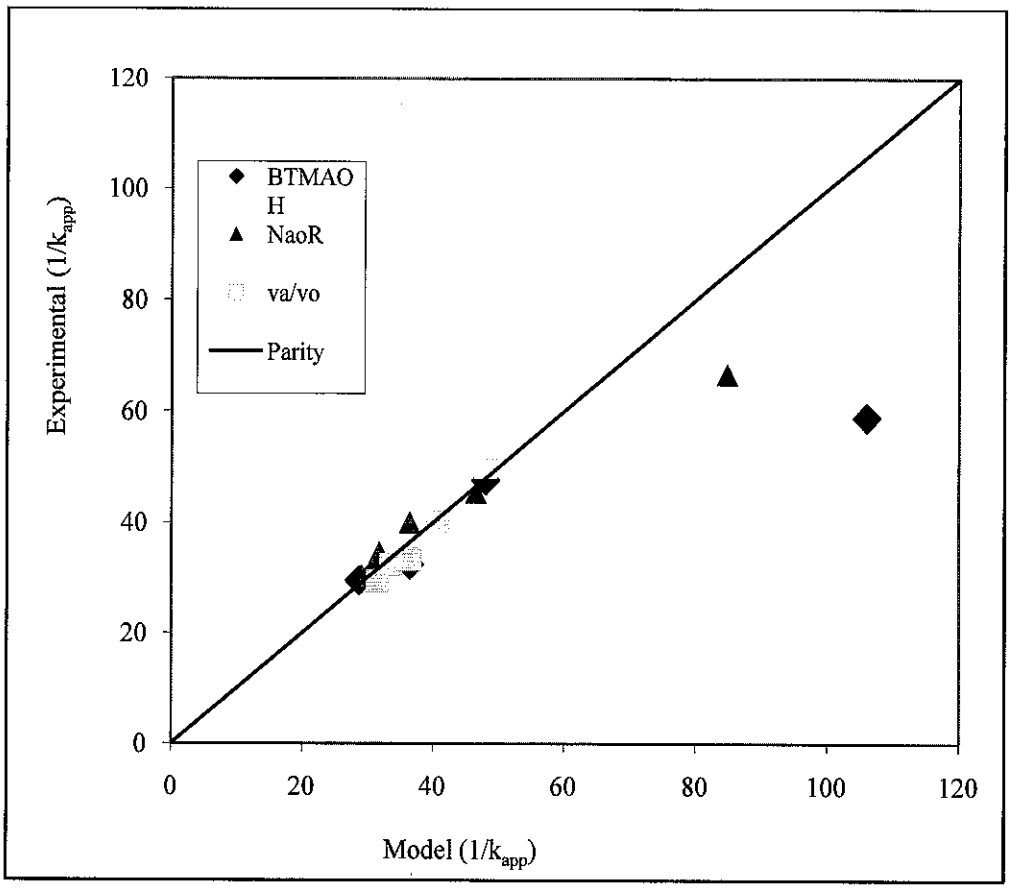


Figure 5.22: the parity plot of experimentally observed apparent rate constant as a function of apparent rate constant obtained by model equation

It can be seen that experimental observations are reasonably well explained by the model equation. The apparent rate equation based on the reaction model can be summarized as

$$k_{app} = \frac{Q_o \left(V_a / V_o \right) [NaOH]}{V_o [TG]_o + 1.8 Q_o V_a [NaOH]} \tag{5.55}$$

And the rate equation (5.39) can be written as

$$-\frac{d[TG]}{dt} = \frac{Q_o\left(V_a/V_o\right)[NaOH]}{V_o[TG]_o + 1.8Q_o V_a[NaOH]}[TG]_o \qquad (5.56)$$

Conversion of triglycerides and hence yield of biodiesel with time can be expressed as

$$\frac{[TG]_o - [TG]}{[TG]_o} = X_{TG} = 1 - e^{-k_{app}t} \qquad (5.57)$$

With:

$$k_{app} = \frac{Q_o\left(V_a/V_o\right)[NaOH]}{V_o[TG]_o + 1.8Q_o V_a[NaOH]}$$

Conversion of triglycerides as a function of reaction time can be estimated with alcohol to oil ratio (Va/Vo), concentration of PTC (Qo), concentration of NaOH as parameters by equation 5.57 at a reaction temperature of 30°C. Conversions based on equation 5.57 compare well with the experimental observations as shown in Figure 5.23.

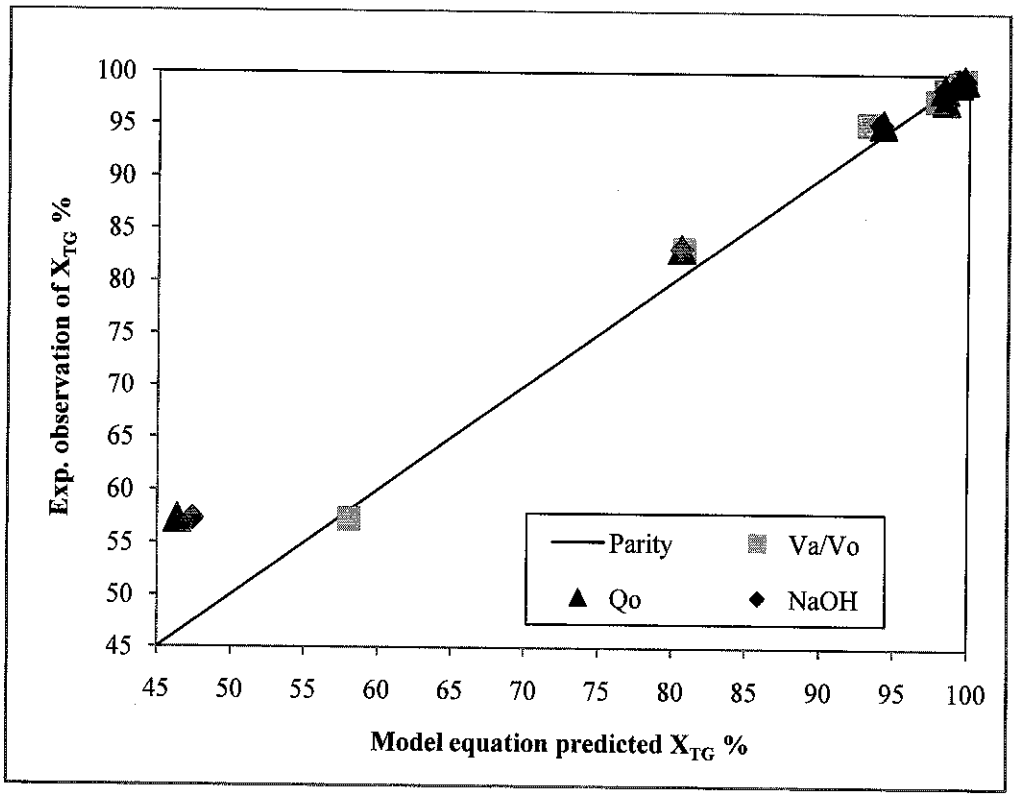


Figure 5.23: Comparison of experimental observed triglycerides conversion with model based equation (5.57) at different values of Va/Vo, PTC (Qo) and NaOH

This equation is developed based on experiments carried out at 30°C. This can be extended to incorporate the effect of temperature through Arrhenius law as;

$$k_{app.T} = \left[\frac{Q_o \left(V_a / V_o \right) [NaOH]}{V_o [TG]_o + 1.8 Q_o V_a [NaOH]} \right]_{T=303} \times e^{-\left[\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{303} \right) \right]} \qquad 5.58$$

In principle, the yield of biodiesel with time can be related to the conversion of triglycerides as;

$$[BD] = 3(TG)_0\left[1 - e^{-k_{app}\,t}\right] \tag{5.59}$$

With:

$$k_{app} = \left(\frac{Q_o\left(V_a / V_o\right)[NaOH]}{V_o[TG]_o + 1.8Q_o V_a[NaOH]} \times e^{-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{303}\right)}\right)$$

However, as triglycerides get converted to diglycerides and monoglycerides before getting converted to biodiesel, yield of biodiesel can be lower; yield may also be lower due to saponification reactions. Experimentally observed yield are compared with the expected yield from the conversion of triglycerides using model equation (5.59) as shown in Figure.5.24. Yields predicted by statistically established RSM model equation (4.2) is also plotted in Figure 5.24 for comparison with model equation (5.59).

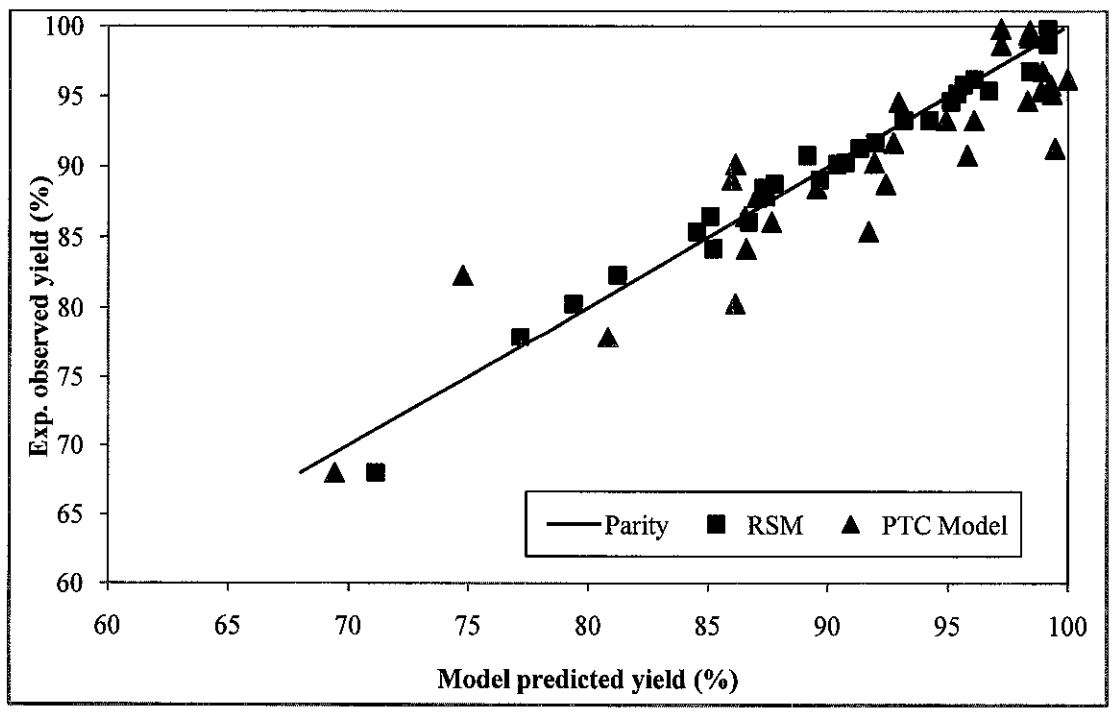


Figure 5.24: The parity plot of experimentally observed yield versus RSM and PTC model equation predicted yield

Experimentally observed yield of biodiesel with estimates from RSM model equation (4.2) and PTC model equation (5.59) are compared and presented in Figure 5.24. In general, the model predictions compare well with experimental observations. However, in some cases the PTC model predictions are slightly higher than experimentally observed biodiesel yields as expected; this can be either due to soap formation (at higher temperatures) or incomplete conversion of di- and mono-glycerides (at low reaction times).

5.5 Summary

Reaction kinetics of alkaline in-situ methanolysis and ethanolysis in the presence of BTMAOH as a PTC were investigated in a batch reactor by measuring the conversion of triglycerides with time at different temperatures to determine reaction rate. Order of the reaction by differential analysis was observed to be nearly one for in-situ methanolysis as well as in-situ ethanolysis at various reaction temperatures investigated. Assuming first order kinetics, the reaction rate constant was revaluated by differential analysis and Arrhenius activation energy of the reactions were estimated. The empirical first order kinetic equations explained well the observed experimental triglycerides conversion with time.

Effect of microwave pretreatment of jatropha seeds on reaction kinetics of alkaline in-situ methanolysis and ethanolysis in the presence of BTMAOH as a PTC were investigated in a batch reactor by measuring the conversion of triglycerides with time at different temperatures to determine reaction rate equation. Microwave pretreatment of seed particles enhanced the apparent reaction rate constant of triglycerides conversion from 0.01637 to 0.04328min^{-1} for in-situ methanolysis and 0.03013 to 0.05497min^{-1} for in-situ ethanolysis for a reaction conducted at 30°C reaction temperature.

Based on the reaction mechanism of phase transfer catalysis of transesterification reactions, kinetics model equations for reaction apparent rate constant, triglycerides conversion and yield of biodiesel were developed. Experimental observations on the effect of each process variables (agitation speed, reaction temperature, ratio of alcohol

to oil seed particles, PTC concentration and NaOH concentration) on triglycerides conversion were evaluated using the model equation. Based on the experimental observation of the effect of each reaction variables, the model parameters of complex formation, partition coefficient and intrinsic reaction rate constant were evaluated to describe the apparent reaction rate constant. Model equation predictions on triglycerides conversion and yield of biodiesel compare well with the experimental results.

CHAPTER 6

CONCLUSION AND RECOMMENDATION

The effects of phase transfer catalysis as well as the effect of microwave irradiation pretreatment of jatropha curcas seed particles on the reaction rate of in-situ transesterification and yield of biodiesel were investigated. Section 6.1 presents the conclusion drawn from the research work. Section 6.2 discusses the contribution of this research work while recommendations and future direction of the research work is described in Section 6.3.

6.1 Conclusion

In-situ methanolysis as well as in-situ ethanolysis transesterification of jatropha oil seed particles were investigated using cetyltrimethylammonium bromide (CTMAB) as phase transfer catalysts at different NaOH concentrations, ratios of alcohol to seed particles, reaction temperatures, mixing speeds and reaction time. Use of cetyltrimethylammonium bromide (CTMAB) as a phase transfer catalyst increased the yield of FAME from 49.7 % w/w to 89.2 % w/w while reducing the consumption of methanol by 16.67%, NaOH by 24% at a shorter reaction time and lower reaction temperature of 40°C as compared to in-situ methanolysis in the presence of only NaOH as alkaline catalyst of the same reaction condition. Similarly, for in-situ ethanolysis reaction, the yield of FAEE increased from 87.4 % w/w to 99.5% w/w while reducing the consumption of ethanol by 16.7%, NaOH by 33.3% at a shorter reaction time and lower temperature of 30°C when cetyltrimethylammonium bromide (CTMAB) was used as phase transfer catalyst in conjunction with NaOH as alkaline catalyst.

Encouraged by the positive result of CTMAB as a PTC on enhancing in-situ transesterification reaction rate, two more phase transfer catalysts of benzyltrimethylammonium hydroxide (BTMAOH) and crown ether (CE) were also investigated along with cetyltrimethylammonium bromide (CTMAB) for choosing PTC with better catalytic performance. BTMAOH exhibited better catalytic performance as compared to CTMAB and CE.

For in-situ methanolysis, use of BTMAOH as a PTC together with NaOH as alkaline catalyst increased the yield of FAME from 79.8 % w/w to 91.2% w/w while reducing the reaction time from 150 minutes to 90 minutes as compared to the reaction conducted with BTMAOH alone as a catalyst; similarly, for in-situ ethanolysis use of BTMAOH as a PTC together with NaOH as alkaline catalyst increased the yield of FAEE from 95.7% w/w to 99.6% w/w while reducing the reaction time from 120 minutes to 90 minutes as compared to the reaction conducted with BTMAOH alone as a catalyst. Thus, experimental observation demonstrated that better catalytic performance of BTMAOH as a PTC was achieved when it was used together with alkaline catalyst in a reduced reaction time as compared to using it alone as a PTC.

The effect of microwave heat pretreatment of jatropha curcas seed particles on the reaction rate of in-situ methanolysis and in-situ ethanolysis in the presence of alkaline BTMAB as a PTC were investigated and the results were compared with microwave heat untreated jatropha curcas seed particles in-situ transesterification reaction. Statistical model equation were developed for predicting the yields of FAME/FAEE and establishing optimum reaction condition for maximum FAME/FAEE yields a function of different reaction variables combination designed using response surface methodology (RSM).

At optimal condition for in-situ methanolysis of microwave untreated jatropha curcas seed particles, 91.7% w/w maximum yield of FAME was predicted by model equation (4.1) and compared with 89.8±0.7% w/w FAME yield observed experimentally at optimal reaction time of 103 minutes; similarly, for in-situ ethanolysis of microwave untreated jatropha curcas seed particles, 99.74% w/w

maximum FAEE yield was predicted by model equation (4.2) and compared with 99.4±0.4% w/w of FAEE yield observed experimentally at optimal reaction time of 95 minutes. However, for microwave heat pretreated jatropha curcas seed particles in-situ methanolysis, 96.75% w/w FAME yield was predicted by the model equation (4.3) and compared with 93.7±1.53% w/w FAME yield observed experimentally in 37 minutes of optimal reaction time; similarly, for in-situ ethanolysis of microwave heat pretreated jatropha curcas seed particles in the presence of alkaline BTMAB as a PTC, 99.61% w/w FAEE yield was predicted by the model equation (4.4) and compared with 99.5±0.12% w/w FAEE yield experimentally observed in 30 minutes of optimal reaction time.

Thus, it was observed that in-situ transesterification reaction rates were drastically increased when jatropha curcas seed particles was pretreated with microwave heat while reducing the reaction time from 103 minutes to 37 minutes for in-situ methanolysis and from 95 minutes to 30 minutes for in-situ ethanolysis reaction. Comparisons of model equations predicted yields with experimentally observed yields also demonstrated that model equations are adequate enough to predict the yield of FAME/FAEE for microwave untreated in-situ transesterification as well as microwave pretreated jatropha curcas seed particles in-situ transesterification.

Reaction kinetics of alkaline in-situ methanolysis and in-situ ethanolysis in the presence of BTMAOH as a PTC for the conversion of triglycerides in a batch reactor at different reaction temperatures were investigated. Order of the reaction rate obtained by differential reaction rate analysis demonstrated that the order of the reaction is nearly one for in-situ methanolysis as well as in-situ ethanolysis at each reaction temperature investigated. Arrhenius activation energy of the reactions were estimated to be 21641J/mole and 17078J/mol for in-situ methanolysis and in-situ ethanolysis of microwave untreated jatropha curcas seed particles; however, for microwave heat treated seed particles the activation energy were estimated to be 11224 J/mole and 7320J/mole for in-situ methanolysis and ethanolysis respectively.

As compared to microwave heat untreated in-situ transesterification, microwave pretreatment of seed particles enhanced the apparent reaction rate constant of triglycerides conversion from 0.01637 to 0.04328min^{-1} for in-situ methanolysis and

0.03013 to 0.05497min^{-1} for in-situ ethanolysis for a reaction conducted at 30°C reaction temperature. Triglycerides conversion estimated by the empirical first order kinetic equation compared well with the experimentally observed triglycerides conversion for both microwave untreated and pretreated in-situ methanolysis as well as in-situ ethanolysis reaction.

Based on the reaction mechanism developed for alkaline phase transfer catalysis transesterification of jatropha curcas oils, phase transfer catalysis transesterification reaction kinetics model equations were developed. The effect of each process variables (agitation speed, reaction temperature, ratio of alcohol to oil seed particles, PTC concentration and NaOH concentration) on triglycerides conversion were evaluated using the model equations and the results were compared with experimental observations. Based on the experimental observation of the effect of each reaction variables, the model parameters of rate of complex formation, partition coefficient and intrinsic reaction rate constant were evaluated to describe the apparent reaction rate constant. Model equations prediction on triglyceride conversion and yield of biodiesel compare well with the experimental results.

6.2 Contributions of the research work

The main contributions of the present research are;

i) *Phase transfer catalysis for in-situ transesterification reaction*:

For the first time, phase transfer catalysis technique was applied to in-situ transesterification reaction to increase the conversion of triglycerides with reduced consumption of alcohol and catalyst concentration in shorter reaction time at ambient temperature. This can improve the economic viability of biodiesel technology.

ii) *Microwave irradiation heat pretreatment of seed particles along with phase transfer catalysis for in-situ transesterification reaction:*

For the first time, application of microwave pretreatment of jatropha seed particles is shown to enhance triglycerides conversion to biodiesel using in-situ transesterification at a reduced consumption of alcohol and catalyst concentration in shorter reaction time at ambient temperature. The reaction time was drastically reduced to about 30 minutes.

iii) *Statistical model by response surface methodology for identification of optimum operating conditions:*

Individual and interaction effect of process variables on the yield of biodiesel with microwave pretreatment of seed particles and use of phase transfer catalysis on in-situ transesterification of jatropha curcas was investigated using response surface methodology (RSM) to develop model equations for FAME and FAEE yields and optimum operating conditions to obtain maximum yield.

iv) *Develop reaction mechanism and kinetics model*:

Based on the reaction mechanism developed for alkaline phase transfer catalysis transesterification of fatty oils, for the first time phase transfer catalysis of transesterification reaction kinetics model equation was developed and compared with the experimental observations on the effect of each process variables to evaluate the model parameters to describe the apparent reaction rate constant. Model predictions on triglycerides conversion and yield of biodiesel compare well with the experimental results.

6.3 Recommendation and future direction

Currently, the central issue of biodiesel to be used as renewable and substitute of petro-diesel is its economics. Research on biodiesel processing technology improvement will remain pursuant. Cost of raw materials and size of processing units

determine the economic viability of biodiesel technology. Transesterification of non-edible oil seeds can reduce the cost of raw materials. In the present study, in-situ transesterification technique was used to eliminate the lengthy oil extraction and purification processes to simplify the process steps and reduce cost of production. Microwave heat pretreatment of jatropha seed particles and use of phase transfer catalysis technique were also investigated to enhance the rate of reaction. Thus, development of continuous process for in-situ transesterification along with a phase separation unit to recover biodiesel is necessary to reduce the cost of biodiesel production. At this junction, the researcher recommends to continue the present research work to develop laboratory size new type of continuous *wet girder-mixer-reactor* that combines the seed grinding and reactive-extraction processes simultaneously along with phase separation unit to recover biodiesel using the reactor-separator concepts demonstrated by Uker et al., [206]. It is also recommended that the research work of the proposed new *wet-girder-mixer-reactor* may take in to consideration the following points;

i) Design and study of the hydrodynamic and bed to wall heat transfer behavior of the reactor using soft ware simulation technique such as COMSOL.

ii) Conduct modeling of reaction kinetics.

iii) Laboratory or prototype reactor design, manufacture and testing.

iv) Generate laboratory data that can help for scale up the reactor to commercial level.

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Journals and conferences extracted and published from the PhD research work.

I. Journals

1. S. M. Hailegiorgis, S. Mahadzir, and D. Subbarao, "Parametric Study and Optimization of In Situ Transesterification of Jatropha curcas l Assisted by Benzyltrimethylammonium Hydroxide as a Phase Transfer Catalyst via Response Surface Methodology" *Journal of Biomass and Bioenergy, vol.49, pp. 63-73, 2013* ***(Science Direct Elsevier - Impact Factor 3.646).***

2. S. M. Hailegiorgis, S. Mahadzir, and D. Subbarao, "Enhanced in situ ethanolysis of Jatropha curcas L. in the presence of cetyltrimethylammonium bromide as a phase transfer catalyst " *Renewable Energy vol. 36, pp. 2502-2507, 2011* ***(Science Direct Elsevier -Impact Factor 2.978)***

3. S. M. Hailegiorgis, S. Mahadzir, and D. Subbarao, " In situ transesterification of non-edible oil in the presence of cetyltrimethylammonium bromide", *International Journal of Global Environmental Issues, Vol. 12, PP 161-170 2012* ***(Inderscience Publisher:-Scopus and Biobase Elsevier Indexed).***

4. S. M. Hailegiorgis, S. Mahadzir, and D. Subbarao, "A reaction kinetic model for transesterification of jatropha curcas in the presence of phase transfer catalysts " *Submitted to Journal of Applied Catalysis A:General:-Under Final Review* ***(Science Direct Elsevier - Impact Factor 3.903).***

5. S. M. Hailegiorgis, S. Mahadzir, and D. Subbarao, "Effect of microwave heat treatment of jatropha curcas seed particles and use of phase transfer catalysis on the in-situ transesterification jatropha curcas oil and reaction kinetics study", *International Journal of Applied Science-under review* ***(Scopus Elsevier Indexed).***

II. Conference proceedings

1. S.M. Hailegiorgis, S. Mahadzir, and D. Subbarao, "Reactive extraction of jatropha curcas l assisted by phase transfer catalyst for the production of biodiesel " *National post graduate conference(npc2011),Print ISBN: 978-1-*

4577-1882-3, INSPEC Accession Number: 12494954 Digital Object Identifier : 10.1109/NatPC.2011.6136271 245 .

2. S. M. Hailegiorgis, S. Mahadzir, and D. Subbarao, "In situ ethanolysis and kinetics study of jatropha curcas oil in the presence of phase transfer catalyst" *2012 The Second International Conference on Process Engineering and Advanced Material (ICPEM2012), ISBN:9789832271666.*

3. S. M. Hailegiorgis, S. Mahadzir, and D. Subbarao, "In situ transesterification of non-edible oil seeds in the presence of cetyltrimethylammonium bromide" *International Conference on Environment 2010; Green Technologies for the Benefits of Bottom Billions, 13- 15th December 2010, Penang, Malaysia.*

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III. Award

Best paper ward for the paper entitled "Reactive extraction of jatropha curcas l assisted by phase transfer catalyst for the production of biodiesel" presented at *National post graduate conference (npc2011).*

APPENDIX A

EXPERIMENTAL PROCEDURE FOR THE DETRIMINATION OF ACID VALUE, SAPONIFICATION VALUE AND IODIN VALUE

A-1: Laboratory procedures for determination of acid value

Acid value is the number of milligram of potassium hydroxide necessary to neutralize the free acids in one gram of sample.

a) Apparatus

1. Erlenmeyer flasks, 250ml
2. Magnetic stirrer
3. Burette, 10ml graduated in 0.05ml division with a tip drawn to a fine opening and extending at least 10cm below the stopcock.
4. Analytical balance, accurate to 0,0001g.

b) Reagents

1. Potassium hydroxide (KOH), 0.1N, i.e., reagent grade KOH with NIST traceable standardization to ±1 part in 1000 in water, methanol and ethanol.
2. Solvent mixture consisting of equal parts by volume of isopropyl alcohol and toluene.
3. Phenolphthalein indicator solution, 1% in isopropyl alcohol.

c) Procedure

1. An indicator solution was added to the solvent in the ratio of 2ml to 125ml s olvent and neutralize with alkali to a faint but permanent pink color.
2. The sample size of 5g was weighed to an accuracy of ±0.02 into an Erlenmeyer flask and well mixed.
3. 125ml of the neutralized solvent mixture was added and well mixed until the s ample is completely dissolved in the mixture.
4. The sample was vigorously shaked while titrating with standard alkali to the first permanent pink color of the same intensity of the neutralized solvent before the later was added to the sample. The color persists for 30 second.

5. Blank titration was also performed using 125ml of the neutralized solvent mixture.

The acid value was calculated using the relation:

$$Saponification\ value, mg of\ KOH / g = (A - B) * \frac{N * 56.1}{w}$$

Where: A = KOH solution required for titration of the sample, ml

B = KOH solution required for titration of the blank, ml

N = Normality of standard alkali KOH solution (mol/l)

W = the amount of sample used, g.

A-2: Laboratory procedures for determination of saponification value

Saponification value is the amount of alkali necessary to saponify a definite quantity of the sample. It is expressed as the number of milligram of potassium hydroxide (KOH) required to saponify one gram of the sample. It is the measure of the average molecular weight of all the fatty acid present.

a) Apparatus

1) Erlenmeyer flasks, 250ml
2) Hot plate
3) Magnetic stirrer
4) Burette, 10ml graduated in 0.05ml division with a tip drawn to a fine opening and extending at least 10cm below the stopcock.
5) Analytical balance, accurate to 0,0001g.

b) Reagents

1) Potassium hydroxide (KOH), 0.1N, i.e., reagent grade KOH with NIST traceable standardization to ±1 part in 1000 in water, methanol and ethanol.
2) Standard hydrochloric acid (0.5M) standardized to detect molarity change of 0.0005by titrating with KOH.
3) Solvent mixture consisting of equal parts by volume of isopropyl alcohol and toluene.
4) Phenolphthalein indicator solution, 1% in isopropyl alcohol.

c) Procedure

1) 2g of oil was added to 250ml conical flask
2) 25ml of KOH solution was added to in to the oil in the 250ml conical flask

3) A reflux condenser was attached to the conical flask and the mixture in the conical flask was heated by putting in a steam bath for about 25minutes with occasional shaking.
4) 2-4 drops of phenolphthalein indicator solution was added to the solvent while the mixture was hot.
5) 0.5 M HCl was taken in a burette and the mixture was titrated until a color change from pink to colorless was observed.
6) The final result was registered for calculation.
7) Blank titration was also performed using 25ml of 0.5 M KOH in a conical flask in which 2-4 drops phenolphthalein indicator solution was added and titration was made using o.5 M HCl in a burette.

The saponification value was calculated using the relation:

$$Saponification\ value, mg of\ KOH / g = (A - B) * \frac{N * 56.1}{w}$$

Where: w = weight of sample taken, g

A = volume of KOH required for blank titration, ml

B = volume of KOH required for sample titration, ml

N = normality of KOH solution, mol/l

A-3: Laboratory procedures for determination of iodine value

Iodine value or iodine number is a measure of the total amount of unsaturated fatty acids in the oil. It is a measure of the number of grams of iodine which will combine with 100 grams of the oil.

a) Apparatus

1. 500 flask with stopper
2. Magnetic stirrer
3. Burette, 10ml graduated in 0.05ml division with a tip drawn to a fine opening and extending at least 10cm below the stopcock
4. Analytical balance, accurate to 0,0001g.

b) Reagents

1. Wijs solution;
2. De-ionized water;
3. Carbon tetrachloride, CCl_4 ;
4. 10% potassium iodide, KI;
5. 0.1 mol/L Sodium thiosulphate, $Na_2S_2O_3$
6. Potassium iodate, KIO_3
7. Demineralized water
8. Sodium thiophosphate

c) Procedure

1. 2ml of sample was mixed in 20-25ml of carbon tetrachloride in a beaker and dissolved completely;
2. The solution was transferred to 500ml flask and 25ml of wij□s solution was added; the stopper was put on the flask and shaken.
3. The glass was kept in a dark for 30 minutes.

4. 20 ml of potassium iodide solution and 100ml of de-ionized water were added and well mixed.
5. 0.1 N of sodium thiosulphate solution was filled in a burette
6. Starch solution was added and titration was conducted. The color was noted until it turned from blue to white and the result was recorded for calculation.
7. Blank titration was also performed using 25ml of wij□s solution and kept in dark place for 30 minutes with occasional shaking, 20ml of KI solution along with the starch indicator was added and the titration was performed with 0.1 N sodium thiosulphate. The result was recorded for calculation.

The iodine number was calculated using the relation:

$$Iodinevalue = (A - B) * \frac{N * 12.69}{w}$$

Where: N = Normality of sodium thiosulphate ($Na_2S_2O_3$) used; mol/l

A = Volume of sodium thiosulphate used for blank; ml

B = Volume of sodium thiosulphate used for determination,ml

w = Mass of the sample, g.

APPENDIX B

GAS CHROMATOGRAPH (GC) CALIBRATION REULTS AND

GROMATOGRAPH PEAKS OF SAMPLES AT OPTIMUM CONDITION

B-1: Details of calibration results

Standard 1:

Compound Name	Retention time	Peak area	Height	concentration
Glycerin	4.071	35663	10203	12.2580
Mono-olein	16.038	265079	34890	20.6531
Tricaprin (IS)	19.373	1914338	688557	0.0000
Di-olein	20.711	99849	34784	10.1399
Tri-olein	23.328	27734	3722	9.1506

Standard 2:

Compound Name	Retention time	Peak area	Height	concentration
Glycerine	4.132	113615	32116	43.0054
Mono-olein	16.038	711683	95419	49.7353
Tricaprin (IS)	19.372	1925820	688077	0.0000
Di-olein	20.711	717515	76597	19.7091
Tri-olein	23.330	84206	11745	21.8390

Standard 3:

Compound Name	Retention time	Peak area	Height	concentration
Glycerine	4.133	185323	53227	54.1306
Mono-olein	16.043	1478835	196732	99.9909
Tricaprin (IS)	19.371	1923408	690325	0.0000
Di-olein	20.710	466885	168456	40.1409
Tri-olein	23.328	163808	22727	39.8233

Standard 4:

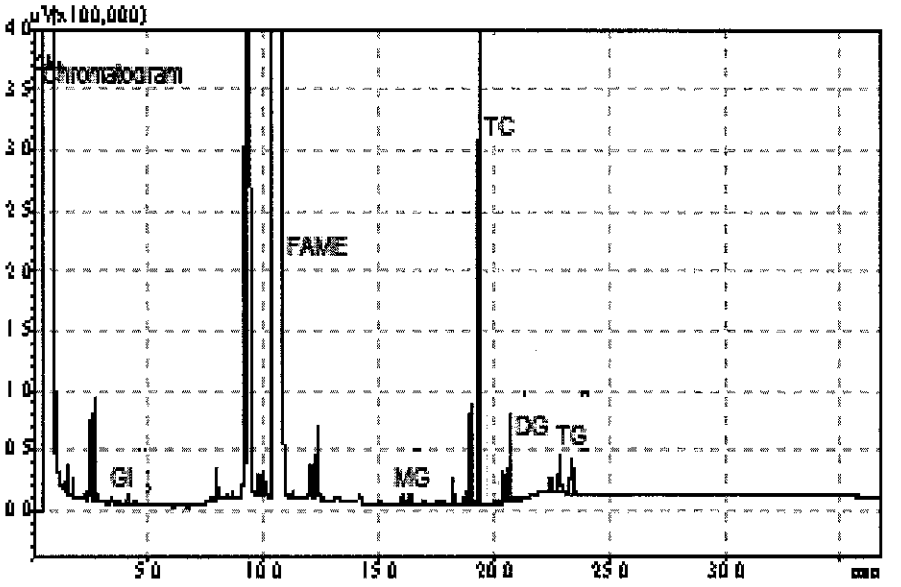
Compound Name	Retention time	Peak area	Height	concentration
Glycerine	4.122	212464	58522	77.3958
Mono-olein	16.023	1577124	235117	148.1609
Tricaprin (IS)	19.361	1522653	550782	0.0000
Di-olein	20.701	659140	233967	70.0742
Tri-olein	23.299	228529	31615	67.9973

Standard 5:

Compound Name	Retention time	Peak area	Height	concentration
Glycerin	4.116	298224	83160	113.4102
Mono-olein	16.016	2272572	298288	201.1597
Tricaprin (IS)	19.357	1444999	520429	0.0000
Di-olein	20.697	899635	320997	99.9359
Tri-olein	23.291	327394	45299	101.1897

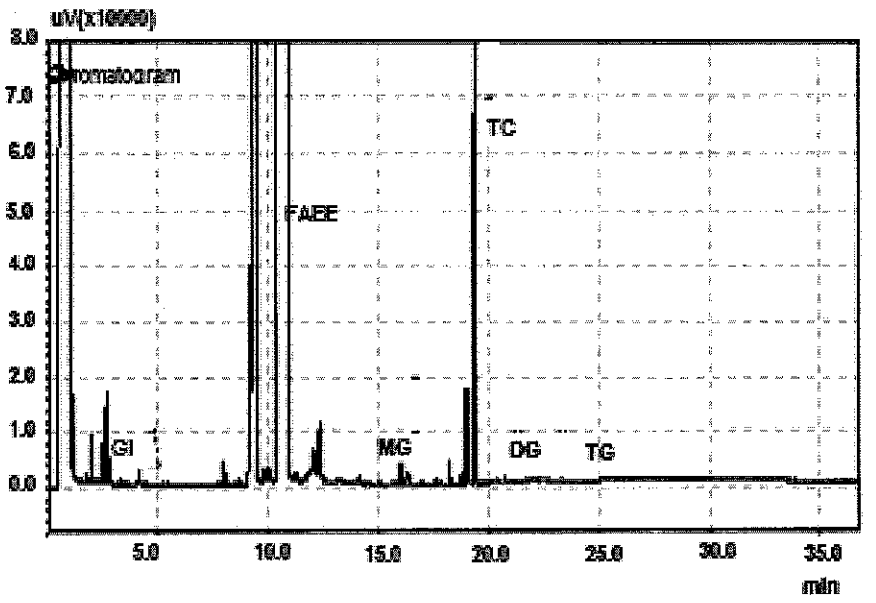
B-2: GC peaks of fatty acid methyl esters (FAME)and ethyl esters(FAEE) produces at optimal condition

1. GC peaks of FAME and FAEE for in situ transestrification of Jatropha curcas in the presence of benzyl trimethylammonium hydroxide (BTMAOH) as a phase transfer catalyst (PTC)



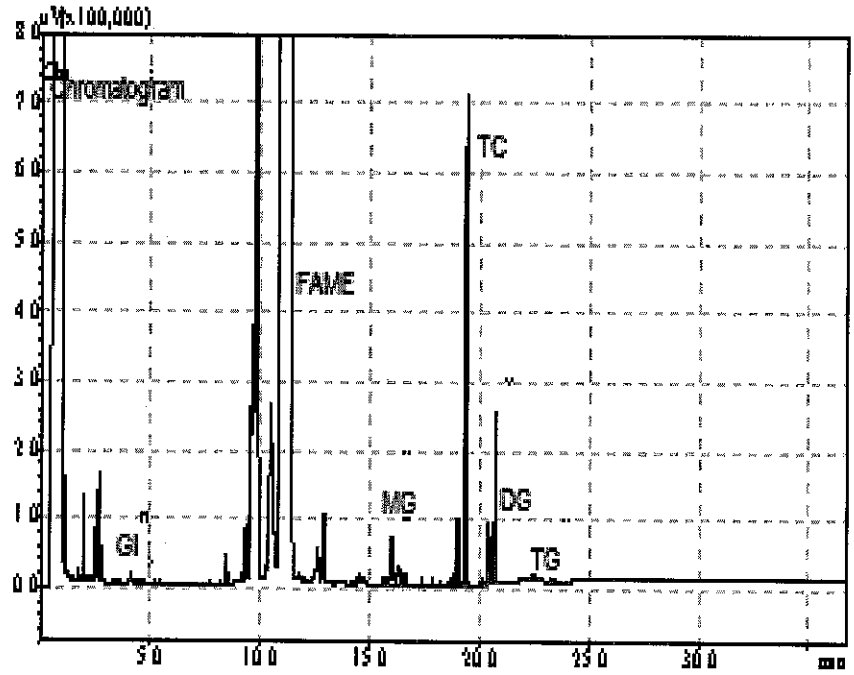
a) GC plots of FAME produced at optimal condition

b)

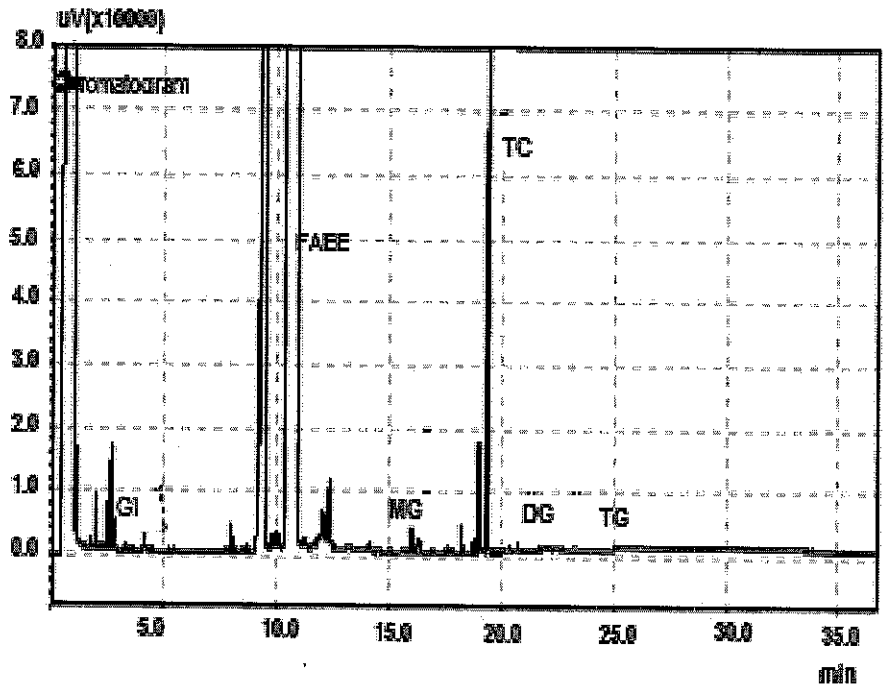


b) GC of FAEE produced at optimal condition

2. GC peaks of FAME and FAEE for microwave radaition treated in situ transestrification of Jatropha curcas in the presence of benzyl trimethylammonium hydroxide (BTMAOH) as a phase transfer catalyst (PTC)



a) GC chromatograms for FAME



b) GC chromatograms for FAME

APPENDIX C

EXPERIMENTAL DATA OF IN SITU TRANSESTRIFICATION REACTION

C-1: Results from alkaline in situ transesterification using CTMAB as a PTC experiment

1. In-situ methanolysis

Quantity of FAME produced from 20g of jatropha curcas seed particles:

i) at different molar ratio of CTMAB to NaOH concentration :

Run: at 7.5 ml/g methanol to jatropha curcas seeds, 0.68 % w/w of NaOH, 30oC, 300 rpm and 150 minutes of reaction time.

CTMAB/NaOH (mole/mole)	Amount of FAME produced (gram)		
	Exper-1	Exper-2	Average
0	5.67	5.25	5.46
0.5	6.85	6.49	6.67
1	9.18	8.85	9.01
1.5	9.18	9.42	9.30
2	9.46	9.19	9.32
2.5	9.10	9.51	9.31

ii) at different ratio of NaOH to jatropha curcas seeds in % w/w

Run: at 7.5 ml/g methanol per jatropha curcas seeds, 1 molar ratio of PTC, 30°C, 300 rpm and 150 minutes of reaction time

NaOH/JCL (% w/w)	Amount of FAME produced without CTMAB (gram)			Amount of FAME produced with CTMAB (gram)		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
0.068	1.92	1.58	**1.75**	5.11	4.73	**4.92**
0.338	2.93	2.62	**2.77**	7.13	6.58	**6.85**
0.675	4.30	4.38	**4.34**	8.95	8.81	**8.88**
1.013	6.22	5.90	**6.06**	9.32	9.62	**9.47**
1.35	6.12	6.38	**6.25**	9.16	9.45	**9.30**
1.688	6.33	6.05	**6.19**	9.31	9.06	**9.19**

iii) at different ratio of methanol to jatropha curcas seeds in ml/g

Run: at 1 molar ration of CTMAB, 0.68 % w/w of NaOH, 30°C, 300 rpm and 150 minutes of reaction time

Methanol per JCL (ml/g)	Amount of FAME produced without CTMAB (gram)			Amount of FAME produced with CTMAB (gram)		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
3	2.18	1.82	2.00	4.66	5.16	4.91
4.5	3.96	3.53	3.74	6.60	6.97	6.79
6	5.16	4.55	4.86	9.05	9.46	9.26
7.5	5.76	6.11	5.93	9.30	9.57	9.44
9	6.58	5.99	6.28	9.39	9.06	9.22
10.5	6.59	6.02	6.30	8.71	9.10	8.91

iv) At different reaction temperature in °C

Run at: 7.5 ml/g methanol per jatropha curcas seeds, 1 molar ration of CTMAB, 0.68 % w/w of NaOH, 300 rpm and 150 minutes of reaction time

Reaction Temp. (°C)	Amount of FAME produced without CTMAB (gram)			Amount of FAME produced with CTMAB (gram)		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
30	5.12	5.48	5.3	9.57	9.35	9.46
40	5.58	5.83	5.71	9.64	9.38	9.51
50	6.59	6.22	6.41	9.17	9.41	9.29
60	6.95	6.52	6.74	9.08	8.94	9.01
70	6.14	6.62	6.38	8.17	8.53	8.35

v) at different mixing speed in rpm

Run: at 7.5 ml/g methanol per jatropha curcas seeds, 1 molar ration of CTMAB, 0.68 % w/w of NaOH, 30°C and 150 minutes of reaction time

Mixing speed (rpm)	Amount of FAME produced without CTMAB (gram)			Amount of FAME produced with CTMAB (gram)		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
200	3.77	4.18	3.98	4.66	5.16	4.91
300	5.60	5.49	5.54	6.60	6.97	6.79
400	6.55	6.17	6.36	9.05	9.46	9.26
500	6.70	6.63	6.66	9.30	9.57	9.44
600	6.63	6.78	6.71	9.39	9.06	9.22
700	6.66	6.41	6.54	8.71	9.10	8.91

vi) at different reaction time in minutes

Run: at 7.5 ml/g methanol per jatropha curcas seeds, 1 molar ration of CTMAB, 0.68 % w/w of NaOH, 30°C and 400 rpm

Reaction Time (minute)	Amount of FAME produced without CTMAB (gram)			Amount of FAME produced with CTMAB (gram)		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
30	1.25	1.50	1.37	5.29	5.03	5.16
60	2.30	1.96	2.13	7.52	7.21	7.37
90	3.55	3.14	3.34	8.75	8.33	8.54
120	5.66	5.04	5.35	9.02	9.22	9.12
150	6.07	5.73	5.90	9.68	9.43	9.56
180	6.27	6.09	6.18	9.62	9.30	9.46
210	6.96	6.41	6.68	9.35	9.64	9.49
240	6.72	6.52	6.62	9.18	9.48	9.33

2. In-Situ Ethanolysis

Quantity of FAEE produced from 20g of jatropha curcas seed particles:

i) At different molar ratio of CTMAB to NaOH concentration

Run: at 7.5 ml/g ethanol per jatropha curcas seeds, 0.68 % w/w of NaOH, 30°C, 300 rpm and 150 minutes of reaction time

CTMAB/NaOH (mole/mole)	Amount of FAEE produced (gram)		
	Exper-1	Exper-2	Average
0	9.37	9.26	9.31
0.5	9.92	9.98	9.95
1	10.48	10.54	10.51
1.5	10.33	10.46	10.40
2	10.41	10.35	10.38
2.5	9.77	9.94	9.85

ii) at different ratio of NaOH to jatropha curcas seeds in % w/w

Run : at 7.5 ml/g ethanol per jatropha curcas seeds, 1 molar ratio of PTC, 30°C, 300 rpm and 150 minutes of reaction time

NaOH/JCL (% w/w)	Amount of FAEE produced without CTMAB (gram)			Amount of FAEE produced with CTMAB (gram)		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
0.068	2.45	2.85	2.65	6.27	6.02	6.15
0.338	5.25	4.84	5.05	8.40	8.90	8.65
0.675	8.42	8.71	8.57	10.51	10.23	10.37
1.013	9.70	9.28	9.49	9.85	10.25	10.05
1.35	9.29	9.34	9.31	9.26	9.77	9.51
1.68	8.75	9.01	8.88	7.62	8.11	7.87

iii) At different ratio of methanol to jatropha curcas seeds in ml/g

Run: at 1 molar ration of CTMAB, 0.68 % w/w of NaOH, 30°C, 300 rpm and 150 minutes of reaction time

Ethanol per JCL (ml/g)	Amount of FAEE produced without CTMAB (gram)			Amount of FAEE produced with CTMAB (gram)		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
3	4.82	5.20	5.01	7.61	7.17	7.39
4.5	7.97	7.65	7.81	9.03	8.77	8.90
6	8.33	8.56	8.45	10.44	10.22	10.33
7.5	9.06	8.75	8.91	10.45	10.52	10.49
9	9.43	9.22	9.33	10.52	10.38	10.45
10.5	9.12	9.48	9.30	10.51	10.26	10.39

iv) At different reaction temperature in °C

Run: at 7.5 ml/g ethanol per jatropha curcas seeds, 1 molar ration of CTMAB, 0.68 % w/w of NaOH, 300 rpm and 150 minutes of reaction time

Reaction Temp. (°C)	Amount of FAEE produced without CTMAB (gram)			Amount of FAME produced with CTMAB(gram)		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
30	8.92	8.97	8.94	10.41	10.51	10.46
40	9.17	9.10	9.13	10.17	10.05	10.11
50	9.55	9.39	9.47	10.22	10.36	10.29
60	9.06	6.52	7.79	9.93	10.00	9.96
70	8.78	6.62	7.70	8.70	8.64	8.67

v) At different mixing speed in rpm

Run: at 7.5 ml/g ethanol per jatropha curcas seeds, 1 molar ration of CTMAB, 0.68 % w/w of NaOH, 30°C and 150 minutes of reaction time

Mixing speed (rpm)	Amount of FAEE produced without CTMAB (gram)			Amount of FAME produced with CTMAB (gram)		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
200	8.52	8.30	8.41	9.16	8.93	9.04
300	8.76	8.55	8.66	9.54	9.79	9.66
400	9.08	8.91	9.00	10.35	10.54	10.44
500	8.91	9.21	9.06	10.31	10.05	10.18
600	9.43	9.19	9.31	9.30	9.09	9.20
700	8.78	8.52	8.65	8.15	7.93	8.04

vi) At different reaction time in minutes

Run: at 7.5 ml/g ethanol per jatropha curcas seeds, 1 molar ration of CTMAB, 0.68 % w/w of NaOH, 30°C and 400 rpm

Reaction Time (minute)	Amount of FAEE produced without CTMAB (gram)			Amount of FAME produced with CTMAB (gram)		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
30	4.63	4.56	4.59	7.61	7.31	7.46
60	7.16	7.24	7.20	9.40	9.22	9.31
90	8.03	8.10	8.06	10.34	10.15	10.24
120	8.72	8.63	8.68	10.39	10.49	10.44
150	8.92	9.01	8.97	10.54	10.44	10.49
180	9.23	9.19	9.21	9.83	9.73	9.78
210	9.07	9.26	9.17	9.24	9.18	9.21
240	8.93	6.52	7.72	8.03	8.49	8.26

C-2: Results from different PTC experiment

1. Without alkaline catalyst (NaOH)

i) Quantity of FAME in gram produced by in situ methanolysis from 20 gram of seed particles

Run: at 7.5 ml/g methanol per jatropha curcas seeds, 1 % w/w of CTMAB, 30°C and 400 rpm

Reaction Time (minute)	CTMAB			BTMAOH			Crown Ether		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
30	4.17	3.90	4.03	5.77	5.51	5.64	0.83	0.69	0.76
60	4.42	4.53	4.48	6.27	6.42	6.35	1.66	1.78	1.72
90	5.02	4.92	4.97	7.09	7.33	7.21	2.30	2.44	2.37
120	5.96	6.14	6.05	8.28	8.04	8.16	3.18	3.29	3.24
150	6.56	6.47	6.52	8.35	8.23	8.29	3.92	3.88	3.90
180	6.78	6.67	6.73	8.35	8.16	8.26	4.41	4.55	4.48
210	6.59	6.68	6.64	8.26	8.15	8.21	4.85	5.03	4.94

ii) Quantity of FAEE in gram produced by in situ methanolysis from 20 gram of seed particles

Run: at 7.5 ml/g ethanol per jatropha curcas seeds, 1% w/w of CTMAB, 30°C and 400 rpm

Reaction Time (minute)	CTMAB			BTMAOH			Crown Ether		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
30	5.65	5.42	5.53	6.65	6.92	6.79	3.82	4.06	3.94
60	7.17	7.65	7.41	7.88	8.22	8.05	5.62	6.00	5.81
90	8.70	8.28	8.49	9.23	9.04	9.13	6.61	6.22	6.41
120	8.75	8.93	8.84	9.23	9.59	9.41	7.23	7.56	7.39
150	9.18	8.95	9.07	9.51	9.74	9.63	7.65	7.96	7.81
180	9.22	9.03	9.13	9.71	9.44	9.57	7.80	8.21	8.00
210	9.36	9.05	9.21	9.74	9.43	9.59	7.93	8.23	8.08

2. With alkaline catalyst (NaOH)

i) Quantity of FAME in gram produced by in situ methanolysis from 20 gram of seed particles

Run: at 7.5 ml/g methanol per jatropha curcas seeds, 1 molar ration of CTMAB, 0.68 % w/w of NaOH, 30°C and 400 rpm

Reaction Time (minute)	CTMAB + NaOH			BTMAOH + NaOH			CE + NaOH		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
30	5.10	5.21	49.3	5.15	7.58	7.66	7.62	2.80	2.46
60	7.47	7.28	68.9	7.37	8.84	8.70	8.77	3.41	3.72
90	8.41	8.64	81.8	8.52	9.73	9.60	9.66	4.75	4.40
120	9.23	9.04	85.6	9.13	9.96	9.91	9.93	6.08	5.83
150	9.67	9.47	89.7	9.57	10.09	10.16	10.12	7.30	7.01
180	9.37	9.59	90.8	9.48	9.94	10.07	10.01	7.76	7.93
210	9.35	9.55	90.4	9.45	9.87	9.95	9.91	7.83	8.10

ii) Quantity of FAEE in gram produced by in situ methanolysis from 20 gram of seed particles

Run: at 7.5 ml/g ethanol per jatropha curcas seeds, 1 molar ration of CTMAB, 0.68 % w/w of NaOH, 30°C and 400 rpm

Reaction Time (minute)	CTMAB			BTMAOH			Crown Ether		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
30	7.37	7.49	7.43	8.53	8.40	8.46	5.85	6.21	6.03
60	9.46	9.27	9.36	9.99	9.85	9.92	7.79	7.61	7.70
90	10.15	10.33	10.24	10.46	10.48	10.47	9.07	8.89	8.98
120	10.30	10.49	10.39	10.07	10.52	10.29	9.28	9.54	9.41
150	10.46	10.51	10.49	10.09	10.51	10.30	9.83	9.75	9.79
180	9.68	10.07	9.88	10.29	10.40	10.35	10.05	9.87	9.96
210	9.13	9.55	9.34	10.26	10.37	10.31	9.48	9.76	9.62

C-3: Results from microwave pretreated jatropha curcas particles experiment

Quantity of FAME and FAEE in gram produced from 20 gram of seed particles

1. **With alkaline catalyst (with NaOH)**

i) In-situ methanolysis

Run at: 7.5 ml/g methanol per jatropha curcas seeds, 0.68 % w/w of NaOH, 30°C and 400rpm

R. time (min)	MWH untreated particles			MWH pretreated particles		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
15	0.81	0.98	0.90	3.72	3.82	3.77
30	1.35	1.40	1.38	5.65	5.44	5.54
60	2.50	2.23	2.37	7.28	6.75	7.01
90	3.39	3.14	3.27	8.22	8.43	8.32
120	4.89	4.56	4.73	8.94	8.84	8.89
150	5.34	4.96	5.15	8.78	8.84	8.81
180	5.40	5.14	5.27	8.82	8.95	8.89
210	5.23	5.58	5.40	8.90	8.976	8.93

ii) In-situ ethanolysis

Run: at 7.5 ml/g ethanol per jatropha curcas seeds, 0.68 % w/w of NaOH, 30°C and 400rpm

R. time (min)	MWH untreated particles			MWH pretreated particles		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
15	2.41	2.59	2.50	5.62	5.11	5.36
30	4.71	4.58	4.64	7.56	7.76	7.66
60	7.05	7.20	7.13	8.68	8.90	8.79
90	7.95	8.06	8.01	9.24	9.49	9.37
120	8.98	8.68	8.83	9.83	9.95	9.89
150	8.81	8.97	8.89	9.89	9.89	9.89
180	9.10	9.23	9.16	9.79	9.87	9.83
210	9.36	9.21	9.28	9.81	9.92	9.86

2. With BTMAOH and alkaline catalyst (with BTMAOH + NaOH)

i) In-situ methanolysis

Run: at 7.5 ml/g methanol per jatropha curcas seeds, 0.68 % w/w of NaOH, 1% w/w PTC, 30°C and 400 rpm

Reaction time (min)	Microwave heat untreated particles			Microwave heat treated particles		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
15	3.77	4.15	3.96	6.89	6.99	6.94
30	7.69	7.74	7.71	9.98	9.66	9.82
60	7.99	8.56	8.28	9.92	9.92	9.92
90	9.20	9.47	9.34	9.84	9.99	9.92
120	9.64	9.74	9.69	9.79	10.00	9.89
150	9.77	9.60	9.69	9.62	9.89	9.76

ii) In-situ ethanolysis

Note: at 7.5 ml/g ethanol per jatropha curcas seeds, 0.68 % w/w of NaOH, 1 molar ratio of PTC, 30oC and 400 rpm

Reaction time (min)	MWH untreated particles			MWH pretreated particles		
	Exper-1	Exper-2	Average	Exper-1	Exper-2	Average
15	4.52	4.58	4.55	7.41	7.22	7.32
30	8.30	8.40	8.35	10.41	10.51	10.46
60	9.69	9.85	9.77	10.52	10.48	10.50
90	10.07	10.25	10.16	10.48	10.52	10.50
120	10.44	10.41	10.43	10.46	10.52	10.49
150	10.39	10.42	10.41	10.46	10.50	10.48